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STEREOCHEMISTRY AND MECHANISM OF THE ASYMMETRIC HYDROGENATION OF UNSATURATED CARBOXYLIC ACIDS CATALYZED BY BINAP—RUTHENIUM(II) DICARBOXYLATE COMPLEXES

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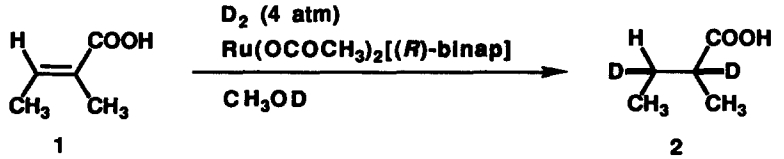
Summary: The stereochemical course and pattern of deuterium incorporation of the hydrogenation of unsaturated carboxylic acids catalyzed by $Ru(OCOCH_3)_2$(binap) indicate operation of a mechanism involving metal monohydride complexes.

We have reported that BINAP—Ru(II) complexes (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) serve as excellent catalysts for asymmetric hydrogenation of a series of functionalized olefins and ketones.[1] The scope is wider than that of hydrogenations with any other chiral transition-metal complexes so far reported.[2] The mechanism of the hydrogenation catalyzed by d^6 Ru(II) species differs from that of the well studied d^8 Rh(I)-promoted reaction.[3] We here describe some experimental results relevant to the mechanism of the asymmetric hydrogenation of unsaturated carboxylic acids[4] catalyzed by BINAP—Ru dicarboxylate complexes.[5]

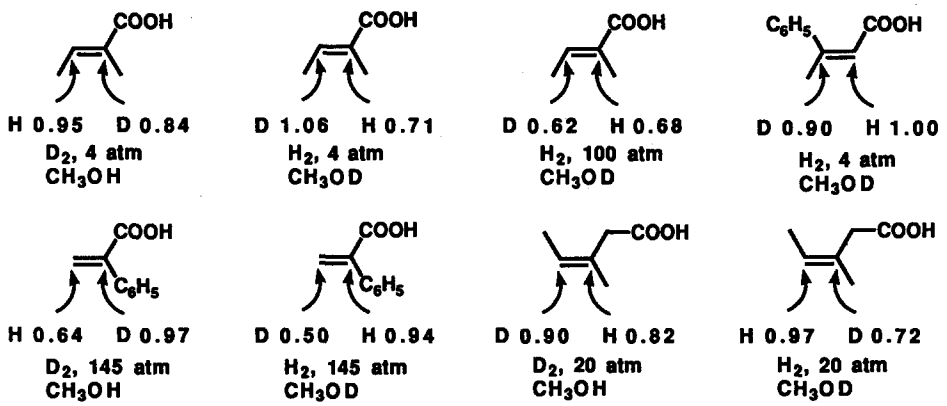
First, we examined stereochemistry of the hydrogenation. When reaction of (*E*)-cinnamic acid was performed under D_2 atmosphere (4 atm) in CH_3OD containing 0.9 mol % of $Ru(OCOCH_3)_2$[(*S*)-binap] for 168 h at 20 °C, *threo*-3-phenylpropionic acid-2,3-d_2[6,7] was obtained in quantitative yield. The threo configuration determined by the ^2D noise-decoupled ^1H NMR spectrum giving $J_{C(2)H\text{-}C(3)H}$ = 6.4 Hz (cf. 9.1 Hz for the erythro stereoisomer)[6] indicates that deuterium addition across the olefinic bond occurs with cis stereochemistry. Similarly, deuteration of tiglic acid (**1**) gave the cis product **2** having 2*R*,3*R* configuration in 91% *ee*.[8] The relative configuration was confirmed by comparison of the ^1H NMR spectrum with that of a sample obtained by reaction using $RhCl[P(C_6H_5)_3]_3$ as catalyst[9] and the 2*R* configuration was deduced from the structure of the product obtained with H_2 and CH_3OH.[4a]



1 **2**

In order to elucidate the origin of hydrogens incorporated in the products, the reaction of unsaturated acids was carried out under H_2 or D_2 atmosphere in CH_3OH or CH_3OD.[10] The extent of deuterium incorporation was determined by ^1H NMR analysis after distillation of the products. Although the results listed in Chart I are somewhat complicated because of kinetic isotope effects, substituent effects on stability and reactivity of intermediates, Ru-catalyzed isotope exchange between hydrogen gas and methanol,[11] etc., it is clear that, in the hydrogenation of acrylic acid derivatives, gaseous hydrogens are mainly introduced to the α positions and protons from solvents are incorporated into the β positions.[12] As the hydrogen pressure increases, the extent of incorporation of gaseous hydrogen at the β position increases. Notably, the pattern of hydrogenation of (Z)-3-methyl-3-pentenoic acid, a β,γ-unsaturated acid, is different; γ-hydrogens originate from gaseous hydrogens and β-hydrogens from protic molecules.

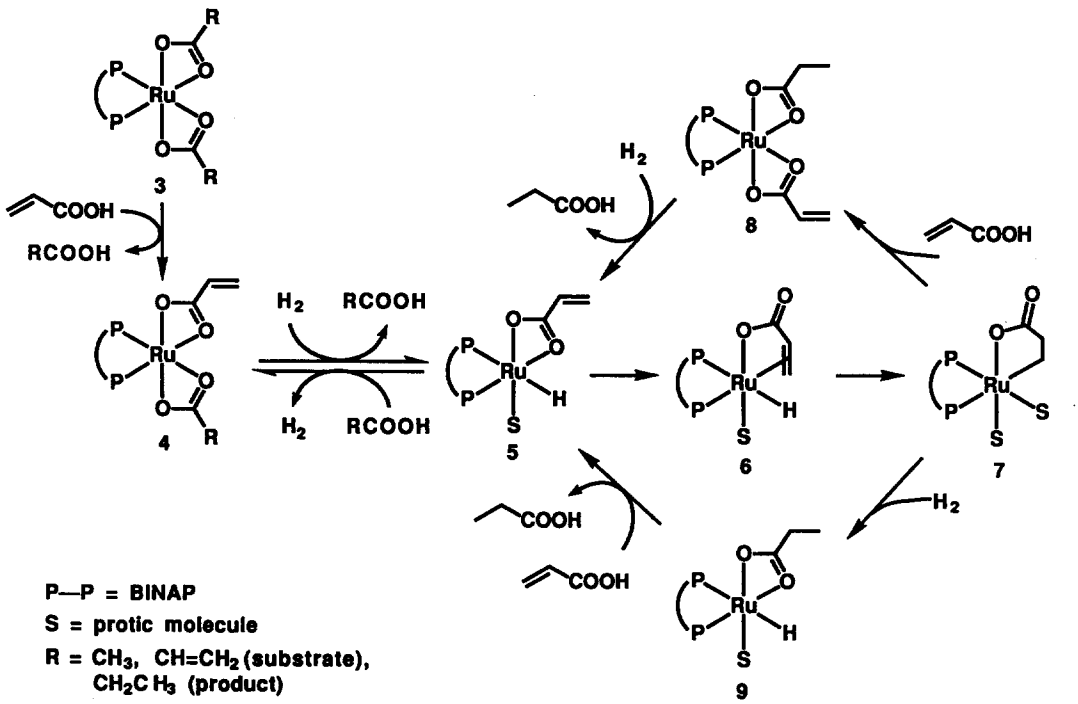
Chart I. Pattern of Hydrogen Incorporation



These facts suggest that the reaction of acrylic acids proceeds by a mechanism involving monohydride complexes[1c,13,14] and five-membered chelate complexes with alkyl—Ru bonds, as outlined in Chart II. The Ru diacetate complex **3** (R = CH_3) acting as catalyst precursor readily undergoes ligand exchange with acrylic acid substrate forming **4**.[12,15] Reaction of the dicarboxylate complex and dihydrogen eliminates a carboxylic acid molecule to generate Ru monohydride **5**, which in turn rearranges to form the olefin/RuH complex **6**. The olefin insertion leads to Ru—alkyl compound **7** having a five-membered structure,[16] whose metal—carbon bond is cleaved by either coordinated methanol or carboxylic acid to afford **8**. Reaction of the dicarboxylate complex **8** and dihydrogen gives the saturated product and **5**, completing the catalytic cycle. Under high hydrogen pressure, intermediate **7** may suffer hydrogenolysis to give **9**. The latter could undergo ligand exchange with unsaturated substrate giving back **5** or, alternatively, react with a carboxylic acid to regenerate the dicarboxylate

complex 4. In any event, the reaction is characterized by the operation of the monohydride mechanism. As a consequence, two hydrogen atoms are introduced to olefinic faces in a cis fashion from different sources (dihydrogen and solvent or two different dihydrogen molecules), in sharp contrast to the Rh(I) catalyzed reaction causing successive delivery of hydrogen atoms from the same hydrogen molecules.[3]

Chart II. Possible Reaction Pathway



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6. N. A. Dunham and M. C. Baird, *J. Chem. Soc., Dalton*, **1975**, 774.
7. The absolute configuration (2*R*,3*R* or 2*S*,3*S*) and *ee* value of the product have not been determined.
8. The *ee* value was determined by HPLC analysis (Chemco Nucleosil) of the amide derived from **2** and (*R*)-1-(1-naphthyl)ethylamine.
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10. The reactions were carried out in an autoclave under H_2 or D_2 in CH_3OH or CH_3OD containing 4.0 x 10^{-4}—8.7 x 10^{-4} *M* of $Ru(OCOCH_3)_2$(binap) and 0.17—0.26 *M* of the substrate.
11. For example, J. P. Collman, P. S. Wagenknecht, R. T. Hembre, and N. S. Lewis, *J. Am. Chem. Soc.*, **112**, 1294 (1990).
12. A similar result was obtained by J. Halpern. Personal communication to R. Noyori.
13. Monohydride mechanisms have been advanced for hydrogenation using Ru chloride catalysts. See: (a) D. Evans, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Nature*, **208**, 1203 (1965). (b) J. Halpern, J. F. Harrod, and B. R. James, *J. Am. Chem. Soc.*, **88**, 5150 (1966). (c) B. R. James, "Homogeneous Hydrogenation," J. Wiley, New York, 1973. (d) B. R. James, L. D. Markham, and D. K. W. Wang, *J. Chem. Soc., Chem. Commun.*, **1974**, 439. See also ref. 4b.
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15. Chart II does not refer to the configurations of intermediary complexes. Although the carboxylate ligands are assumed to form four-membered chelate rings for the sake of simplicity, methanol can act as ligand cleaving the chelate structure. $Ru(OCOCH_3)_2$(binap) having C_2 symmetry in solid state[5] exhibited in a 5:1 CD_3OD—CD_2Cl_2 mixture major ^{31}P NMR signals at δ 66.55 and 67.21 with an AB pattern (-70 °C) and ^1H NMR signals at δ 1.65 and 1.75 due to the acetate ligands (singlet, -80 °C), which indicate nonequivalency of the two phosphorus nuclei.[12] ^{31}P NMR spectrum of a mixture of $Ru(OCOCH_3)_2$(binap) and tiglic acid (1:1.5 mole ratio) in CD_3OD exhibited a singlet at δ 64.90 due to $Ru(OCO(CH_3)C{=}CHCH_3)_2$(binap) and an AB quartet centered at δ 64.39 and 65.41 (J_{AB} = 46.0 Hz) due to $Ru(OCOCH_3)(OCO(CH_3)C{=}CHCH_3)$(binap) in addition to a singlet at δ 64.95 due to the starting complex. The addition of a large excess of tiglic acid to this mixture resulted in only a singlet at δ 64.90. No substantial change in ^1H and ^{31}P NMR spectra has been observed in the course of the hydrogenation. We could not observe the formation of Ru hydride species by reaction of **3** (R = CH_3) and H_2.[12]
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