Structural Characterisation of a Transient Intermediate in Rhodium-catalysed Asymmetric Homogeneous Hydrogenation

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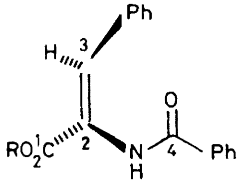
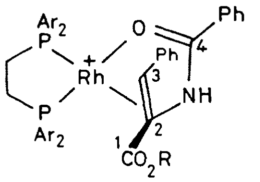
Summary An unstable rhodium alkyl has been characterised by n m r spectroscopy at low temperatures under the conditions of homogeneous hydrogenation

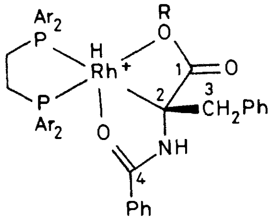
In previous papers we have described the formation of rhodium complexes derived from dehydroamino acids and their characterisation by phosphorus and carbon n m r spectroscopy [1] Thus (*RR*)-1,2-bis-(*o*-methoxyphenylphenylphosphino)ethane[2] rhodium complexes of α-benzamidocinnamic acid (**1a**) and its methyl ester (**1b**) exist as two diastereomers in ratio 10:1 at room temperature These are co-ordinated to rhodium through olefinic and amide groups[3] and differ in configuration of bound olefin At room temperature they disappear concomitantly on exposure to hydrogen



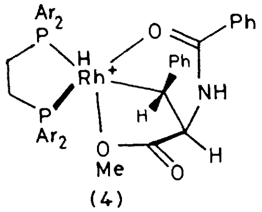
(1)a; R = H
b; R = Me



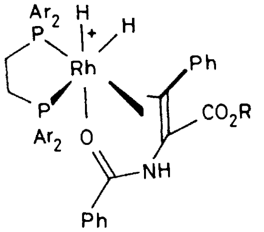
(2)a; R = H
b; R = Me



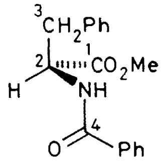
(3)a; R = H
b; R = Me



(4)

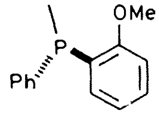


(5)



(6)

PAr$_2$ =



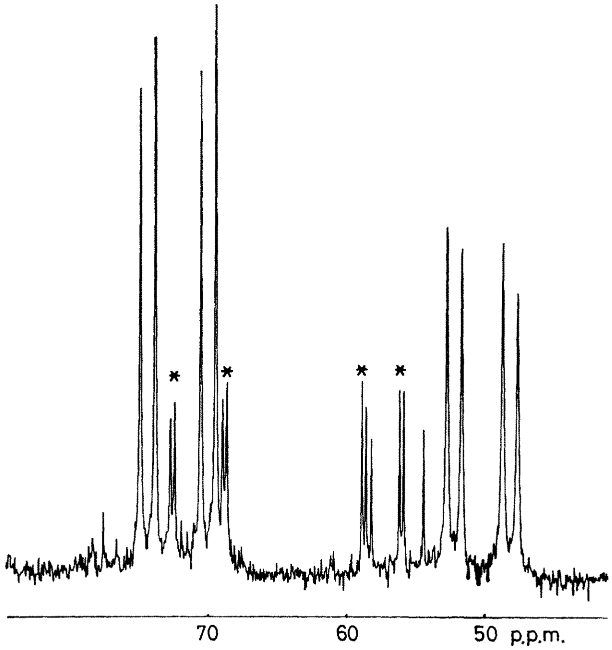


Figure. The phosphorus-31 n.m.r. spectrum of (**2b**) in methanol at 230 K under hydrogen. Signals due to (**3**) are asterisked and a small quantity of (dipamp)$_2$Rh$^+$† is apparent at 56 p.p.m. Spectral parameters: δ_2 70·7, δ_1 57·1 p.p.m., $J_{P(2)-Rh}$ 137, $J_{P(1)-Rh}$ 97, $J_{P(1)-P(2)}$ 11 Hz.

If the enamide complex [either acid (**2a**) or its methyl ester (**2b**)] is prepared under hydrogen at 195 K and allowed to warm to 220 K slowly then a new species is formed, to the extent of 30% under the most favourable conditions. It is distinguished (Figure) by very small $J_{P(1)-P(2)}$ and $J_{Rh-P(1)}$ values, suggestive of 5- or 6-co-ordination, and of an alkyl or hydride group *trans* to the high-field phosphine.[4] Above 230 K the transient species gradually disappears and studies with ^{13}C-labelled dehydroamino acids (*vide infra*) demonstrate that the hydrogenation product appears simultaneously. Addition of an excess of NEt$_3$ or HBF$_4$ increases the rate of disappearance of the transient to some extent. A similar intermediate may be observed in low-temperature hydrogenation of enamide complexes derived from rhodium bis(diphenylphosphino)ethane but not those from chiraphos[5a] or diop.[5b]†

The structure of this labile species is shown to be (**3**) by studies with carbon-13-labelled (**1**). Using criteria established earlier[1] it may be seen that both ester and amide groups are co-ordinated, the carbonyl ^{13}C resonances being shifted downfield by 12·1 and 9·2 p.p.m. respectively relative to the free ligand (Table). Both are coupled to the high-field phosphine, and C(1) also to rhodium. The 3-carbon has a chemical shift consistent with an sp^3-benzylic site. In addition, the use of C-1, C-3 doubly labelled enamides shows a very small (<1 Hz) C–C coupling constant in the intermediate, suggesting saturation of the double bond.[6] Halpern and co-workers have recently reported the ^{31}P spectra of enamide complexes derived from methyl α-acetamido[2-^{13}C]cinnamate and we have independently observed the 24·5 Hz P(1)–C(2) coupling in (**2b**). In (**3b**) this is increased to 82 Hz and although there are no analogies in rhodium chemistry,[7] there is a precedent for large *trans*-phosphine couplings in platinum alkyls.[8] Taken together this evidence uniquely defines the structure of the intermediate to be (**3**).

Table. N.m.r. data for (**1b**), (**2b**), (**3b**), and (**6**). Comparable values are observed in the dehydroamino acid sequence.

	(**1b**)	(**2b**)[a]	(**3b**)[b]	(**6**)
δ (^{13}C)/p.p.m.				
C(1)	167·2	170·5	179·3	172·6
C(2)	126·9	82·2	73·6	56·0
C(3)	136·4	81·6	45·1	38·1
C(4)	169·8	181·3	179·0	170·3
$J_{C(1)-C(3)}$/Hz	5·6	5	<1	<1

Coupling constants (in Hz): [a] P(1)–C(1) 5, P(1)–C(2) 24·5, P(1)–C(4) 8, P(2)–C(4) 2·5, Rh–C(2) 7, Rh–C(3) 15; [b] P(1)–C(1) 3·5, P(1)–C(2) 82, P(1)–C(3) *ca.* 2, P(1)–C(4) 8, P(2)–C(4) 2·5, Rh–C(1) 2·5, Rh–C(2) 22·5.

Enamide binding is slow at 220 K and when a deficiency of either (**1a**) or (**1b**) is employed, up to 35% of the minor diastereomer is observed, since equilibration is also slow under these conditions. If hydrogen is then admitted to

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† Chiraphos = (*SS*)-2,3-bis(diphenylphosphino)butane; diop = *trans*-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyldioxolan; dipamp = (*RR*)-1,2-bis-(*o*-methoxyphenylphosphino)ethane.

the n m r tube without raising the temperature then (**3**) appears gradually over 30 min at the exclusive expense of the minor diastereomer, and does not increase in intensity after the latter has disappeared If the enamide complex is formed at 265 K (at which temperature equilibration is rapid and the minor diastereomer virtually absent) and then hydrogenated at 220 K, (**3**) is evident only at very low concentrations These experiments require that the rhodium alkyl is formed predominantly[9] from the minor diastereomer of (**2**), contrary to our earlier supposition Additionally, they show that the chelate enamide structure is maintained during hydrogen transfer, since the alternative alkyl (**4**) is not formed Hydrogenation involves firstly *cis*-addition of hydrogen to rhodium, giving (**5**) (or a Rh stereoisomer) and then intracomplex hydride transfer giving a cationic alkyl monohydride At 220 K the rate-determining step in the overall hydrogenation reaction is breakdown of (**3**) and requires a rapid[10] hydride transfer to give (**6**) If this is the mechanism under catalytic conditions at room temperature then a number of earlier observations, such as the requirement for terdentate substrates in dipamp-Rh$^+$† promoted hydrogenations[2,11] are explicable The rhodium alkyl (**3**) is in any event a very simple model for the transition-state of asymmetric hydrogenation

Since this manuscript was accepted for publication, a bis(diphenylphosphino)ethane analogue of (**3**) has been reported[12] and the ^{1}H n m r spectrum recorded Although undetected earlier, we have now observed a weak hydride signal from (**3b**), δ -19 3 p p m , $J_{H-P,Rh}$ 11, 23, 34 Hz Unlike the intermediate described by Chan and Halpern,[12] (**3b**) does not react with MeCN ($\geqslant$ 1 equiv , 230 K) but their evidence requires caution concerning the precise role of the methoxy carbonyl group

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