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SYNTHESIS AND EVALUATION OF A NOVEL DIRHODIUM TETRAPROLINATE CATALYST CONTAINING BRIDGING PROLINATE LIGANDS

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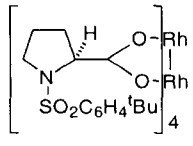
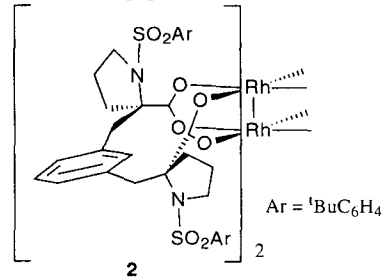
*Abstract: The D_2 symmetric dirhodium prolinate complex **2** is an effective catalyst for asymmetric vinylcarbenoid cyclopropanations* © 1997 Elsevier Science Ltd.

Rhodium(II) prolinates such as Rh_2(*S*-TBSP)$_4$ (**1**) have been shown to be excellent chiral catalysts for asymmetric cyclopropanation (up to 98% ee) by vinyldiazoacetates[1] and phenyldiazoacetates.[2] Considering that the generally held view has been that the rhodium(II) tetracarboxylate framework is far from ideal as a template for chiral catalyst design,[3,4] further studies were carried out to understand how **1** could induce such high levels of asymmetric induction. A predictive model has been presented to rationalize the asymmetric induction caused by **1**.[1c] In this model the complex is considered to exist in a D_2 symmetric conformation in which the arylsufonyl groups align in an up-down-up-down arrangement. If this was the case, this would offer an exciting approach for designing D_2 symmetric catalysts. Instead of the traditional method which requires the synthesis of complex ligands of D_2 symmetry,[5] one could design much simpler ligands which would arrange appropriately in the complex to form a structure of D_2 symmetry. In order to test the validity of the predictive model, a novel dirhodium tetraprolinate catalyst **2** was prepared, in which pairs of prolinates are tethered. The overall effect of the tethered prolinates is to force the arylsulfonyl groups to align in an up-down-up-down arrangement. The synthesis of **2** and its evaluation as a chiral catalyst is described in this paper.



Rh_2(*S*-TBSP)$_4$

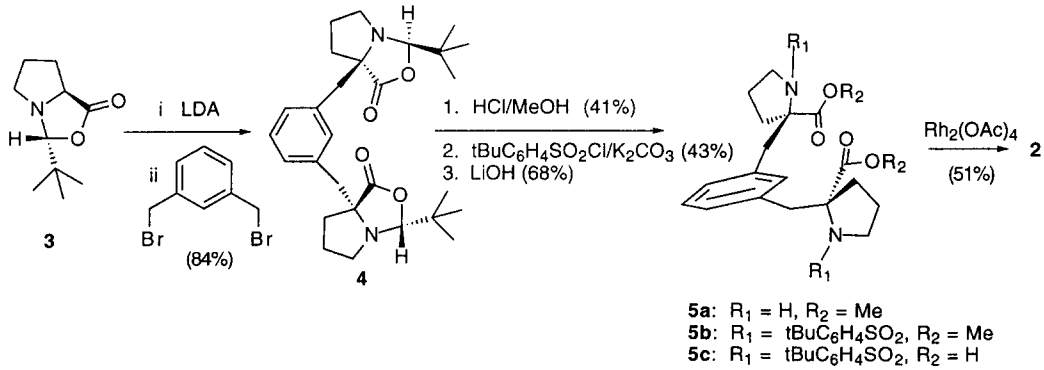
1



2

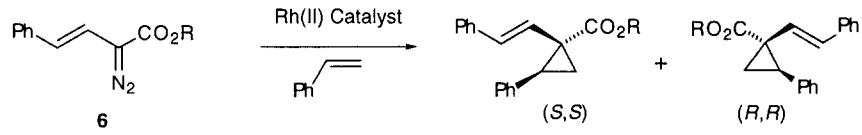
The general strategy that was used to prepare **2** is based on the chemistry developed by Seebach[6] for the stereospecific alkylation of proline. The cyclic aminal **3** is readily derived from the condensation of (*S*)-proline with pivalaldehyde.[6] Alkylation of an excess of the enolate derived from **3** with α,α'-dibromo-*m*-xylene resulted in the formation of a single diastereomer of the bis-functionalized derivative **4** in 84% yield. The stereochemistry of **4** is assigned on the basis of the well-established studies by Seebach.[6] The hydrolysis of sterically crowded 1-aza-3-oxabicyclo[3.3.0]octan-4-ones can be difficult,[6] and in the case of **4**, an indirect method was required for the hydrolysis. Methanolysis of **4** under acidic conditions generated the diester **5a** in 41% yield which was successfully sulfonated to **5b** (43% yield) and then hydrolyzed to the diacid **5c** (68% yield). High temperature ligand exchange between rhodium(II) acetate and **5c** resulted in the formation of the dirhodium complex **2**[7] as a green powder in 51% yield. The HRMS FAB data indicated that **2** was a dirhodium complex containing two of the bidentate ligands. 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.[8]

Scheme 1



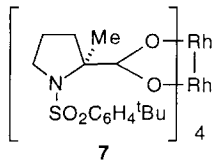
Comparison studies of the efficiency of **1** and **2** as chiral catalysts for cyclopropanation of styrene by the vinyldiazoacetate **6** are summarized in Table 1. Even though the standard prolinate catalyst **1** results in the highest levels of asymmetric induction, the bidentate catalyst **2** is an effective catalyst for asymmetric cyclopropanation resulting in asymmetric induction of 83% ee when the reaction was carried out in CH_2Cl_2 at -50 °C. However, the asymmetric induction profile of **2** is very different to the profile of **1**. The most striking difference between **1** and **2** is that the asymmetric induction by **2** is opposite in every case to that by **1**. Furthermore, the asymmetric induction with **1** is highly dependent on the nature of the ester group on the carbenoid and the reaction solvent but this is not the case with **2**. The use of a non-polar solvent with **1** has a dramatic effect on the asymmetric induction (from 74% ee in CH_2Cl_2 to 90% ee in pentane) but virtually no solvent effect was observed with **2**

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

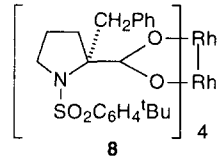


Entries	R	Solvent	Temp	Catalyst	%ee (abs config)[9]	yield, %
1	Me	CH_2Cl_2	25	**1**	74 (1*S*, 2*S*)[2c]	60
2	Me	CH_2Cl_2	25	**2**	59 (1*R*, 2*R*)	81
3	Me	CH_2Cl_2	-50	**1**	92 (1*S*, 2*S*)	62
4	Me	CH_2Cl_2	-50	**2**	83 (1*R*, 2*R*)	52
5	Me	pentane	25	**1**	90 (1*S*, 2*S*)[2c]	76
6	Me	pentane	25	**2**	56 (1*R*, 2*R*)	78
7	^{t}Bu	CH_2Cl_2	25	**1**	9 (1*S*, 2*S*)[2c]	38
8	^{t}Bu	CH_2Cl_2	25	**2**	49 (1*R*, 2*R*)	59
9	Me	pentane	25	**7**	52 (1*S*, 2*S*)	81
10	Me	pentane	25	**8**	6 (1*R*, 2*R*)	65

(from 59% ee in CH_2Cl_2 to 56% ee in pentane). It has been suggested that the solvent effect for **1** may be due to changes in either ligand conformation[2b] or the transition state for the non-synchronous cyclopropanation.[1c] The lack of solvent effect in the asymmetric induction by **2**, which would be expected to be conformationally locked, is indicative that the solvent effect for **1** is due to changes in ligand conformation. A second trend that was observed for **1** is a dramatic drop in asymmetric induction on using a bulky ester on the carbenoid (from 74% ee for Me to 9% ee for ^{t}Bu). In the case of **2**, the asymmetric induction was fairly independent of ester size (from 59% ee for Me to 49% ee for ^{t}Bu). The substituted prolinates **7** and **8** were also evaluated as model compounds in order to probe why the asymmetric induction is opposite on going from **1** to **2**. The methyl derivative **7** caused a significant drop in the enantioselectivity compared to **1** (from 90% ee to 52% ee) while the benzyl derivative **8** resulted in a slight preference for the other enantiomer of the cyclopropane. Therefore, it appears that introduction of functionality at the C-2 position of the proline tends to decrease or even reverse the asymmetric induction in the cyclopropanation. A possible explanation of this interesting effect could be that the 2-substituent alters the preference of the binding orientation of the carbenoid to the complex.[1c]



7



8

In summary, the bidentate prolinate catalyst **2**, represents a novel D_2 symmetric catalyst that has been used to probe why Rh_2(*S*-TBSP)$_4$ (**1**) is such an effective chiral catalyst for asymmetric cyclopropanations. The difference in the asymmetric induction profile between **2** and **1** appears to be due to the fact that **2** is rigid while **1** has greater conformational flexibility. Further studies are in progress to design other bidentate prolinate complexes as catalysts for asymmetric transformations.

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7. Spectral data for **2:** IR (neat) 2962, 1598, 1396, 1339 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, 8 H, *J* = 8.6 Hz), 7.52 (d, 8 H, *J* = 8.6 Hz), 7.07 (t, 2 H, *J* = 7.6 Hz), 6.87 (d, 4 H, *J* = 7.6 Hz), 6.78 (s, 2 H), 4.03 (d, 4H, *J* = 13.5 Hz), 3.45-3.41 (m, 4 H), 3.20-3.29 (m, 4 H), 2.66 (d, 4 H, *J* = 13.5 Hz), 2.43-2.34 (m, 4 H), 1.95-1.40 (m, 12 H), 1.35 (s, 36 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 191.0, 155.9, 138.5, 136.6, 128.9, 128.3, 127.6, 125.8, 74.5, 50.1, 42.6, 38.7, 34.9, 31.0, 22.31; HRMS(FAB) calcd for $C_{76}H_{93}N_4O_{16}Rh_2S_4$ (M + H), 1651.3580, found (m + H) 1651.3603.

8 Modeling studies of **5c** bound to dirhodium show that the up-down arrangement of the sulfonyl groups is 27 Kcal/mole more stable than the up-up arrangement.

9. The enantiomeric excess was determined by chiral HPLC (Chiral OD column, 25 x 0.46 cm), flow rate 1.0 mL/min, 0.5% 2-propanol in hexanes; UV 254 nm; T_R = 14 min (1*R*, 2*R*), 17 min (1*S*, 2*S*).

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