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Novel dirhodium tetraprolinate catalysts containing bridging prolinate ligands for asymmetric carbenoid reactions

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Abstract

The D_2-symmetric dirhodium prolinate complex **3** is an effective catalyst for asymmetric vinylcarbenoid and phenylcarbenoid cyclopropanations. © 1999 Elsevier Science Ltd. All rights reserved.

Rhodium(II) prolinates, such as Rh_2(*S*-DOSP)$_4$ (**1**), have been shown to be excellent chiral catalysts for asymmetric cyclopropanation (up to 98% ee) by vinyldiazoacetates[1] and phenyldiazoacetates.[2] A predictive model has been presented to rationalize the asymmetric induction caused by Rh_2(*S*-DOSP)$_4$.[1c] In this model the complex is considered to exist in a D_2-symmetric conformation in which the arylsulfonyl groups preferentially align in an up-down–up-down arrangement. In order to test this model, the dirhodium tetraprolinate catalyst **2** was evaluated.[3] In **2**, pairs of prolinates are tethered at the C-2 position, which forces the arylsulfonyl groups to align in an up-down–up-down arrangement. Complex **2** performed as a reasonable chiral catalyst resulting in cyclopropanation of up to 83% ee, but was inferior to Rh_2(*S*-DOSP)$_4$ as a chiral catalyst.[3] In this communication, we describe the synthesis of a new series of bridged prolinate complexes **3**, tethered at the C-5 position. This new class of catalyst offers a major advantage over Rh_2(*S*-DOSP)$_4$ because it can achieve high asymmetric induction in reactions carried out in non-hydrocarbon solvents, which is not the case with Rh_2(*S*-DOSP)$_4$.[1c]

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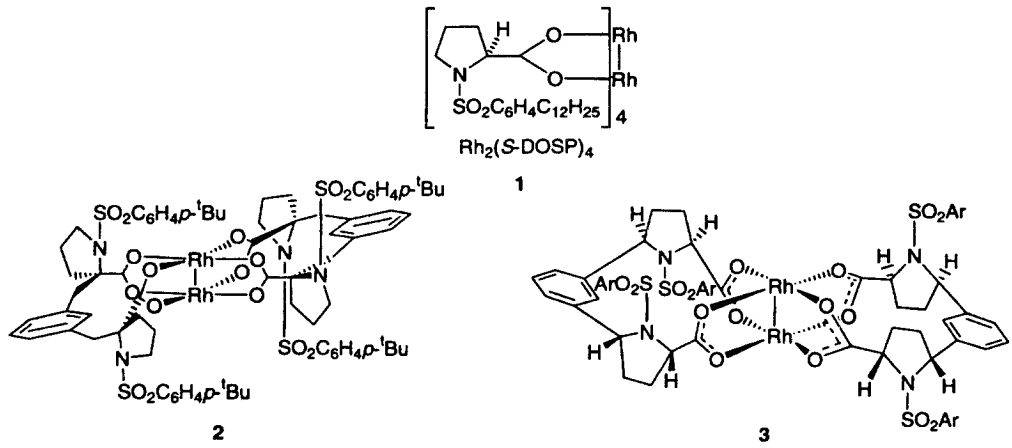
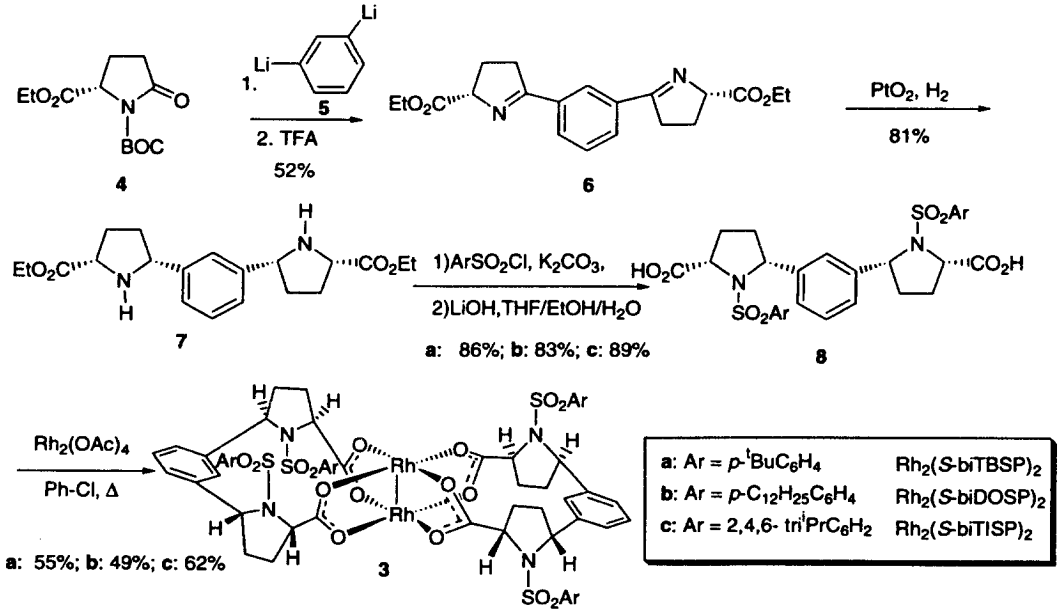


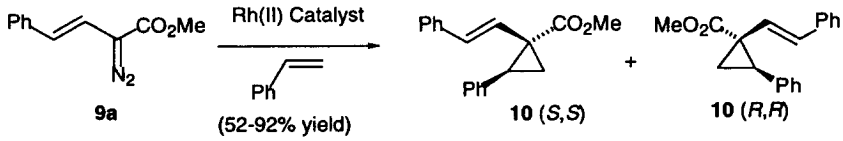
The direct synthetic strategy that was used to prepare **3** is shown in Scheme 1. The key step is alkylation of (*S*)-pyroglutamate derivative **4**[4] with 1,3-dilithiobenzene (**5**)[5] to form the bis-imine **6**. It is well established that the reaction of **4** with aryl Grignard reagents followed by reduction is an effective method to prepare *cis*-5-arylproline derivatives.[6] Platinum(IV) oxide catalyzed hydrogenation of **6** generated the bis-proline **7**, with an overall 42% yield from the pyroglutamate. Treatment of **7** with arylsulfonylchlorides, followed by saponification generated bis-sulfonated ligands **8**, which were readily incorporated into the dirhodium complex **3** by a ligand exchange reaction using $Rh_2(OAc)_4$. The HRMS FAB data indicated that the dirhodium complexes **3** contain two of the bridged ligands.[7] Furthermore, due to the bridging nature of the ligands, the arylsulfonyl groups are forced to adopt an up-down–up-down arrangement, generating a complex of D_2 symmetry.



Scheme 1.

A comparative study of the new-bridged catalysts **3** with Rh_2(*S*-DOSP)$_4$ and the original bridged catalyst **2** is summarized in Table 1. The standard reaction that was used for this comparative study was the cyclopropanation of styrene by the vinyldiazoacetate **9a**. One of the most distinctive features

Table 1
Asymmetric cyclopropanation of styrene using rhodium(II) prolinate catalysts

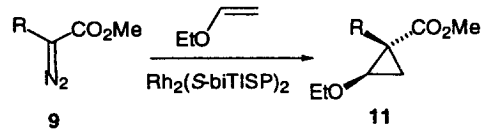


solvent	temp, °C	%ee for the formation of **10** by Rh(II) catalysts				
		Rh_2(*S*-biTBSP)$_2$	Rh_2(*S*-biDOSP)$_2$	Rh_2(*S*-biTISP)$_2$	Rh_2(*S*-DOSP)$_4$	**2**
n-alkane	25	55(*S,S*)	53 (*S,S*)	74 (*S,S*)	90 (*R,R*)[1c]	56 (*S,S*)[3]
CH_2Cl_2	25	63 (*S,S*)	68 (*S,S*)	90 (*S,S*)	74 (*R,R*)[1c]	59 (*S,S*)[3]
CH_2Cl_2	-50	—	—	**98 (*S,S*)**	**88 (*R,R*)**	83 (*S,S*)[3]

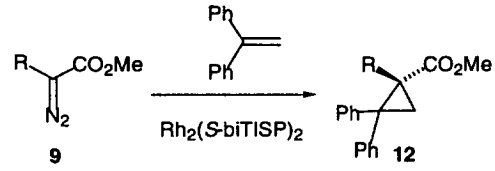
of Rh_2(*S*-DOSP)$_4$ catalyzed reactions is that they exhibit higher enantioselectivity when carried out in hydrocarbons such as hexane or pentane rather than CH_2Cl_2 as solvent. In the case of the bridged catalysts **3**, the opposite is seen in each case with the highest enantioselectivity being obtained when CH_2Cl_2 is used as solvent. The structure of the arylsulfonyl substituent has a fairly limited effect on the asymmetric induction for the tetraprolinate catalysts related to Rh_2(*S*-DOSP)$_4$.[1c] However, for the bridged catalysts **3**, the arylsulfonyl group has a major effect with the 2,4,6-triisopropylphenyl derivative, Rh_2(*S*-biTISP)$_2$ (**3c**), resulting in the highest asymmetric induction. Reaction of **9a** with Rh_2(*S*-biTISP)$_2$ in the presence of stytene at –50°C in CH_2Cl_2 resulted in the formation of the cyclopropane **10** in 98% ee.[8] One of the most intriguing features of both series of bridged catalysts **2** and **3** is that the asymmetric induction in their reactions is opposite to that observed with Rh_2(*S*-DOSP)$_4$. The most reasonable explanation for this effect at this stage is that the carbenoid binds in a different staggered orientation in **2** and **3** compared to Rh_2(*S*-DOSP)$_4$.

Two illustrative examples of the synthetic utility of Rh_2(*S*-biTISP)$_2$ are shown in Scheme 2. Reaction of the vinyldiazoacetate **9a** or the phenyldiazoacetate **9b** with ethyl vinyl ether, catalyzed by Rh_2(*S*-biTISP)$_2$, resulted in cyclopropanation to form **11a** (87% ee) or **11b** (79% ee). Reaction of **9a** or **9b** with diphenylethylene, catalyzed by Rh_2(*S*-biTISP)$_2$, resulted in cyclopropanation to form **12a** or **12b** in >97% ee. In each case, the asymmetric induction is comparable but opposite to that obtained with Rh_2(*S*-DOSP)$_4$.[1e,d] Further studies are in progress to determine the range of utility of Rh_2(*S*-biTISP)$_2$ in asymmetric cyclopropanation, Si-H insertions[9] and C-H insertions[10] of vinyldiazoacetates[1,11] and phenyldiazoacetates.[2]

In summary, the demonstration that the rigid bridged prolinate complex, Rh_2(*S*-biTISP)$_2$ (**3c**), is an excellent catalyst for asymmetric cyclopropanation adds further support to the concept that the efficiency of Rh_2(*S*-DOSP)$_4$ as a chiral catalyst is due to the arrangement of the ligands in a D_2-symmetric arrangement. The binding of identical low symmetry ligands around a central core to form complexes of high symmetry is an exciting new approach for chiral catalyst design. Rh_2(*S*-biTISP)$_2$ is expected to be of great utility in the emerging field of vinyldiazoacetate and phenyldiazoacetate transformations because it can achieve high asymmetric induction in reactions carried out in non-hydrocarbon solvents, which was not the case for Rh_2(*S*-DOSP)$_4$.



	temp, °C	R	yield, %	ee, %
a	-50	CH=CHPh	53	87
b	-50	Ph	86	79



	temp, °C	R	yield, %	ee, %
a	25	CH=CHPh	94	91
a	-50	CH=CHPh	32	>97
b	-50	Ph	81	>97

Scheme 2.

Acknowledgements

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7. Spectral data for **3c**: IR (NaCl) 2966, 2929, 2871, 1603, 1417, 1321, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 8H), 6.97 (t, 2H, *J*=7.4 Hz), 6.81 (d, 4H, *J*=8.4 Hz), 6.80 (s, 2H), 4.63 (t, 4H, *J*=8.2 Hz), 4.39 (d, 4H, *J*=7.6 Hz), 3.47 (sept, 8H, *J*=6.4 Hz), 2.96 (sept, 4H, *J*=6.8 Hz), 2.41 (dd, 4H, *J*=12.2, 6.0 Hz), 2.24–2.14 (m, 4H), 2.14–2.00 (m, 4H), 1.76–1.63 (m, 4H), 1.31 (d, 12H, *J*=6.8 Hz), 1.29 (d, 12H, *J*=6.8 Hz), 1.05 (d, 24H, *J*=6.8 Hz), 0.94 (d, 24H, *J*=6.0 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 190.5, 153.1, 151.4, 141.6, 130.5, 127.1, 127.0, 124.7, 123.6, 64.7, 62.3, 34.9, 34.0, 29.3, 27.8, 25.0, 24.6, 23.5, 23.5; HRMS (FAB) calcd for $C_{92}H_{125}N_4O_{16}S_4Rh_2$ $(m+H)^+$: 1875.6084, found $(m+H)^+$: 1875.6076.
8. **General procedure for Rhodium(II)-catalyzed decompositions of diazo in the presence of alkenes**: a solution of the diazo compound (0.5 mmol, 1 equiv.) in CH_2Cl_2 (10 mL) was added over 1–2 h to a stirred solution of the alkene (5.0 equiv.) and Rh(II) catalyst (0.01 equiv.) in CH_2Cl_2 (5 mL) at −50°C under an argon atmosphere. The mixture was then stirred for 24 h at −50°C and then warmed to rt. The mixture was concentrated in vacuo and the residue was purified on silica using ether/petroleum ether as the eluent.
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