151. Tetrakis[(4*S*)-4-phenyloxazolidin-2-one]dirhodium(II) and Its Catalytic Applications for Metal Carbene Transformations

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The synthesis and X-ray structure of the binuclear complex tetrakis[(4*S*)-4-phenyloxazolidin-2-one]-dirhodium(II) ([Rh_2{(4*S*)-phox}$_4$]) are reported. Structure-selectivity comparisons are made for typical metal carbene transformations, such as inter- and intramolecular cyclopropane formation, intermolecular cyclopropene formation and intramolecular C–H insertions of diazoacetates and diazoacetamides. The enantioselectivity achieved in the [Rh_2{(4*S*)-phox}$_4$]-catalyzed reactions is intermediate between that of [Rh_2{(5*S*)-mepy}$_4$] and [Rh_2{(4*R*)-bnox}$_4$], which were described previously (mepy = methyl 5-oxopyrrolidine-2-carboxylate; bnox = 4-benzyloxazolidin-2-one). In contrast to other catalyzed intermolecular cyclopropane formations, those using [Rh_2{(4*S*)-phox}$_4$] result preferentially in formation of the *cis*-cyclopropane.

Introduction. – We previously reported that dirhodium(II) catalysts possessing chiral methyl 5-oxopyrrolidine-2-carboxylate ligands[1]), [Rh_2{(2*S*)-mepy}$_4$] and [Rh_2{(2*R*)-mepy}$_4$], are exceptionally effective for highly enantioselective metal carbene transformations [1–7]. These catalysts were prepared by ligand substitution from dirhodium(II) acetate, and their design places 2 O and 2 N donor atoms from the four amide ligands on each octahedral Rh-atom in a *cis*-configuration. The asymmetric center of the chiral oxopyrrolidinecarboxylate ligand is the sp^3-hybridized C-atom bonded to the N donor atom, and this structural design places the ring attachment in the intermediate metal carbene over the carbene C-atom. With allyl diazoacetates, intramolecular cyclopropane formation in the presence of the [Rh_2(mepy)$_4$] catalysts occurred in high yield and with enantiomeric excesses that were often greater than 90% [2]. Homoallylic diazoacetates were recently reported to also undergo intramolecular cyclopropane formation with high enantioselectivity [8], and similar results were obtained for intramolecular C–H insertion reactions [3] and for intermolecular cyclopropene formation from alk-1-ynes [4]. Dirhodium(II) carboxamide catalysts whose ligand-ring substituent is benzyl or isopropyl do not approach [Rh_2(mepy)$_4$] in their effectiveness for controlling enantioselectivities [1].

In our effort to prepare dirhodium(II) carboxamides whose ligand-ring substituents could offer greater steric bias for enantioselective metal carbene reactions, we synthesized tetrakis[(4*S*)-4-phenyloxazolidin-2-one]dirhodium(II) ([Rh_2{(4*S*)-phox}$_4$]). This catalyst was expected to control selectivity by sterically restricting approach of the substrate to the carbene C-atom rather than by electronic interaction with the carbene C-atom, as was

[1]) These ligands were formerly called 'methyl 2-pyrrolidone-5-carboxylates', *e.g.* Rh_2(5*S*-MEPY)$_4$.

suggested for the $[Rh_2(mepy)_4]$ [9] catalyst. We now wish to report the synthesis and characterization of $[Rh_2\{(4S)\text{-phox}\}_4]$, including its X-ray crystal structure, as well as its effectiveness for enantioselective carbene transformations.

Results and Discussion. – *Synthesis and Structure of* $[Rh_2\{(4S)\text{-phox}\}_4]$. Tetrakis[(4*S*)-4-phenyloxazolidin-2-one]dirhodium(II) was prepared by acetate displacement from $[Rh_2(OAc)_4]$ in refluxing chlorobenzene. In this procedure, AcOH was trapped by Na_2CO_3 in a *Soxhlet* extractor, thereby forcing the ligand substitution to completion. Both the ^1H- and ^{13}C-NMR spectra, with two resonance signals for protons and C-atoms in the two nonequivalent sets of ligands, suggest the *cis*-arrangement of the N donor ligands. Confirmation of this structure was obtained by X-ray crystallography. The structure corresponds closely to those of the previously reported tetrakis(carboxamidate)-dirhodium(II) compounds $[Rh_2\{(2R)\text{-mepy}\}_4]$ and $[Rh_2\{(4S)\text{-bnox}\}_4]$ (bnox = 4-benzyloxazolidin-2-one) [4]. *Fig. 1* clearly shows the expected *cis*-arrangement of the ligands in $[Rh_2\{(4S)\text{-phox}\}_4]$, consistent with the NMR data.

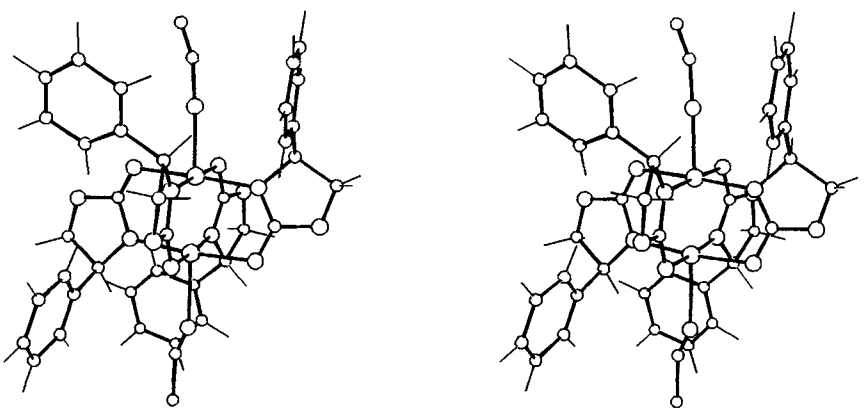


Fig. 1. *Stereoscopic view of* $[Rh_2\{(4S)\text{-phox}\}_4]$

The complex crystallizes with four MeCN molecules, two of which are coordinated on the Rh-atoms, and two are interstitional. All of them show large atomic displacement parameters leading to a deformed average geometry. This particularly affects the coordi-

Table 1. *Selected Bond Lengths* [Å] *and Bond Angles* [°] *for* $[Rh_2\{(4S)\text{-phox}\}_4]$. For numbering, see *Fig. 2*.

Rh(1)–Rh(2)	2.471(1)	Rh(1)–N(1d)	2.01(1)	Rh(2)–O(2c)	2.076(7)
Rh(1)–O(2a)	2.08(1)	Rh(1)–N(101)	2.19(1)	Rh(2)–O(2d)	2.09(1)
Rh(1)–O(2b)	2.071(8)	Rh(2)–N(1a)	2.02(1)	Rh(2)–N(201)	
Rh(1)–N(1c)	1.996(9)	Rh(2)–N(1b)	2.01(1)		
O(2a)–Rh(1)–O(2b)	88.3(4)	N(1c)–Rh(1)–N(1d)	92.9(4)	N(1b)–Rh(2)–O(2c)	173.1(4)
O(2a)–Rh(1)–N(1c)	91.2(4)	N(1c)–Rh(1)–N(101)	92.2(5)	N(1b)–Rh(2)–O(2d)	87.8(4)
O(2a)–Rh(1)–N(1d)	174.6(4)	N(1d)–Rh(1)–N(101)	97.4(5)	N(1b)–Rh(2)–N(201)	95.2(4)
O(2a)–Rh(1)–N(101)	86.1(4)	N(1a)–Rh(2)–N(1b)	91.6(4)	O(2c)–Rh(2)–O(2d)	88.7(3)
O(2b)–Rh(1)–N(1c)	176.9(5)	N(1a)–Rh(2)–O(2c)	91.2(4)	O(2c)–Rh(2)–N(201)	90.6(4)
O(2b)–Rh(1)–N(1d)	87.4(4)	N(1a)–Rh(2)–O(2d)	173.4(5)	O(2d)–Rh(2)–N(201)	88.9(4)
O(2b)–Rh(1)–N(101)	90.8(4)	N(1a)–Rh(2)–N(201)	97.7(5)		

Table 1 (cont.)

	ligand a	ligand b	ligand c	ligand d
O(1)–C(2)	1.36(2)	1.41(2)	1.39(2)	1.40(2)
O(1)–C(3)	1.41(2)	1.38(1)	1.40(1)	1.37(1)
O(2)–C(3)	1.15(2)	1.27(2)	1.20(2)	1.25(2)
N(1)–C(1)	1.44(2)	1.43(2)	1.48(2)	1.48(2)
N(1)–C(3)	1.36(2)	1.30(2)	1.33(2)	1.31(2)
C(1)–C(2)	1.57(2)	1.59(2)	1.58(2)	1.53(2)
C(1)–C(4)	1.56(1)	1.51(2)	1.50(2)	1.50(2)
C(2)–O(1)–C(3)	112(1)	105(1)	108(1)	110(1)
C(1)–N(1)–C(3)	114(1)	111(1)	111.2(9)	108(1)
N(1)–C(1)–C(2)	99(1)	101(1)	100(1)	104(1)
N(1)–C(1)–C(4)	114.8(9)	116(1)	113(1)	112(1)
C(2)–C(1)–C(4)	111(1)	111(1)	112(1)	110(1)
O(1)–C(2)–C(1)	105(1)	106.7(8)	106.6(8)	104(1)
O(1)–C(3)–O(2)	123(1)	114(1)	118(1)	117(2)
O(1)–C(3)–N(1)	106(1)	116(1)	112(1)	113(2)
O(2)–C(3)–N(1)	131(1)	130(1)	130.8(9)	129(1)

nated MeCN molecules, for which the observed N–C–C angles are 157 and 159°, respectively. The geometrical parameters around the Rh-atoms (*Table 1*; see also *Fig. 2*) are very similar to those observed in the methyl 5-oxopyrrolidine-2-carboxylate complex $[Rh_2\{(2S)\text{-mepy}\}_4]$ [10], except for the Rh–NCMe bond distances, for which the mean value is slightly longer in $[Rh_2\{(4S)\text{-phox}\}_4]$. The differentiation between the Rh–O and

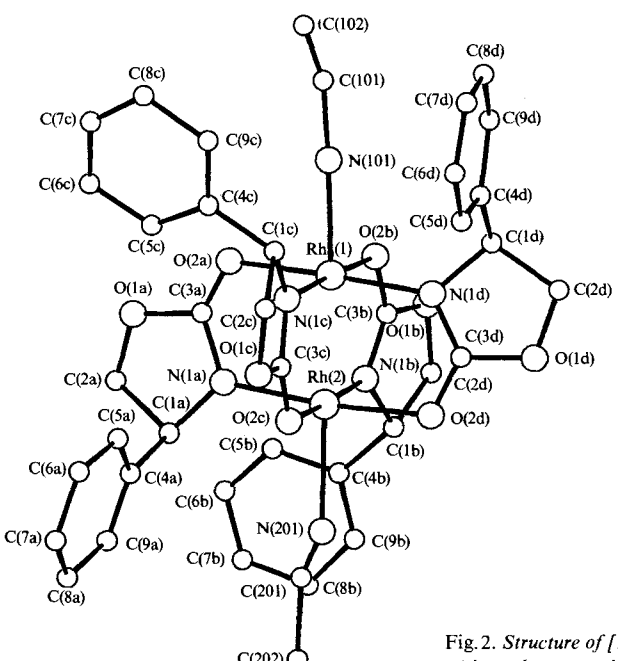


Fig. 2. *Structure of* $[Rh_2\{(4S)\text{-phox}\}_4]$ *with numbering used in* Table 1

Rh–N bond length in the main coordination plane is coherent (mean values: Rh–O = 2.079(8), Rh–N = 2.009(10) Å). The mean planes, calculated through the four atoms bonded to each Rh-atom, are parallel (0.8(3)°) and show maximum deviations of *ca.* 0.006 Å, whereas the Rh-atoms deviate from these planes towards the coordinated MeCN by 0.059 and 0.113 Å for Rh(1) and Rh(2), respectively.

The coordination sites of the Rh-atom on both sides of the complex for MeCN are believed to be also the coordination sites for the carbene in the catalyzed carbene transformations [10]. These coordination sites are related by a pseudo two-fold symmetry axis perpendicular to the Rh–Rh bond and oriented parallel to the bisector of the O–Rh–N bond angle (see also *Fig. 3*). Both 'active sites' around the Rh-atoms are chiral and may be described as an open half box constituted by three orthogonal planes. Two of them are delimited by the perpendicular Ph groups of the ligands, and this third one is defined by the main coordination plane of the Rh. The oxazolidinone rings adopt flattened envelope conformations with the C(2) atom out of plane. No short contact nor stacking interactions were observed in the molecular packing.

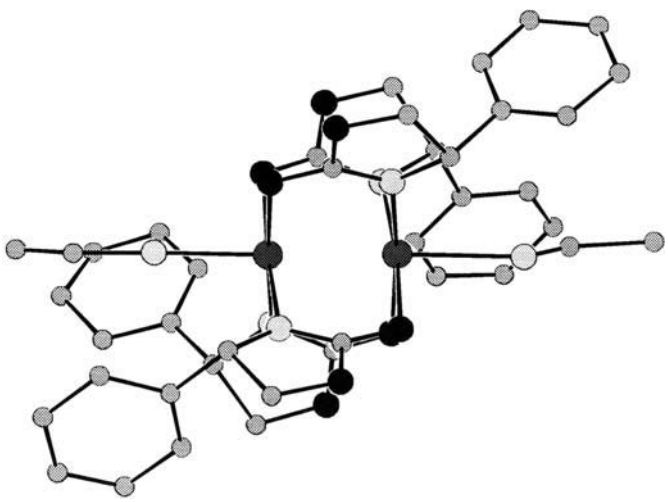
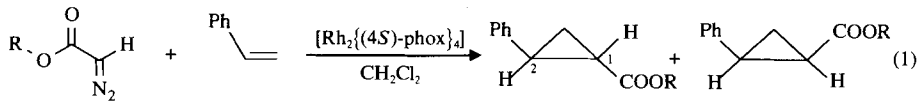


Fig. 3. *Projection of the structure of [Rh_2\{(4S)-phox\}$_4$] along the two-fold pseudo-symmetry axis*

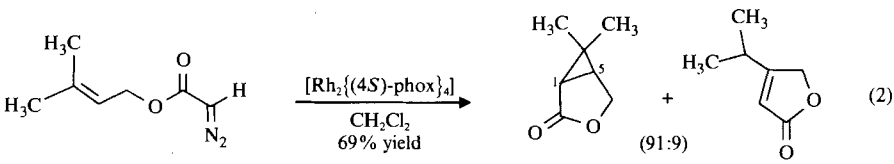
Enantioselective Carbene Transformations with [Rh_2\{(4S)-phox\}$_4$]. The effectiveness of [Rh_2\{(4*S*)-phox\}$_4$] for enantioselective carbene transformations was evaluated by intermolecular cyclopropane formation from (–)-L- and (+)-D-menthyl diazoacetate (**1a** and **1b**, resp.) or ethyl diazoacetate (**1c**) and styrene (see *Eqn. 1*: →**2a–c**/**3a–c**), intramolecular cyclopropane formation from 3-methyl-but-2-en-1-yl diazoacetate (**4**; see *Eqn. 2*: →**5** + **6**), and intermolecular cyclopropane formation from hept-1-yne (**7**) and methyl diazoacetate (see *Eqn. 3*: →**8**). The models selected for intramolcular C–H insertions were 2-methoxyethyl diazoacetate (**9**; see *Eqn. 4*: →**10**), *N*-(butyl)-*N*-(*tert*-butyl)-diazoacetamide (**11**; see *Eqn. 5*: →**12** + **13**), and (**14**; see *Eqn. 6*: →**15–17**). Absolute configurations of all reaction products, where known, are given in parentheses. The results were compared with those obtained using the catalysts [Rh_2\{(2*S*)-mepy\}$_4$] and [Rh_2\{(4*R*)-bnox\}$_4$] (see *Table 2*).



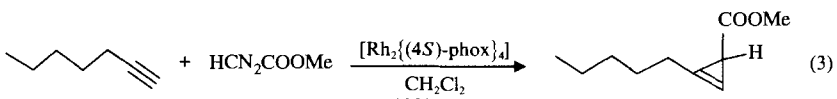
1a R = (–)-L-menthyl
b R = (+)-D-menthyl
c R = Et

2a–c **3a–c**

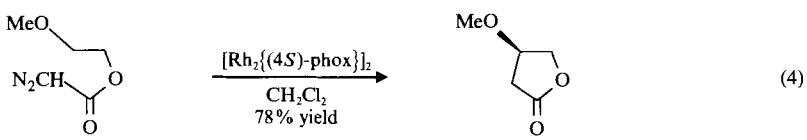
R	Yield [%] of **2**/**3**	**2**/**3**	ee(de)[%] of **2**	ee(de)[%] of **3**
a (–)-menthyl	19	0.37	40 (1*R*,2*R*)	72 (1*R*,2*S*)
b (+)-menthyl	24	1.44	4 (1*S*,2*S*)	6 (1*R*,2*S*)
c Et	41	0.52	24 (1*R*,2*R*)	57 (1*R*,2*S*)



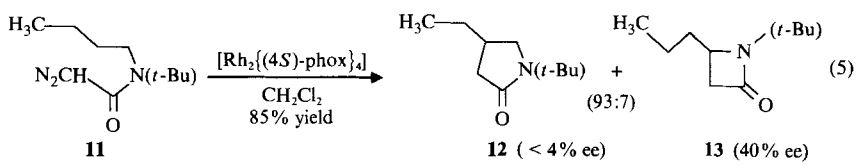
4 **5** (68% ee; (1*R*,5*S*)) **6**



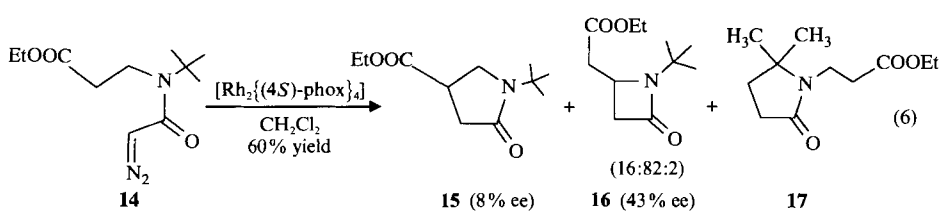
7 **8** (38% ee)



9 **10** (55% ee; *R*)



11 **12** (< 4% ee) **13** (40% ee)



14 **15** (8% ee) **16** (43% ee) **17**

Table 2 reveals that, in the vast majority of the metal carbene transformations that were examined, [Rh$_2${(4*S*)-phox}$_4$] lies between [Rh$_2${(2*S*)-mepy}$_4$] and [Rh$_2${(4*R*)-bnox}$_4$] in its overall effectiveness for enantioselectivity. In addition, unlike the other catalysts, [Rh$_2${(4*S*)-phox}$_4$] produced the *cis*-isomer **3a** as the predominant product (**2a**/**3a** 27:73),

Table 2. *Comparative Selectivities for Dirhodium(II) Catalysts with Chiral Carboxamide Ligands in Representative Metal Carbene Transformations*[a])

Diazo compound	Product	$[Rh_2\{(4S)\text{-phox}\}_4]$		$[Rh_2\{(2S)\text{-mepy}\}_4]$[b])		$[Rh_2\{(4R)\text{-bnox}\}_4]$[b])	
		ee (de) [%]	ratio	ee (de) [%]	ratio	ee (de) [%]	ratio
1a	**2a**	40	**2a/3a** 27:73	56	**2a/3a** 52:48	4	**2a/3a** 62:38
	3a	72		79		25	
1b	**2b**	4	**2b/3b** 59:41	48	**2b/3b** 57:43	34	**2b/3b** 67:33
	3b	6		86		62	
1c	**2c**	24	**2c/3c** 34:66	58	**2c/3c** 56:44	8	**2c/3c** 46:54
	3c	57		33		13	
4	**5**	68	**5/6** 91:9	98	**5/6** > 99:1	56	**5/6** 81:19
7	**8**	38		57[c])		5[c])	
9	**10**	55		91		11	
11	**12**	< 4	**12/13** 93:7	63	**12/13** 88:12	< 2	**12/13** 92:8
	13	40		73		0	
14	**15**	8	**15/16/17** 16:82:2	–	**15/16/17** 2:9:89	16	**15/16/17** 12:88: < 1
	16	43		44		20	

[a]) Reactions were performed in CH_2Cl_2 under identical conditions. [b]) Absolute configurations of products were opposite to those obtained from reactions catalyzed by $[Rh_2\{(4S)\text{-phox}\}_4]$. With the exception of $[Rh_2\{(4R)\text{-bnox}\}_4]$-catalyzed cyclopropane formation from styrene and **1c**, data were taken from [2] [3] [5] [7]. [c]) For hex-1-yne and **1c** in refluxing CH_2Cl_2.

when intermolecular cyclopropane formation was performed with **1a**. This high *cis*-selectivity is unique among dirhodium(II) or copper catalysts [11–14] and was reported only for cyclopropane formations catalyzed by select rhodium(III) porphyrinates [15] [16]. In his recent communication on cyclopropane formation from styrene and ethyl diazoacetate (**1c**), catalyzed by a 'chiral wall' and 'chiral fortress' Rh^{III} complex, *Kodakek* reported **2c/3c** ratios of 30:70 and 29:71, respectively, but enantiomeric excesses for **3c** were < 15% rather than the ee of 57% obtained with the use of $[Rh_2\{(4S)\text{-phox}\}_4]$ and **1c**. Preliminary experiments indicated that the preference for formation of *cis*-cyclopropanes is general and characteristic for $[Rh_2\{(4S)\text{-phox}\}_4]$-catalyzed reactions of diazoacetates. A detailed study of this phenomenon is underway and will be reported in due course.

A remarkable difference in catalyst selectivity occurred also in the formation of β-lactams and γ-lactams from diazoacetamides. With **11**, all catalysts studied exhibited a strong (*ca.* 9:1) preference for γ-lactam **12**, but in the case of **14**, β-lactam **16** was the principal product with $[Rh_2\{(4S)\text{-phox}\}_4]$ and the structurally similar $[Rh_2\{(4R)\text{-bnox}\}_4]$. Use of $[Rh_2\{(2S)\text{-mepy}\}_4]$, however, resulted mainly in formation of **17**, from insertion into one of the Me groups of the *t*-Bu substituent [5].

In general, the chemical yields achieved in the intramolecular cyclopropane formations and C–H insertions catalyzed with $[Rh_2\{(4S)\text{-phox}\}_4]$ were competitive with those obtained with $[Rh_2\{(2S)\text{-mepy}\}_4]$ and $[Rh_2\{(4R)\text{-bnox}\}_4]$ [10], but they were much less satisfactory in the case of intermolecular cyclopropane and cyclopropene formation. In these latter cases, one observed a higher amount of carbene dimers, and for this reason it appears justified to attribute the low cyclopropane yield to steric hindrance towards the approach of the alkene to the coordinated carbene. The sterically more demanding Ph

substituents of the oxazolidinone ligand phox not only block the approach of the alkene, but also enforce the thermodynamically less favorable *cis*-arrangement of the cyclopropane substituents in the product, while the catalysts having the less crowding benzyl substituent in the ligand (bnox catalyst) or the oxopyrrolidecarboxylate ligand (mepy catalyst) produce preferentially the more stable *trans*-cyclopropane. There is clearly a subtle balance between the interactions of the catalyst with the substituents of the carbene and of the olefin on one hand, and between the substituents of the carbene and the olefin on the other. The lower control of enantioselectivity generally observed with $[Rh_2\{(4S)\text{-phox}\}_4]$ as compared to that with $[Rh_2\{(2S)\text{-mepy}\}_4]$ indicates that increased steric crowding does not necessarily improve enantioselectivity, and that the higher performance of the mepy catalyst should be ascribed to other causes.

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Experimental Part

General. Dirhodium(II) tetraacetate was obtained commercially or prepared from rhodium(III) chloride hydrate [17]. The syntheses of $[Rh_2\{(2S)\text{-mepy}\}_4]$ and $[Rh_2\{(4R)\text{-bnox}\}_4]$ were described in [10]. Chlorobenzene, MeCN, and CH_2Cl_2 were distilled from CaH_2 prior to use, 1,2-dichloroethane was distilled from P_2O_5. (–)-L-Menthyl diazoacetate (**1a**) and (+)-D-Menthyl diazoacetate (**1b**) [12c] were prepared from their corresponding menthyl diazoacetoacetates [18] by deacylation in $MeCN/H_2O$ using LiOH (3.0 equiv.). The diazo compounds and **7** were added to the catalyst soln. through a syringe pump. IR Spectra (cm^{-1}): FT instrument, resolution of $\pm$ 1 cm^{-1}. NMR Spectra: ^1H at 300 and ^{13}C at 75 MHz; δ in ppm rel. to Me_4Si (= 0 ppm), J in Hz. MS: quadrupole instrument; ionizing voltage of 70 eV.

Tetrakis[(4S)-4-phenyloxazolidin-2-one] dirhodium(II) $[Rh_2\{(4S)\text{-phox}\}_4]$. A mixture of rhodium(II) acetate (200 mg, 0.466 mmol) and (4*S*)-4-phenyloxazolidin-2-one (670 mg, 4.11 mmol) in 20 ml of anh. chlorobenzene was refluxed under N_2 and under a *Soxhlet* extraction apparatus. The thimble was charged with 5 g of an oven-dried mixture of Na_2CO_3/sand 1:1 (*v/v*). After 72 h, the resulting blue soln. was cooled to r.t., the solvent evaporated, and the resulting solid purified by chromatography (10 g of *J.T. Baker Bondapak-CN*-capped silica gel). After elution of excess ligand with MeOH (100 ml), the pure catalyst (single red band) was obtained with MeOH/MeCN 99:1 (*v/v*). 0.25 g (57%) of a blue glass, after evaporation. Recrystallization from MeCN gave $[Rh\{(4S)\text{-phox}\}_4]\cdot(MeCN)_4$ which was used in all experiments. $[\alpha]_D^{23} = 323 \pm 3$ (MeCN, $c = 0.128$). ^1H-NMR ($CDCl_3$): 7.6–6.9 (*m*, 20H); 4.74 (*s*, 2H); 4.72 (*q*, $J = 9.3$, 2H); 4.28–4.12 (*m*, 4H); 3.77 (*t*, $J = 7.8$, 2H); 2.80 (*dd*, $J = 9.3$, 1.4, 2H). ^{13}C-NMR ($CDCl_3$): 168.1; 145.2; 128.8; 128.0; 127.9; 127.5; 127.3; 127.0; 73.4; 65.3; 64.8.

X-Ray Structure of $[Rh_2\{(4S)\text{-phox}\}_4]\cdot(MeCN)_4$. Single crystals of $[Rh_2\{(4S)\text{-phox}\}_4]\cdot(MeCN)_4$ were obtained by slow evaporation from MeCN soln. and mounted in *Lindemann* capillaries with supernatant liquid to prevent degradation. The cell parameters (from 20 reflections with $22° < 2\theta < 33°$) and diffracted intensities ($-8 < h < 8$, $0 < k < 28$, $0 < l < 10$, and all antireflections of these) were measured at r.t. on a *Philips-PW-1100* diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å). Two reference reflections measured every 60 min showed variations less than $3.5\sigma(I)$. Data were collected for *Lorentz* and polarization effects and for absorption [19]. The structure was solved by direct methods using MULTAN 87 [20], all other calculations used XTAL [21] and ORTEP [22] programs. Atomic scattering factors and anomalous dispersion terms were taken from [23]. The chirality/polarity of the structure was refined, and the absolute structure parameter [24] converged to $x = -0.01(4)$. All coordinates of the H-atoms were calculated. A summary of crystal data, intensity measurements, and structure refinement is given in *Table 3*. Crystallographic data were deposited with the *Cambridge Crystallographic Data Center*, University Chemical Laboratory, Union Road, Cambridge, CB2 1EZ, England.

Intermolecular Cyclopropane Formation from Styrene and (–)- and (+)-Menthyl Diazoacetate (**1a** and **1b**). To a blue soln. of styrene (2.5 mmol) and $[Rh_2\{(4S)\text{-phox}\}_4]$ (0.01 mmol) in 25 ml of refluxing CH_2Cl_2 under N_2 was added **1a** or **1b** (0.50 mmol) in CH_2Cl_2 (5 ml; 0.4 ml/h). After addition was complete, the catalyst was filtered off through a 1-cm plug of silica gel and the silica gel washed with additional CH_2Cl_2 (30 ml). A standard, ethyl *trans*-2-phenylcyclopropanecarboxylate (0.191 mmol), was added and the mixture analyzed by GC (30-m capillary

Table 3. *Crystal Data, Intensity Measurement, and Structure Refinement for [Rh_2{(4S)-phox}$_4$]*

Formula	$[Rh_2(C_9H_8NO_2)_4](MeCN)_4$	$((\sin\theta)/\lambda)_{max}$ [Å^{-1}]	0.53
Mol. wt.	1018.7	Temperature [K]	298
Crystal system	Monoclinic	No. measured reflections	5908
Space group	$P2_1$	No. observed reflections	4469
a [Å]	8.198(3)	R_{int} for equiv. reflections	0.040
b [Å]	27.482(9)	Criterion for observed	$\|F_o\| > 4\sigma(F_o)$
c [Å]	10.395(3)	Refinement (on F)	Full-matrix
β [°]	107.81(1)	No. parameters	559
V [Å^3]	2230(1)	Weighting scheme	$\omega = 1/\sigma^2(F_o)$
Z	2	Max. and average Δ/σ	0.26, 0.04
$F(000)$	1036	Max. and min. $\Delta\varrho$ [e·Å^{-3}]	1.11, −1.02
D_c [g·cm^{-3}]	1.52	x	−0.01(4)
$\mu(MoK_\alpha)$ [mm^{-1}]	0.786	S	2.20
A^* (min, max)	1.195, 1.229	R, ωR	0.043, 0.029

methylsilicone column). The order of elution of the diastereoisomers (base-line separation) was *(1R,2S)-*, *(1S,2R)-*, *(1S,2S)-*, and *(1R,2R)-menthyl 2-phenylcyclopropanecarboxylate* (**2a**; from **1a** and **3a**) and *(1S,2R)-*, *(1R,2S)-*, *(1R,2R)-*, and *(1S,2S)-menthyl 2-phenylcyclopropanecarboxylate* (**2b** and **3b**; from **1b**).

Intermolecular Cyclopropane Formation from Styrene and Ethyl Diazoacetate (**1c**). To a light blue soln. of styrene (20.0 mmol) and [Rh_2{(4*S*)-phox}$_4$] (0.01 mmol) in anh. CH_2Cl_2 (20 ml) refluxing under N_2 was added **1c** (2.0 mmol) in CH_2Cl_2 (5 ml; 0.4 ml/h). After the addition was complete, the solvent was evaporated and the product purified by chromatography (10 g of silica gel). Gradient elution (hexane→AcOEt/hexane 1:4) yielded pure **2c**/**3c** in 41% yield. The enantiomeric excess was determined by GC (30-m *Chiraldex* permethylated β-cyclodextrin column, 140°). The order of elution was *(1S,2R)-*, *(1R,2S)-*, *(1R,2R)-*, and *(1S,2S)-ethyl 2-phenylcyclopropanecarboxylate* (**2c** and **3c**).

Intramolecular Cyclopropane Formation from 3-Methylbut-2-en-1-yl Diazoacetate (**4**). To a light blue soln. of the [Rh_2{(4*S*)-phox}$_4$] (0.009 mmol) in refluxing anh. CH_2Cl_2 (20 ml) was added, under N_2, **4** (0.83 mmol) in CH_2Cl_2 (5 ml; 0.40 ml/h). After addition was complete, the soln. was filtered through a 1-cm silica-gel plug and the plug eluted with additional CH_2Cl_2 (30 ml). The resulting CH_2Cl_2 soln. was evaporated under reduced pressure and the residue purified by column chromatography (silica gel, hexane → hexane/AcOEt 3:1). The resulting mixture was then analyzed as previously described [10] by GC (30-m *Chiraldex* γ-cyclodextrin trifluoroacetate capillary column) from which the enantiomeric excess for (−)-*(1R,5S)-6,6-dimethyl-3-oxabicyclo[3.1.0]hexan-2-one* (**5**) was calculated to be 67.9% (69% yield). In addition to **5**, *4-isopropylfuran-2(5H)-one* (**6**) was formed in 9% yield.

Intermolecular Cyclopropene Formation from Hept-1-yne (**7**) *and Methyl Diazoacetate.* To a stirred soln. of [Rh_2{(4*S*)-phox}$_4$] (0.023 mmol) and **7** (4.80 g, 50 mmol) in CH_2Cl_2 (20 ml) was added, at 25°, methyl diazoacetate (500 mg, 5.0 mmol) in CH_2Cl_2 (5.0 ml) over 21 h. After the addition was complete, stirring was continued for 1 additional h. The mixture was filtered through a 1-cm plug of silica gel which was eluted with CH_2Cl_2. After evaporation of solvent and unreacted **7**, the product was purified by prep. TLC (silica gel, hexane/AcOEt 3:1): 162 mg (19%) of *methyl 2-pentylcycloprop-2-ene-1-carboxylate* (**8**). The enantiomeric excess (38%) was determined by ^{1}H-NMR using [Eu(hfc)] as shift reagent on the *s* at 3.66 ppm (MeO). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.8–1.0 (*t*, 3H); 1.2–1.7 (*m*, 6H); 2.12 (*d*, J = 1.6, 1H); 2.40–2.50 (*m*, 2H); 3.66 (*s*, 3H); 6.31 (*m*, 1H).

Intramolecular C−H Insertion of 2-Methoxyethyl Diazoacetate (**9**). To a light blue soln. of [Rh_2{(4*S*)-phox}$_4$] (0.007 mmol) in anh. refluxing CH_2Cl_2 (20 ml) under N_2 was added **7** (0.7 mmol) in CH_2Cl_2 (5 ml) over 24 h. The solvent was evaporated and the residue purified by bulb-to-bulb distillation to afford *4,5-dihydro-4-methoxyfuran-2(3H)-one* (**10**; 78%) which was analyzed as previously reported [10] by GC (30-m *Chiraldex* γ-cyclodextrin trifluoroacetate capillary column).

Intramolecular C−H Insertion of N-*Butyl*-N-*(*tert*-butyl)diazoacetamide* (**11**). To a light blue soln. of [Rh_2{(4*S*)-phox}$_4$] (0.004 mmol) in refluxing anh. CH_2Cl_2 (15 ml) under N_2 was added **11** (0.37 mmol) in CH_2Cl_2 (5 ml; 0.4 ml/h). After addition was complete, the blue CH_2Cl_2 soln. was evaporated and the residue distilled: 56 mg of a colorless oil (85%) consisting of N-*(*tert*-butyl)-4-ethylpyrrolidin-2-one* (**12**: 93%) and N-*(*tert*-butyl)-4-propylazetidin-2-one* (**13**; 7%). Enantiomeric excesses were obtained by GC (*Chiraldex* γ-cyclodextrin trifluoroacetate column). For characterization of **12** and **13**, see [10].

*Intramolecular C−H Insertion of Ethyl 3-[*N-*(*tert*-Butyl)*-N-*(diazoacetyl)amino]propanoate* (**14**). To a light blue soln. of [Rh_2{(4*S*)-phox}$_4$] (0.005 mmol) in refluxing anh. CH_2Cl_2 (10 ml) was added, under N_2, **14** (0.54

mmol) in CH_2Cl_2 (5 ml; 0.7 ml/h). After addition was complete, the blue-grey mixture was evaporated and the residue distilled: 78 mg (68%) of a colorless oil consisting of **15** (16%), **16** (82%), and **17** (2%). Enantiomeric excesses were determined by GC (γ-cyclodextrin trifluoroacetate column). The principal by-product was that from H_2O insertion. Separation of products was performed by column chromatography (silica gel, gradient hexane/AcOEt 4:1 → 2:1).

Ethyl N-(tert-*Butyl*)-*5-oxopyrrolidine-3-carboxylate* (**15**): ^{1}H-NMR ($CDCl_3$, 300 MHz): 4.18 (*q*, J = 7.1, 2H); 3.66 (*d*, J = 8.1, 2H); 3.11 (br. *quint.*, J = 8.1, 1H); 2.67 (*dd*, J = 16.6, 8.0, 1H); 2.60 (*dd*, J = 16.6, 9.7, 1H); 1.40 (*s*, 9H); 1.28 (*t*, J = 7.1, 3H). MS: 214 (0.6, $[M + 1]^+$), 213 (4.9, M^+), 199 (10), 198 (100), 170 (22), 113 (13), 84 (25), 70 (49), 57 (25).

Ethyl N-(tert-*Butyl*)-*4-oxoazetidine-2-acetate* (**16**): ^{1}H-NMR ($CDCl_3$, 300 MHz): 4.16 (*q*, J = 7.2, 2H); 4.11–3.92 (*m*, 1H); 3.04 (*dd*, J = 14.9, 5.2, 1H); 2.96 (*dd*, J = 14.9, 3.9, 1H); 2.55 (*dd*, J = 15.6, 1.8, 1H); 2.51 (*dd*, J = 15.6, 9.5, 1H); 1.35 (*s*, 9H); 1.27 (*t*, J = 7.2, 3H). MS: 214 (0.2, $[M + 1]^+$), 213 (0.8, M^+), 198 (51), 156 (32), 141 (19), 126 (30), 114 (21), 113 (23), 84 (40), 58 (56), 57 (100). Anal. calc. for $C_{12}H_{21}NO_2$: C 68.21, H 10.02, N 6.63; found: C 68.26, H 10.03, N 6.58.

Ethyl 2,2-Dimethyl-5-oxopyrrolidine-1-propanoate (**17**): IR (neat): 1730, 1675. ^{1}H-NMR ($CDCl_3$, 300 MHz): 4.14 (*q*, J = 7.0, 2H); 3.42 (*t*, J = 7.8, 2H); 2.62 (*t*, J = 7.8, 2H); 2.37 (*t*, J = 8.0, 2H); 1.87 (*t*, J = 8.0, 2H); 1.26 (*t*, J = 7.0, 3H); 1.24 (*s*, 6H).

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