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New Chiral Rhodium(II) Carboxylates and their Use as Catalysts in Carbenoid Transformations

Leigh Ferris,[a] David Haigh[b] and Christopher J. Moody[a*]

[a]Department of Chemistry, University of Loughborough, Loughborough, Leicestershire LE11 3TU, U.K.

[b] SmithKline Beecham Pharmaceuticals, Great Burgh, Yew Tree Bottom Road, Epsom, Surrey KT18 5XQ, U.K.

Abstract: New chiral dirhodium(II) carboxylates **11-15** have been prepared from the half phthalate esters **6-8** and the pyrroles **9** and **10**, and their use as catalysts for the decomposition of diazocarbonyl compounds **16** and **18** investigated.

The development of chiral catalysts for asymmetric reactions of metal carbenoids has been widely studied[1] since the first report by Nozaki and co-workers that decomposition of ethyl diazoacetate in the presence of a copper(II) complex with a chiral Schiff base ligand resulted in enantioselective cyclopropanation of styrene.[2] Subsequent development of such ligands by Aratani and co-workers resulted in much improved enantioselectivities (>90% e.e.),[3] and more recent work from the groups of Pfaltz,[4] Masamune,[5] and Evans[6] has produced copper catalysts capable of effecting enantioselective cyclopropanations in >99% e.e. Although copper based catalysts are extremely effective in cyclopropanation reactions, dirhodium(II) compounds, first introduced by Teyssié and coworkers,[7] are generally superior catalysts for diazo compound decomposition since they mediate a wider range of carbenoid processes.[8,9]

The chiral dirhodium catalysts reported to date are of three types: (i) chiral rhodium(II) carboxylates **1**, first reported by Noels in 1982,[10] but then used by McKervey[11-14] and Brunner,[15,16] and subsequently developed by Ikegami and Hashimoto[17-21] and Davies,[22,23] effect enantioselective cyclopropanation and C-H insertion reactions; (ii) chiral rhodium(II) carboxamides **2** most notably the dirhodium(II) tetrakis(methyl 2-pyrrolidine-5-carboxylate), $Rh_2(MEPY)_4$, catalyst developed by Doyle and co-workers which effects highly enantioselective cyclopropanation, cyclopropenation and C-H insertion reactions;[24-27] and (iii) the chiral rhodium binaphtholphosphate, developed independently by McKervey[28] and Pirrung[29] which effects a range of rhodium carbenoid transformations. Although rhodium(II) carboxamides **2** are less reactive catalysts for the decomposition of diazo compounds than the carboxylates **1**, they usually exhibit higher enantioselectivities since the chiral centre in the ligand is in closer proximity to the reacting centre in the presumed metal carbenoid intermediate, *e.g.* **3**.[1] We now report the first examples of a new family of chiral rhodium catalysts **4** and **5** which retain the higher catalytic activity of the carboxylates **1**, but place the chiral centre nearer to the reacting carbenoid (Figure 1).

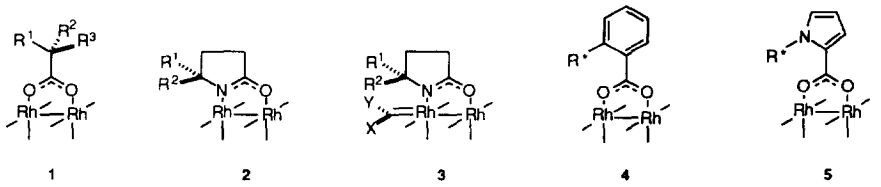
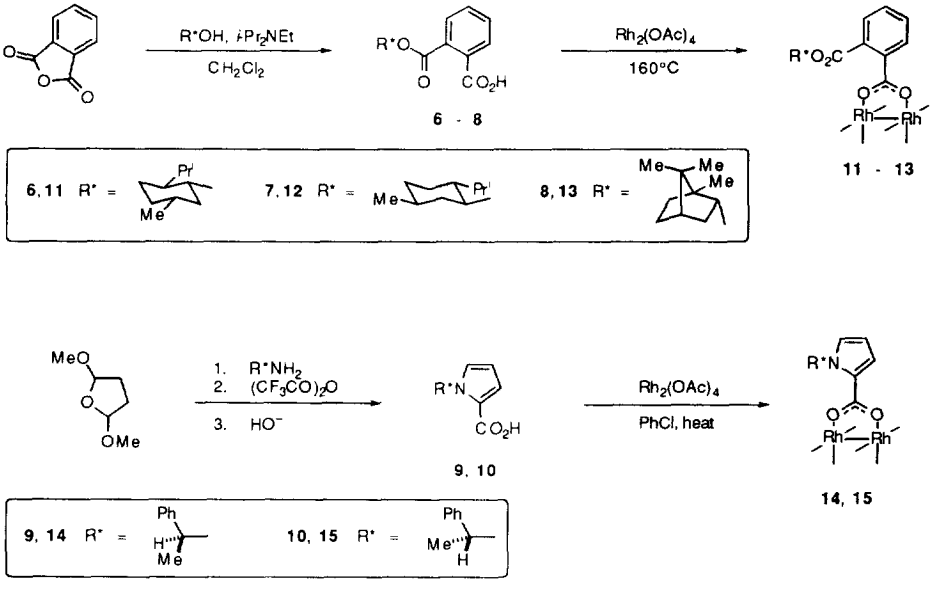


Figure 1. Only one of the four ligands bridging the dirhodium core is shown.

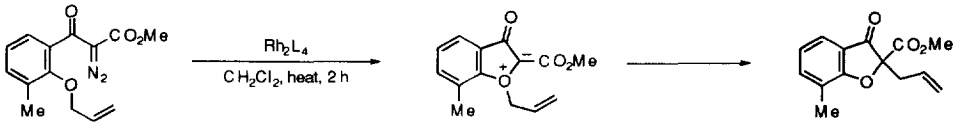
The five carboxylate ligands chosen for initial study were the half esters of phthalic acid derived from (-)- and (+)- menthol **6** and **7**[30] and (-)-borneol **8**,[31] and the pyrrole-2-carboxylates **9** and **10**,[32] containing a chiral substituent on nitrogen. The phthalate half esters were readily prepared from phthalic anhydride and the appropriate alcohol in the presence of Hünig's base. The pyrrole based ligands **9** and **10** were prepared by reaction of (S)- and (R)-1-phenylethylamine respectively with 2,5-dimethoxytetrahydrofuran, followed by reaction with trifluoroacetic anhydride, and hydrolysis of the trifluoroacetyl group. Subsequent 'fusion' of the ligands with rhodium(II) acetate at 160°C or, in the case of **9** and **10**, heating in boiling chlorobenzene gave the corresponding rhodium(II) carboxylates **11-15** as green solids (Scheme 1).



Scheme 1

The catalytic activity of **11-15** in the decomposition of diazocarbonyl compounds and possible asymmetric induction therein was examined in two cases. Firstly following the work of McKervey and co-workers,[28] we studied the decomposition of the diazoketoester **16**, in which the intermediate oxonium ylide undergoes [2,3]-sigmatropic rearrangement to give the benzofuran-3-one **17** (Scheme 2). Thus treatment of **16** with each of the catalysts **11-15** in boiling dichloromethane gave the expected product **17** in good yield. Analysis by HPLC on a chiral column indicated that the product was formed in about 12% e.e. (Table 1),[33]

with the catalysts **11, 12, 14** and **15**. As expected the pairs of enantiomeric catalysts gave the opposite enantioselectivity.



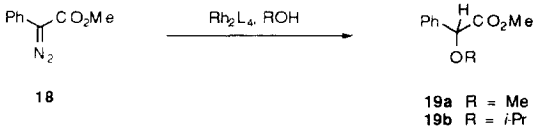
16 **17**

Scheme 2

Table 1

Catalyst	*Origin of ligand*	*Yield 17 /%*	*e.e. /%*
11	(-)-menthol	88	13
12	(+)-menthol	92	13
13	(-)-borneol	90	0
14	(S)-1-phenylethylamine	90	12
15	(R)-1-phenylethylamine	92	12

Having established that the new catalysts did effect asymmetric induction, albeit at a low level, in the above ylide rearrangement, we then investigated their use in O-H insertion reactions. Although the rhodium(II) catalysed decomposition of diazocarbonyl compounds in the presence of hydroxylic compounds usually results in the formal insertion of the carbenoid into the O-H bond in good yield,[34,35] the precise details of the process, and in particular, the stage at which the new metal-free sp^3-centre is established, remain unknown.[36,37] Despite this uncertainty, the diazoester **18** was decomposed in the presence of methanol or 2-propanol using the chiral catalysts **11-15** to give the expected α-alkoxyesters **19** in good yield (90-94%) (Scheme 3). However analyses of the products by NMR using a chiral shift reagent established that they were formed with 0% e.e.[38] The reaction was also carried out using the known chiral rhodium catalysts, rhodium(II) (R)-*N*-benzenesulfonylprolinate and rhodium(II) (S)-MEPY, but again no enantioselectivity was observed. In the only other example of a carbenoid X-H insertion reaction using chiral catalysts, Brunner did observe up to 12% e.e. in the S-H insertion reaction of 3-diazo-2-butanone with thiophenol.[16] This result does not preclude the possibility that O-H insertion reactions should be subject to asymmetric catalysis, and therefore further studies using modified catalysts are underway.



18

19a R = Me
19b R = *i*-Pr

Scheme 3

Acknowledgements

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32. Ligands **9** and **10**; m.p. 83.5-84.5°C; $[\alpha]_D \pm 207.6°$ (c = 0.6, $CHCl_3$).
33. HPLC analysis was carried out on a Chiralcel OD column using 1% 2-propanol in hexane as eluant at a flow rate of 0.3 ml/min. Compound **17** derived from catalyst **11** has $[\alpha]_D + 16.3°$ (c = 2.3, CH_2Cl_2).
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38. NMR Analysis performed in $CDCl_3$ using $Eu(hfc)_3$ (0.5 equiv) as chiral shift reagent.

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