

## Asymmetric Synthesis in Carbon–Carbon Bond Forming Reactions of $\alpha$ -Diazoketones catalysed by Homochiral Rhodium(II) Carboxylates

Michael Kennedy, M. Anthony McKerverey,\* Anita R. Maguire, and Gregory H. P. Roos

Department of Chemistry, University College, Cork, Ireland

Partial asymmetric synthesis has been observed in intramolecular C–H insertion, aromatic cycloaddition, and cyclopropanation reactions of  $\alpha$ -diazoketones catalysed by homochiral rhodium(II) mandelate and rhodium(II) carboxylates derived from L-proline.

Rhodium(II) carboxylates are very efficient catalysts for the decomposition of  $\alpha$ -diazocarbonyl compounds and their use has largely replaced copper-based catalysts in many characteristic reactions such as C–H insertion, cyclopropanation, aromatic cycloaddition, and electrophilic aromatic substitution.<sup>1</sup> Recently we added rhodium(II) mandelate to the range of useful, catalytically active rhodium(II) salts.<sup>2</sup> The introduction of rhodium(II) mandelate for diazoketone decomposition raises the additional interesting prospect of asymmetric catalysis through its use in homochiral form. Although some success has been achieved with chiral copper catalysts for intermolecular cyclopropanation,<sup>3</sup> they are not amenable to C–H insertion or aromatic cycloaddition reactions. We now report preliminary results of the first use of homochiral rhodium(II) catalysts in carbon–carbon bond forming reactions of  $\alpha$ -diazocarbonyl precursors.

Three typical intramolecular diazocarbonyl reactions were chosen, *viz.* aromatic cycloaddition, C–H insertion, and alkene cyclopropanation. In addition to rhodium(II) (*S*)-mandelate (**1**),<sup>4</sup> two new carboxylates (**2**) and (**3**) were prepared by treating *N*-benzenesulphonyl-L-proline and *N*-1-naphthalenesulphonyl-L-proline, respectively, with Na<sub>4</sub>Rh<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>.

Asymmetric synthesis in an aromatic cycloaddition reaction was probed with reference to the synthesis of *trans*-1-methylbicyclo[5.3.0.]decan-2-one (**5**) *via* cyclisation of diazoketone (**6**) to bicyclic trienone (**7**), a reaction already known to be catalysed efficiently by rhodium(II) mandelate. Although some enantioselection was observed with rhodium(II) (*S*)-mandelate, the extent (25%) was rather less than that obtained with proline carboxylate (**3**). Exposure of diazoketone (**6**) to catalyst (**3**) in hot dichloromethane furnished the optically active trienone (**7**) (*ca.* 80%) which did not respond well to NMR chiral shift reagents. However, reduction of (**7**) with lithium tri-*t*-butoxyaluminumhydride in ether furnished alcohol (**8**), [ $\alpha$ ]<sub>D</sub><sup>20</sup> –9.44° (8.81, CH<sub>2</sub>Cl<sub>2</sub>), as a 3 : 1 mixture of epimers which was amenable to NMR analysis. The predominant epimer was presumed to be that with the methyl and hydroxy group *cis* to each other on the basis of steric control of the direction of hydride addition. The epimers were not separated as such, but their <sup>1</sup>H NMR signals were clearly identifiable in the presence of Eu(tfc)<sub>3</sub> [tris(trifluoroacetylcamphorato)europium(II)], which produced a complete separation of the epimeric methyl groups and further resolution of the enantiomers of the *cis* isomer, indicating an

