

Identification of a Further Transient Species relating to Rhodium-complex Catalysed Asymmetric Hydrogenation

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Interconversion of the diastereoisomeric rhodium enamide complexes (1) and (2) occurs by an intramolecular mechanism requiring an olefin dissociated species (3).

Asymmetric hydrogenation of dehydroamino acids may involve the rhodium enamide complexes (1) and (2). When the ligand is (*S,S*)-2,3-bis(diphenylphosphino)butane, *X*-ray structure analysis¹ demonstrates the configuration of the isolated complex (1a) to be opposite that of the product, assuming *cis*-transfer of hydrogen within the co-ordination sphere. This configuration is maintained in solution² and the second diastereoisomer (2a) cannot be detected^{1,3} although it is presumed to carry the flux of catalysis. When the ligand is (*R,R*)-1,2-bis[*o*-methoxyphenyl(phenyl)phosphino]ethane (dipamp) both enamide complexes are present in solution³ but the disfavoured isomer selectively absorbs H₂ at low temperatures to form an alkyrhodium hydride^{4,5} which is transformed to the hydrogenation product above -50 °C. It should be noted that these latter experiments were carried out on a reaction mixture biased from thermodynamic equilibrium in favour of the minor diastereoisomer.

Accurate data have been obtained for the rate of dissociation

of enamide complexes derived from 1,2-bis(diphenylphosphino)ethane applying the DANTE spin-excitation transfer technique⁶ to the ³¹P and ¹³C n.m.r. spectra of the enamide complexes. Dissociation of enamide and recombination from the solute pool⁷ is much faster than catalytic turnover⁵ with rate-constants of 1–20 s⁻¹ for the former step under ambient conditions. Application of the same procedure to the dipamp complex (1b) ⇌ (2b) at 325 K in methanol demonstrates a second process (Figure 1). This involves the direct interconversion of these complexes *without* enamide dissociation. The observation is amply supported by irradiation at several resonances of both diastereoisomers in turn. Nevertheless, there are too many variables (six excitation transfer *k* values and four *T*₁ values) and simplification was sought.

Judicious choice of oscillator frequency and pulse interval permitted simultaneous excitation of pairs of *P*-coupled lines in both resonances of the major diastereoisomer (2b). This

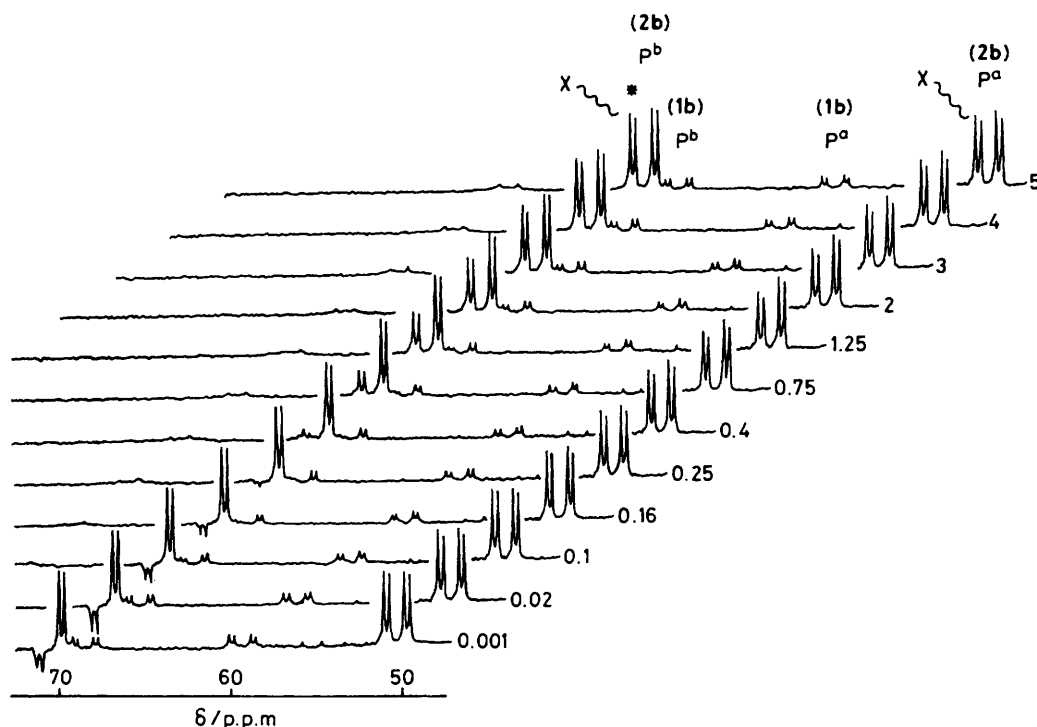
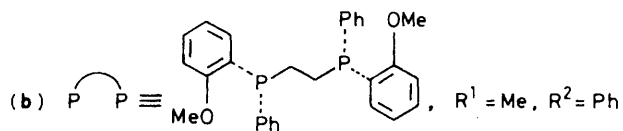
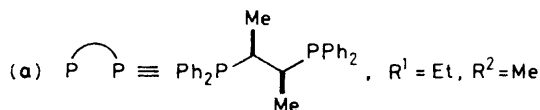
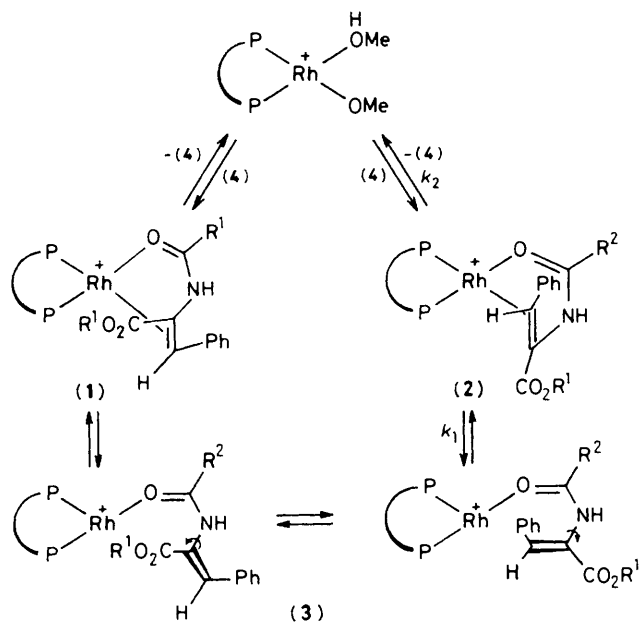
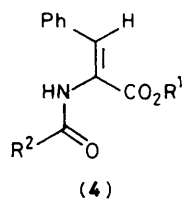


Figure 1. ³¹P N.m.r. spectrum of (1b) ⇌ (2b) at 325 K in MeOH, 121.47 MHz with population inversion at the starred frequency (*). The pre-acquisition delay (s) is indicated to the right of each trace. Peaks marked 'X', see Figure 2.



(c) as (b) but ^{13}C at amide CO



Scheme 1

procedure effectively separates out the major intermolecular process and reduces analysis of reaction (1b) \rightleftharpoons (2b) to a two-site problem (Figure 2), with excellent agreement for k_1 0.65 s^{-1} . Furthermore, the application of DANTE techniques to the ^{13}C n.m.r. spectrum of (1c) \rightleftharpoons (2c) in the presence of excess of enamide with excitation of the ^{13}C resonance due to the major diastereoisomer (2c) gave a good fit to k_1 0.65 s^{-1} and k_2 0.45 s^{-1} , and T_1 values of 12.5 and 25 s for bound and free enamide, respectively.

These results require that olefin dissociation according to Scheme 1 is the major pathway for interconversion of (1b) and (2b) via a dissociated state (3b), which could not have been observed by previous techniques. Halpern has amply demonstrated the critical importance of the 14-electron species $(\text{PPh}_3)_2\text{RhCl}$ in homogeneous catalysis of hydrogenation by Wilkinson's catalyst.⁸ It then seems necessary to consider the possibility that the dissociated species (3) may be involved in the catalytic cycle of asymmetric hydrogenation.

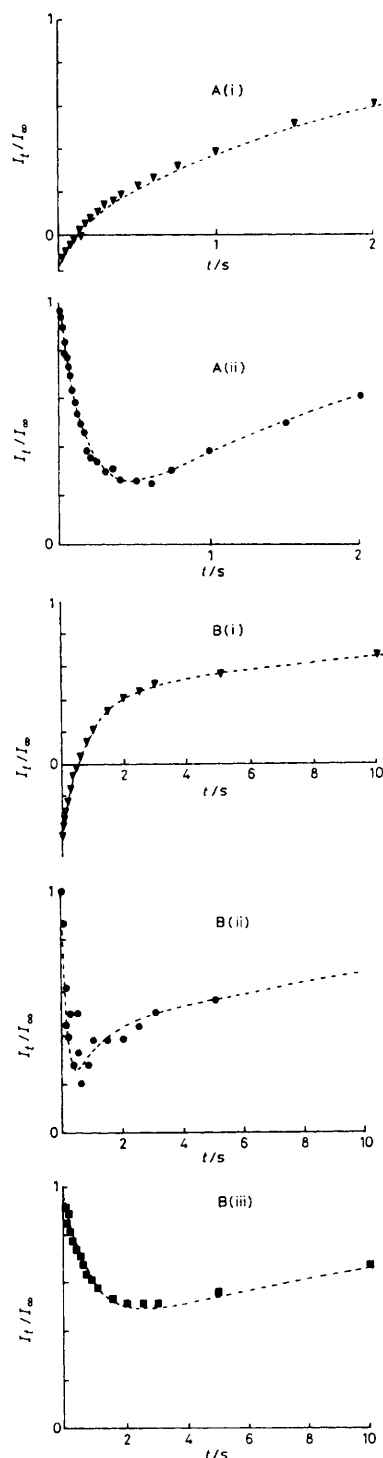


Figure 2. Peak height changes during DANTE experiments vs. time. A. Inversion of both P-coupled pairs labelled 'X' in Figure 1; (i) major diastereoisomer (2b), \blacktriangledown ; (ii) minor diastereoisomer (1b), \bullet . B. Inversion of the ^{13}C resonance of the major diastereoisomer (2c) in the ^{13}C spectrum of (1c) \rightleftharpoons (4) CD_3OD , 325 K; (i) major diastereoisomer (2c) 181.4 p.p.m., \blacktriangledown ; (ii) minor diastereoisomer (1c) 182.5 p.p.m., \bullet ; (iii) free enamide (4) 169.9 p.p.m., \blacksquare . Peak heights are corrected by a factor of 0.67 in the last case to take account of the difference in line-widths of the respective signals. Dashed lines are computer simulations.

tion. At the very least, an intramolecular equilibration of enamide diastereoisomers must counteract the effect of high pressures of hydrogen, which reduce the optical yield by changing the rate-determining stage.^{9,10}

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