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A rigid dirhodium(II) carboxylate as an efficient catalyst for the asymmetric cyclopropanation of olefins

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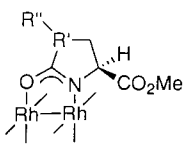
Abstract

The dirhodium(II) complex **7** of (1*S*,3*R*,4*R*)-2-(*p*-*tert*-butylphenylsulphonyl)-2-aza-bicyclo[2.2.1]heptane-3-carboxylic acid (**3**) (or its enantiomer) was synthesised in four steps from cyclopentadiene, (*R*)- or (*S*)-phenylethylamine and methyl glyoxylate. Complex **7** was evaluated as a catalyst in the asymmetric cyclopropanation of alkenes with vinyl- and phenyl-diazoesters, resulting in enantioselectivity of up to 92%. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium; Cyclopropanation; Asymmetric catalysis

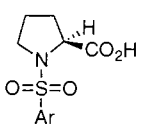
1. Introduction

In 1966, Nozaki et al. presented the first example of an asymmetric carbenoid transfer [1]. With the use of a chiral salicylaldimine–copper(II) complex, a modestly enantioselective cyclopropanation of styrene with ethyl diazoacetate was achieved. Since then, a number of efficient catalytic systems have been developed, mainly based on copper salts [2] and more recently, on rhodium salts [3–5]. Among the most well-known rhodium catalysts are the dirhodium(II) carboxamidates **1** (Chart 1) developed by Doyle and co-workers [3a,b].



1

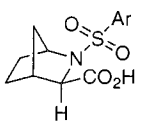
Rh_2(5*S*-MEPY)$_4$ R'=C, R''=H



2

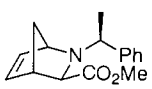
(*S*)-TBSP: Ar= (*p*-*t*-Bu)Ph

(*S*)-DOSP: Ar= (*p*-dodecyl)Ph



3

Ar= (*p*-*t*-Bu)Ph



4

(Chart 1)

The intense studies in the area of asymmetric cyclopropanation can be attributed to the use of the cyclopropane moiety as a building block for organic synthesis [6]. For example, vinylcyclopropanes are known to undergo a variety of stereospecific rearrangements which allow access to complex carbon skeleta that may contain one or more quaternary carbons [7]. Vinylcyclopropanes can be prepared, in a highly diastereoselective manner [8], by using vinyldiazoesters as the carbenoid precursor. However, the presence of a vinyl or aryl substituent in the diazoester decreases its electrophilic character and thereby also its ability to form carbenoid intermediates. The dirhodium carboxamidate catalysts are not active enough to form a carbenoid complex with these diazoesters. Instead, the diazoester rearranges to the corresponding pyrazole [3c]. On the other hand, dirhodium carboxylates are known to be kinetically competent and catalyse the reaction without any rearrangement of the vinyldiazoester [9]. Davies and co-workers started to investigate the proline-derived carboxylic acids **2** (Chart 1), first reported by McKervey and co-workers [3d] as catalysts for the cyclopropanation of olefins with vinyl- and phenyldiazoacetates [3c]. For some olefins, the ligands (*S*)-TBSP and (*S*)-DOSP gave high levels of asymmetric induction. These ligands, which also proved to be useful for other carbene transformations [10], are now commercially available.

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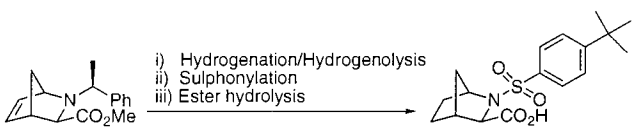
To further improve the results obtained with the ligands **2**, Davies' group developed a rigid D_2 symmetric complex with ligands consisting of two proline moieties [11]. The small rise in stereoselectivity obtained could be more related to the change of solubility of the Rh complex, which allowed the reaction to be run at a lower temperature, than to the change in ligand structure.

Our approach to improve the catalyst performance was to build a Rh dimer based on the rigid 2-azanorbornyl carboxylic acid **3** (Chart 1), which would ideally lead to a catalyst with a highly ordered D_2 symmetry. The 2-aza-norbornene skeleton **4** (Chart 1) has, after some simple modifications, shown remarkable usefulness as chiral ligand [12] and chiral base [13] in the field of asymmetric catalysis.

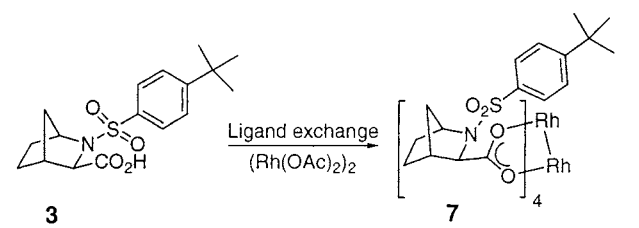
2. Results and discussion

The backbone **4** of the chiral ligand is formed via an aza-Diels–Alder reaction [14] from the starting materials, cyclopentadiene, methyl glyoxylate and (*R*)- or (*S*)-phenylethylamine. The *N*-sulphonylamino acid **3** is then prepared via a three-step procedure from adduct **4**. Reduction of the double bond and subsequent *N*-debenzylation proceeds quantitatively using Pd/C and H_2 (7 atm) in EtOH. After sulphonylation with (4-*tert*-butyl)benzenesulphonyl chloride, the ester **6** is hydrolysed in a refluxing mixture of aqueous NaOH and dioxane. The overall yield of ligand **3** from **4** is 75% (Scheme 1).



4 **3**

Scheme 1. (i) H_2 (7 atm), 5% Pd/C (20 wt.%), EtOH, r.t., 98%. (ii) (4-*tert*-Bu)benzene sulphonyl chloride (one equivalent), Et_3N (two equivalents), CH_2Cl_2, 0°C to r.t., 80%. (iii) NaOH (2 M)/dioxane: 1/1, reflux, 95%.



3 **7**

Scheme 2. $[Rh(OAc)_2]_2$ (one equivalent), **3** (seven equivalents), PhCl, K_2CO_3, reflux, 54%.

The chiral dimeric Rh catalyst **7** was prepared via a ligand exchange reaction from $[Rh(OAc)_2]_2$ and an excess of sulphonylated amino acid **3** (Scheme 2).

The rhodium complex **7** was evaluated in the cyclopropanation reaction of olefins. For the carbene source, the diazoester (**8** or **9**) was used (Table 1).

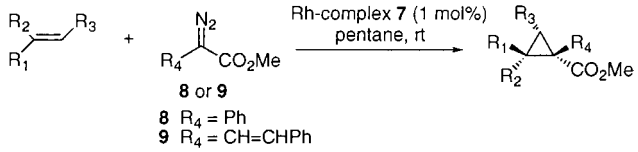
All reactions were run at room temperature with pentane as solvent. These conditions are reported to be optimal for similar catalytic systems [3c] and also proved to be the best with our ligand [15]. The substrates screened were styrene derivatives (Table 1, entries 1–10) and cyclic enol ethers (Table 1, entries 11–14). The best results were obtained with diazoester **8** and *p*-methyl styrene (92% ee, entry 3). Cyclic enol ethers were transformed into the corresponding bicyclic product with enantioselectivity in the range 65–75% (entries 11–14), the ee having no obvious correlation to the size of the ring (five- or six-membered).

With the selectivity model proposed in the literature that assumes a D_2 symmetric arrangement of the active Rh catalyst [3c], our hypothesis was that a more rigid and bulky ligand would better keep the D_2 symmetry of the complex and thereby increase the stereoselectivity in the reaction. Unfortunately, our results suggest this is not the case. The asymmetric induction in the cyclopropanation reaction using our Rh complex **7** is similar to the enantioselectivity obtained by the proline analogue Rh_2-(*S*)-TBSP. A comparison of our results with those presented in the literature [3c,10] shows different trends in the enantiomeric excess when changing the electronic nature of the alkene. Increasing the electron density of the double bond in the substrate (Table 1, entries 1–6, 9 and 10) results in a slightly increased or unaffected enantioselectivity. When using the Rh_2-(*S*)-TBSP catalyst the opposite behaviour is reported [3c]. Lowering the electron density of the double bond results in a dramatic drop in both yield and ee (compare entries 1 and 2 with 7 and 8). When introducing a second substituent on the alkene, the yield in the reaction drops, whereas the ee is slightly higher than with the monosubstituted analogue (compare entries 1 and 2 with 9 and 10). Cyclic enol ethers react with somewhat lower enantioselectivity than reported with the Rh_2-(*S*)-DOSP,[10d] even though the difference in ee could to some extent be explained by the lower solubility of Rh complex **7** in hydrocarbon solvent.

3. Conclusions

As a new member in the group of chiral metal catalysts, complex **7** performs well. The asymmetric induction in the reaction of olefins with vinyl- and

Table 1



Entry	R_1	R_2		R_3	Diazoester	Yield [a] (%)	ee [b] (%)
1	Ph	H		H	**8**	87	65
2	Ph	H		H	**9**	95	82
3	(*p*-Me)Ph	H		H	**8**	65	92
4	(*p*-Me)Ph	H		H	**9**	80	77
5	(*p*-MeO)Ph	H		H	**8**	82	82
6	(*p*-MeO)Ph	H		H	**9**	63	83
7	(*m*-NO_2)Ph	H		H	**8**	60	20
8	(*m*-NO_2)Ph	H		H	**9**	30	50
9	Ph	Me		H	**8**	55	73
10	Ph	Me		H	**9**	45	90
11	H		$-O(CH_2)_2-$		**8**	72	75
12	H		$-O(CH_2)_2-$		**9**	70	68
13	H		$-O(CH_2)_3-$		**8**	85	65
14	H		$-O(CH_2)_3-$		**9**	60	67

[a] The diastereoselectivity is above 20:1 for all substrates in favour of the *trans* product (determined by ^{1}H-NMR spectroscopy).
[b] See Section 4 for determination of enantiomeric excess.

phenyl-diazoacetates is high for substrates containing electron-donating groups and slightly lower for cyclic enol ethers. Both enantiomers of the optically pure bicyclic ligands are easily prepared on a large scale and should thus have a great potential in the field of asymmetric catalysis.

4. Experimental

4.1. General comments

For general experimental information, see Ref. [16]. All reactions were run under N_2, using dry glassware. Pd/C was purchased from Lancaster Chemical or Aldrich. Pentane used as solvent was dried over activated molecular sieves before use. Chlorobenzene was distilled from CaH_2 and stored over activated molecular sieves. ^{1}H- and ^{13}C-NMR spectra were recorded at 400 and 100.4 MHz, respectively, using $CDCl_3$ as solvent. GC analysis was performed on a Varian 3400 capillary gas chromatograph using a CP–Chirasil–Dex CB (25 m/0.25 mm I.D.) column under isothermal conditions, with N_2 as carrier gas and a flame ionisation detector. Mass spectra were recorded under electronic impact (70 eV) using a Finnigan MAT GCQ PLUS system.

The Rh catalyst was prepared in a four-step route as described below.

4.2. (1R,3R,4S)-2-[(1S)-Phenylethyl]-2-aza-bicyclo[2.2.1]hept-5-ene-3-carboxylic acid methyl ester (4)

Compound **4** was prepared via an aza-Diels–Alder reaction using a published procedure [14a]. All the physical and spectroscopic data for compound **4** were in complete agreement with the reported data for the racemic compound [14a]. $[\alpha]_D^{25} = +118.5°$ (*c* 1.51, CH_2Cl_2).

4.3. (1S,3R,4R)-2-Aza-bicyclo[2.2.1]heptane-3-carboxylic acid methyl ester (5)

Hydrogenation and hydrogenolysis of **4** to the amino ester **5** was achieved in quantitative yield following a published procedure [12c]. The crude product was sulphonylated to **6** without further purification.

4.4. (1S,3R,4R)-2-(p-tert-butylphenylsulphonyl)-2-aza-bicyclo[2.2.1]heptane-3-carboxylic acid methyl ester (6)

To the amino ester **5** (0.60 g, 3.6 mmol) and Et_3N (0.72 g, 7.1 mmol) in CH_2Cl_2 (6 ml), a solution of (4-*tert*-butyl)-benzene sulphonyl chloride (0.83 g, 3.6 mmol) in CH_2Cl_2 (4 ml) was added dropwise at 0°C. The reaction mixture was then stirred at room tempera-

ture (r.t.) until all of the amino ester was consumed (2 h, monitored by TLC). The reaction mixture was diluted with Et_2O (20 ml) and washed with HCl (0.1 M, 20 ml), H_2O (20 ml), $NaHCO_3$ (satd., 20 ml) and NaCl (satd., 20 ml). The ethereal solution was then dried with $MgSO_4$ and the solvent evaporated under reduced pressure to obtain the crude product as white crystals (1.24 g, 93%). Purification was performed using flash chromatography (10:1–10:3 pentane–EtOAc) to obtain pure **6** (1.06 g, 80%). R_f 0.37 (3:1 pentane–EtOAc); m.p. 100–102°C; $[\alpha]_D^{25} = +52.5°$ (*c* 1.10, $CHCl_3$); IR (KBr, cm^{-1}): 3050, 2854, 1751, 1640, 1460, and 1159; ^{1}H-NMR: δ 7.86 (2H, d, $J = 8.8$ Hz), 7.50 (2H, d, $J = 8.8$ Hz), 4.12 (1H, m), 3.98 (1H, br s), 3.60 (3H, s), 2.71 (1H, dm, $J = 4.5$ Hz), 2.05–1.95 (2H, m), 1.78–1.68 (1H, m), 1.57–1.44 (2H, m), 1.35–1.24 (1H, m), and 1.33 (9 H, s); ^{13}C-NMR: δ 171.1, 156.4, 137.3, 127.6, 125.7, 64.4, 59.9, 52.1, 43.3, 36.3, 35.0, 31.1, 29.4, and 27.7; MS (GC) *m*/*z* (rel. intensity) 352 ($M + H^+$, < 1), 293(19), 292(100), 264(57), 197(29) and 133(14).

4.5. (1S,3R,4R)-2-(p-tert-butylphenylsulphonyl)-2-aza-bicyclo[2.2.1]heptane-3-carboxylic acid (3)

Ester hydrolysis of **6** to form **3** was performed using a 1:1 mixture of NaOH (2 M) and dioxane. The ester **6** (1.24 g, 3.3 mmol) was refluxed in 40 ml of this mixture until the reaction was complete (4 h according to TLC). After cooling to r.t., the solution was acidified (conc. HCl) and the carboxylic acid was extracted from the aqueous phase using CH_2Cl_2 (3 × 20 ml). The organic layers were combined, dried with $MgSO_4$ and evaporated under reduced pressure to afford the protected amino acid **3** (1.06 g, 95%). m.p. 157–159°C; $[\alpha]_D^{25} = +41.5°$ (*c* 1.82, $CHCl_3$); IR (KBr, cm^{-1}): 3436, 2964, 1724, 1642, and 1159; ^{1}H-NMR: δ 7.86 (2H, d, $J = 8.4$ Hz), 7.52 (2H, d, $J = 8.4$ Hz), 4.13 (1H, m), 3.94 (1H, m), 2.87 (1H, d, $J = 4.5$ Hz), 1.96 (1H, m), 1.93–1.84 (1H, m), 1.77–1.68 (1H, m), 1.50–1.42 (1H, m), 1.38–1.30 (2H, m) and 1.34 (9 H, s); ^{13}C-NMR: δ 174.5, 156.9, 136.4, 127.7, 126.0, 64.7, 60.3, 43.2, 36.6, 35.2, 31.1, 28.6, and 27.4; MS *m*/*z* (rel. intensity) 292 ($M^+ - CO_2H$, 33), 264(19), 255(17), 254(100), 198(8), 196(52) and 134(14); Anal. Calc. for $C_{17}H_{23}NO_4S$: C, 60.50; H, 6.87; N, 4.15; Found: C, 60.55; H, 7.00; N, 4.00%.

4.6. [(1S,3R,4R)-2-(p-tert-butylphenylsulphonyl)-2-aza-bicyclo[2.2.1]heptane-3-carboxylate]dirhodium (7)

The sulphonylated amino acid **3** (0.2 g, 0.59 mmol) and $(Rh(OAc)_2)_2$ (37 mg, 0.085 mmol) was dissolved in chlorobenzene. The solution was refluxed over K_2CO_3 (changed every 2 days) using a Soxlet extractor. After 4–6 days of reflux the reaction mixture was concentrated under reduced pressure. The residual was dissolved in CH_2Cl_2 (15 ml), washed with $NaHCO_3$ (10 ml), dried ($MgSO_4$) and concentrated in vacuo to afford the Rh complex **7** (0.1 g, 77%). After flash chromatography (2:1 pentane–EtOAc) the pure product was obtained (70 mg, 54%). R_f 0.69 (1:1 pentane–EtOAc); m.p. 335°C (dec.); $[\alpha]_D^{23} = +224.2°$ (*c* 0.10, $CHCl_3$); IR ($CDCl_3$, cm^{-1}): 3157, 2980, 2244, 1609, 1385, and 1150; ^{1}H-NMR: δ 7.82 (2H, d, $J = 8.9$ Hz), 7.51 (2H, d, $J = 8.9$ Hz), 3.82 (2H, m), 2.67 (1H, m), 1.81 (1H, d, $J = 9.8$ Hz), 1.60–1.14 (3H, m), 1.34 (9H, s), 1.08 (1H, m), and 0.96 (1H, d, $J = 9.8$ Hz);^{13}C-NMR: δ 190.7, 156.0, 137.6, 127.6, 125.8, 66.1, 59.2, 43.7, 36.7, 35.1, 31.1, 28.5, and 27.3; MS *m*/*z* (rel. intensity) 337(4), 293(19), 292(100), 265(14), 264(88), 197(42), 119(40) and 91(51).

4.7. Methyl phenyldiazoacetate (8)

The methyl phenyldiazoacetate was prepared in a one-step procedure [17] from methyl phenylacetate (one equivalent) and *p*-toluenesulphonyl azide (1.2 equivalents) in acetonitrile.

4.8. Methyl (E)-2-diazo-4-phenylbutenoate (9)

The diazoester **9** was prepared from malonic acid and phenylacetaldehyde in a three-step procedure [7a,18].

4.9. Rh(II) catalysed cyclopropanation reaction — general procedure

The olefin (five equivalents) was added to a slurry of Rhodium complex **7** (0.01 equivalents) in pentane (3 ml). The mixture was stirred at r.t. during slow addition (6 h) of a pentane solution of diazoester (one equivalent). After complete addition, another 6 h of stirring followed. The reaction mixture was then concentrated under reduced pressure and purified using flash chromatography (pentane–EtOAc).

The enantiomeric excess of the cyclopropanation products in entry 2–12 and 14 (Table 1) was determined by HPLC analysis using a OD–H column. The solvent system used was 2% *i*-PrOH in hexane and the flow was varied between 0.4 and 0.5 ml min^{-1}. In entry 1, shift reagent was used and in entry 13, a GC-analysis of the ee was performed using a Chirasil DexCB-column.

Acknowledgements

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