Mechanism of Asymmetric Hydrogenation Catalysed by Rhodium(I) *trans*-4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyldioxolan (DIOP) Complexes

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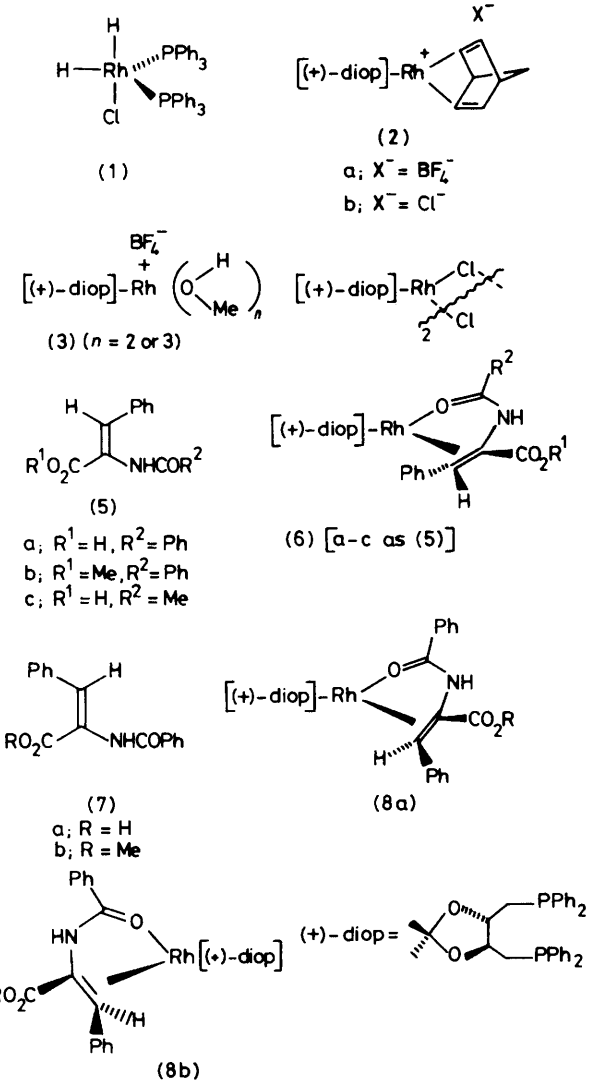
Summary Intermediates in the hydrogenation of (*E*)- and (*Z*)-α-benzamidocinnamic acids and their methyl esters by asymmetric rhodium(I) complexes have been identified by phosphorus-31 n.m.r. spectroscopy.

HOMOGENEOUS hydrogenation of olefins by achiral neutral[1] and cationic[2] rhodium complexes has been extensively studied and the normal reaction pathway involves addition of an olefin molecule to a transient co-ordinatively unsaturated metal dihydride (**1**). Despite the continuing high level of interest in asymmetric hydrogenation,[3] its detailed mechanism remains unclear and most literature discussions rely on argument by analogy with these simpler cases and assume similar intermediates.



Hydrogenation of a 0·04M solution of complex (**2a**) in methanol (1 ml; 1 atm H_2; 5 min; room temp.) causes quantitative conversion into a light yellow solution of the adduct (**3**) which contains no metal-hydride resonances observable by Fourier transform ^1H n.m.r. spectroscopy, even under a hydrogen atmosphere. The starting complex (**2a**) is reformed on addition of excess of norbornadiene. Complex (**2b**) gives a similar product, formulated as the bridged dimer (**4**) (Table). Related triarylphosphine complexes have been reported previously.[1] The absence of

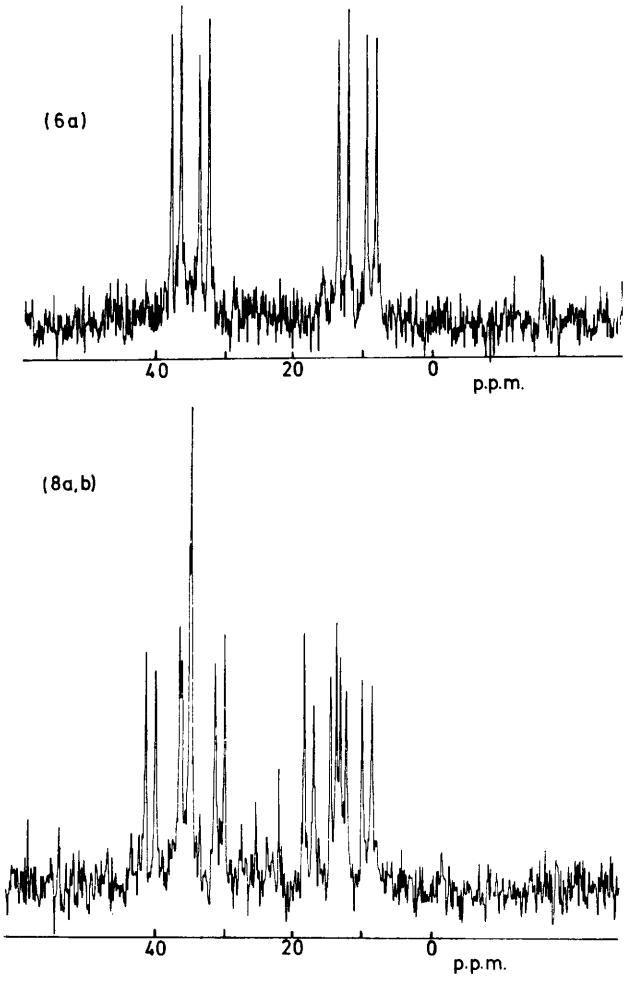


FIGURE. (a) ^{31}P n.m.r. spectrum of (**6a**) in methanol at 230 K; (b) that of (**8**) in methanol at 295 K. On cooling the sample the outer AB quartet diminishes in relative intensity and its upfield signal broadens considerably. Standard conditions for ^{31}P Fourier transform n.m.r. spectra: 6000 Hz sweep width, 8K points, 65° pulse, 1·1 s repetition rate; the proportions of (**8a**) and (**8b**) were unaltered in an experiment conducted with 90° pulses and 10 s repetition rate.

TABLE. ^{31}P n.m.r. spectra of rhodium complexes recorded in p.p.m. downfield from external 85% H_3PO_4. All spectra recorded at 230 K or 265 K are corrected by 3 p.p.m. to compensate for the change in external lock from D_2O to $(CD_3)_2CO$.

Substrate	Complex	Temp./K	Chemical shift/p.p.m.	Coupling constant/Hz	
				J_{P-Rh}	J_{P-P}
	(**3**)	265	43·6	200	
(**5a**)	(**6a**)	230	10·5	151	51
			35·0	151	
(**5b**)	(**6b**)	230	10·8	148	52
			35·1	149	
(**5c**)	(**6c**)	230	9·7	151	51
			35·3	152	
(**7a**)	(**8a**)	295	15·4	170	52
			33·3	178	
	(**8b**)		11·6	166	52
			38·4	178	
(**7b**)	(**6b**)	230	10·7	149	52
			35·0	149	

stable dihydride intermediates derived from (**3**) and (**4**) is in marked contrast to the behaviour of non-chelate phosphine complexes, although Halpern and his co-workers have recently shown[4] that the bisdiphenylphosphinoethane analogue of (**2a**) behaves similarly on hydrogenation.

Admission of a 5-molar excess of (*Z*)-α-benzamidocinnamic acid (**5a**) to an argon-blanketed solution of (**3**) gives a highly air-sensitive orange solution whose ^{31}P n.m.r. spectrum at 230 K is in the Figure. This rhodium-coupled AB quartet is consistent with the unsymmetrical chelate structure (**6a**), only one of two possible diastereoisomers being apparent. This presumably involves complexation of the C(1)-*re* face of (**5a**) for compatibility with the stereochemical course of hydrogenation.[5] Excepting minor changes in chemical shift, the spectrum is unaltered up to 270 K but exchange broadening becomes significant at higher temperatures. Binding of the enamide group is indicated by the lack of detectable complexation of cinnamic acid under similar conditions. (*E*)-α-Benzamidocinnamic acid (**7a**) behaves quite differently in related experiments, and two diastereoisomeric complexes are obtained in approximately equal proportions (Figure) at 295 K, ligand exchange being slow on the n.m.r. time-scale. The lack of selectivity between *re*- and *si*-isomers correlates with the low optical yield observed in asymmetric hydrogenation of (**7a**). On cooling the solution the relative proportions of (**8a**) and (**8b**) alter, one diastereoisomer predominating by 2:1 at 230 K. Interestingly, the colour of (**8**) is temperature-independent, whilst that of (**6a**) fades reversibly on cooling to 195 K.

The ester (**5b**) and (*Z*)-α-acetamidocinnamic acid (**5c**) both react with (**3**) in similar manner to (**5a**) although the resulting complexes differ in their rates of olefin exchange with free ligand, which varies in the sequence (**5c**) > (**5a**) > (**5b**). 1:1 Stoicheiometry of complexation is demonstrated by an experiment in which (**3**) reacts with an equimolar quantity of (**5b**), and the ^{31}P n.m.r. spectrum at 230 K shows (**6b**) with $\leqslant 10\%$ of residual (**3**). The ester (**7b**) initially shows no evidence for complexation, but monitoring the n.m.r. spectrum over several hours demonstrates slow formation of (**6b**) (olefin isomerisation *via* the imine?) with no detectable intermediates.

Several conclusions may be drawn from these experiments, which simulate the conditions of asymmetric hydrogenation closely. Most significantly, its stereochemical course is defined in an olefin-binding step whereby a square-planar chelate intermediate is formed, and the subsequent addition of hydrogen has only a minor influence on the optical yield. The simplicity of this key intermediate will facilitate the design of asymmetric complexes tailored to specific requirements.

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