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INTERMEDIATES IN ASYMMETRIC HYDROGENATION

THE STRUCTURE AND ^{31}P NMR SPECTRA OF RHODIUM ENAMIDE COMPLEXES CONTAINING 1*R*, 2*R*-*TRANS*-1, 2-*BIS*(DIPHENYLPHOSPHINOMETHYL) CYCLOBUTANE

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Abstract—Hydrogenation of bicyclo[2.2.1]heptadiene-1*R*, 2*R*-*trans*-1, 2-*bis*(diphenylphosphinomethyl)cyclobutane rhodium (*I*) tetrafluoroborate in methanol gives a solvent adduct which reacts with *N*-acyldehydroamino acids and their esters to give air-unstable scarlet to yellow complexes. Effects of structure variation in the enamide on the ^{31}P NMR spectra of these species are reported and discussed with reference to (a) the equilibrium between methanol and enamide complexes; (b) the ratio of diastereomeric enamide complexes formed; (c) the temperature dependence of this ratio; (d) the rate of complexation equilibria and (e) the structure of enamide complexes, which are normally bidentate with binding via the olefin and amide groups. In certain cases the complex may be terdentate and *E*-enamides bind through the olefin and carboxyl groups. Each mode of binding gives rise to characteristic ^{31}P NMR spectra with regard to P–P and P–Rh coupling constants.

Previous studies on asymmetric hydrogenation[1] have established that the highest optical yields are obtained when chelating biphosphine rhodium complexes are employed in the reduction of olefins carrying polar functionalities, especially enamides. A considerable range of structural variations in the ligands has been tested, most being based on Ph_2P–*X*–PPh_2, where *X* represents an unspecified asymmetric group. Few guiding principles can be derived from this work although it appears that biphosphines forming 5-ring chelate complexes[2] are superior to biphosphines forming 7-ring chelate complexes because of their greater conformational rigidity.[3] Asymmetric induction arises from chirality,[4] or induced chirality at phosphorus involving preferred *P*-phenyl rotamers.

A series of papers from Be'er Sheva[5] has reported the optical yields in hydrogenation of a range of enamides in which olefin, amide and carboxylate substituents were systematically varied. Most of the earlier work involved complexes of 4*R*, 5*R*-*trans*-*bis*-(diphenylphosphinomethyl)-2, 2-dimethyl-1, 3-dioxolan **1**, normally prepared *in situ*, but more recently other 7-ring chelate biphosphines such as **2** and **3** have been employed. Although formally similar in structure, these complexes gave quite varied optical yields in enamide hydrogenation and show differing responses to change in substrate structure. The results obtained permit a rational description[5] of the role of each substituent on the course of reaction.

Prior work at Oxford has been directed to determining the structure of enamide rhodium complexes in solution by NMR methods.[6] These experiments show that hydrogenation of chelating phosphine rhodium bicycloheptadiene complexes gives first a solvent adduct **4** which reacts the *Z*-enamides to give an intermediate, usually **5**. In appropriate cases both diastereomeric complexes derived from a single prochiral enamide have been simultaneously observed.

This present study was undertaken in order to correlate the optical efficiency in asymmetric hydrogenation with variations in the structure of the enamide. The cyclobutane derived biphosphine **2** was selected for detailed study since the enantiomer excess obtained in hydrogenation is rather sensitive to the precise nature of the substituents in the enamide.

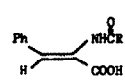
Biphosphine **2** reacted with bicyclo[2.2.1] heptadiene rhodium (I) acetylacetonate and fluoroboric acid to give complex **6**. This was in turn readily hydrogenated in methanol solution to give a solvent adduct **4a**, prepared *in situ* and identified by its ^{31}P NMR spectrum (δ = 46.8 ppm, J_{P-Rh} = 200 Hz). This coupling constant is characteristic of a solvent adduct rather than a dihydride.[7] Addition of a fourfold excess of enamide to this solution led to the formation of a new complex whose ^{31}P NMR spectrum depended on the nature of the enamide. Exchange broadening of signals at room temperature was quite common and it was frequently necessary to cool the sample to 240 K to obtain narrow line spectra. The results obtained provide information on the mode of binding, on trends in stereoselectivity, and on the kinetics and thermodynamics of complexation. All of these are quite sensitive to small changes in the structure of the enamide.

DISCUSSION

(a) *Variation of acyl residue in Z-acylaminocinnamic acids*

Spectral parameters for a series of complexes in which the steric and electronic character of the amide residue is systematically varied, are recorded in Table 1. In all cases except 7-CF_3, enamide formation was complete under the conditions specified. This implies that the

Table 1. ^{31}P NMR spectra of complexes of Z-α-acylaminocinnamic acids



R	Temp °K	Diastereomer 1					Diastereomer 2					Line-width at half height	Ratio of diastereomers	Enantiomer excess in hydrogenation[a]
		δ_{P_1}	J_{RhP_1}	δ_{P_2}	J_{RhP_2}	$J_{P_1P_2}$	δ_{P_1}	J_{RhP_1}	δ_{P_2}	J_{RhP_2}	$J_{P_1P_2}$			
Me	305											60 Hz		86% R
	274	(38.8)	(155)			(49)	(30.1)	(157)				21	(64:36)	
	241	40.3	154	12.9	150	48	30.4	160	14.3	162	49	3	73:27	
Ph	305	(37.1)	(157)									30		67% R
	274	38.4	155	14.6	157	52	30.1	163	16.9	165	45	5	72:28	
	241	39.1	153	14.6	152	50	30.4	162	16.6	165	44	2	80:20	
tBu	305	38.1	159	13.1	160	50	30.4	163	16.1	165	45	10	41:59	49% R
	274	38.5	156	13.3	159	50	30.3	162	15.7	165	44	7	46:54	
	241	38.8	154	13.6	154	50	30.3	162	15.4	165	44	2	52:48	
Adamantyl	305	37.1	157	13.1	160	50	29.5	162	15.6	165	45	7	49:51	44% R
	274	38.2	155	14.0	157	50	30.2	163	16.1	166	45	6	57:43	
	241	38.7	153	14.3	155	50	30.2	162	15.7	165	45	2	65:35	
CF_3[b]	241	49.0	140	33.7	133	40						17		c
	213	49.7	140	33.5	132	41						8		

(a) Ref 17 (b) At 274 K approximately 50% of the phosphorus signal is due to methanol adduct; no second diastereomer is observed
Data in brackets were difficult to estimate accurately due to exchange broadening.
(c) Not determined.

complexation constant K, derived according to eqn (1) is ≥300:

$$\text{Enamide} + \mathbf{4a} \underset{\text{nMeOH}}{\overset{K}{\rightleftharpoons}} \mathbf{5} + \text{nMeOH}. \qquad (1)$$

This value is considerably greater than those reported by Halpern *et al.*[8] for the related equilibrium between methanol complex **4b** and a large range of olefins or arenes, implying a more favourable free energy of binding in the case of enamides.

The characteristic appearance of the ^{31}P NMR spectrum of enamide complexes derived from **4a** is two separate 8-line multiplets. This is because each diastereomer exhibits two distinct phosphorus resonances which are mutually coupled and also coupled to rhodium. The observed J and δ values correspond to those observed in related complexes where it has been demonstrated that both olefin and amide are coordinated to rhodium, as indicated in structure **5**. In all cases (excepting 7-CF_3) the diastereomer with P2 resonating at lower field predominates at low temperatures and in the case of 7-Me and 7-Ph this is also true at ambient temperature. With bulky amide functions 7Bu^t, 7-Ad) the proportion is temperature dependent (Fig. 1) but selectivity is low. These last-named amides possess sharp enamide complex spectra over the temperature range of study, but all others show appreciable exchange broadening at 274 K and above. Since this dynamic process, which is due to interligand exchange between coordinated and free enamides, is very dependent on the bulk of the amide group, it suggests an associative mechanism for the process involving preliminary coordination of the amide carbonyl function.

Trifluoroacetamide 7-CF_3 presents an interesting case. Only one complexed species is formed, with both its phosphorus resonances at unusually low field. The phosphorus–rhodium coupling constants are substantially lower than those observed in the rest of the series. This imples that the rhodium phosphorus π-bond is weakened, consistent with an increased coordination number, and it is possible that both amide and carboxyl groups are bound to rhodium simultaneously. The amide function is very weakly basic and methanol complex **4a** predominates at equilibrium (K ~ 5 at 274K) and exchange broadening persist down to 240K.

(b) *Variation of acyl-residues in methyl Z-α-acylaminocinnamates* **8**

Results for this series are recorded in Table 2. The overall appearance of the spectra, and observed chemical shifts are similar to those obtained for the corresponding acids although exchange broadening is generally less at a given temperature. In all cases there is a much greater excess of one diastereomeric intermediate than observed for the series of acids, this being essentially independent of the nature of the acyl residue and only moderately sensitive to temperature. Thus $\Delta G_0 = 3.0$ kJ mol^{-1} for the enamide derived from **8**-Ad at 305 K and 3.5 kJ mol^{-1} at 241 K. Values of $\Delta G_0 = 0.0$ kJ mol^{-1} at 305 K and $\Delta G_0 = 1.2$ kJ mol^{-1} at 241 K are obtained for the acid 7-Ad. This indicates that ΔS_0, the standard entropy difference between diastereomers is only of the oder of 10–20 J deg^{-1} mol^{-1} implying that their overall structure and mode of binding is similar.

The formamide **8**-H is different in two respects. Firstly, it is bound much more weakly than other members of the series (K ≤ 40 M^{-1}, compared to a general value of 400 M^{-1}). In the case of the N-Me derivative **9** this is even more striking and an enamide complex is only observed at low temperatures. It has been noted previously[4] that N-methylenamides hydrogenate much more slowly than the corresponding secondary amides, this presumably reflecting a weaker metal-substrate interaction. Secondly the complex formed from **8**-H exhibits a much lower Rh-P coupling to the higher field nucleus, and a small P-P coupling. The chemical shifts are quite distinct from those obtained for the rest of the series, and the spectrum is consistent with tridentate binding of the

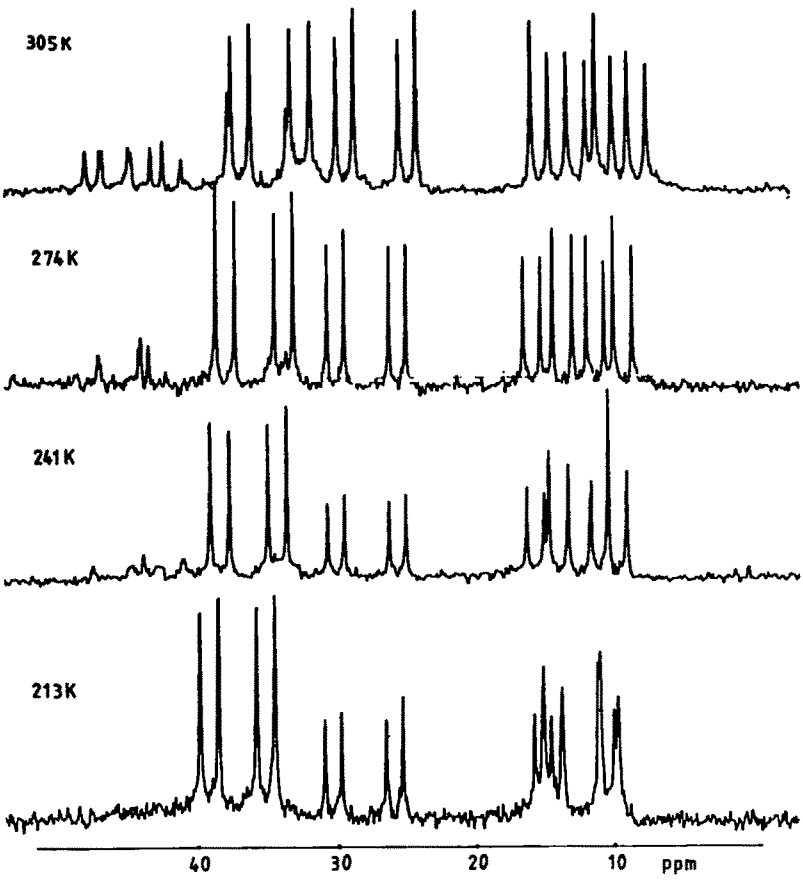
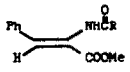


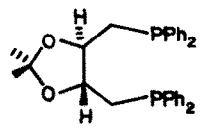
Fig. 1. ^{31}P NMR spectrum of enamide complex 7-Ad in methanol solution at various temperatures. An impurity which is apparent in the spectrum at ambient temperature is asterisked.*

Table 2. ^{31}P NMR spectra of complexes of methyl Z-α-acylaminocinnamates 8



R	Temp °K	Diastereomer 1 δ_{P_1}	J_{RhP_1}	δ_{P_2}	J_{RhP_2}	$J_{P_1P_2}$	Diastereomer 2 δ_{P_1}	J_{RhP_1}	δ_{P_2}	J_{RhP_2}	$J_{P_1P_2}$	Line-width at half height	Ratio of diastereomers	% Methanol complex	Enantiomer excess in hydrogenation[a]
H	274	b										60 Hz		60	55% R
	241	43.9	153	8.1	128	40	No second species was observed					5		17	
H	305	b					No second species was observed					15		100	c
(N-Me	274	b												71	
formamide)	241	37.9	152	15.5	152	54								65	
Ne	305	b										30		0	44% R
	274	38.4	153	14.7	154	51	b					9	91±9	0	
	241	39.5	152	13.6	150	50	31.3	160	14.7	159	45	3	93±7	0	
Ph	305	36.9	157	14.3	158	50	b					9	b	0	20% R
	274	38.1	153	14.7	155	52	30.8	160	17.8	163	46	3	95±5	0	
	241	38.8	152	14.6	151	50						3	97±3	0	
Adamantyl	305	36.8	155	13.8	160	51	30.1	160	16.3	162	46	7	77±23	0	18% R
	274	38.0	153	14.6	156	52	30.7	160	16.9	163	46	5	83±17	0	
	241	38.7	150	14.7	152	52	30.7	160	16.4	162	46	3	85±15	0	

(a) Ref. 17 (b) The signals were either too broad or too weak for accurate data to be obtained.
(c) Not determined.



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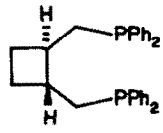

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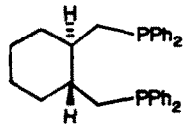

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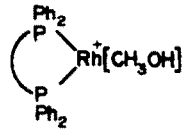

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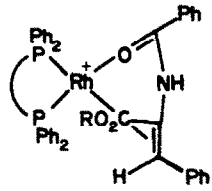
4a from 2

4b from DIPHOS



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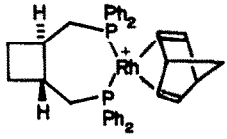

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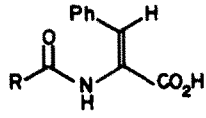
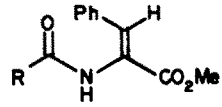
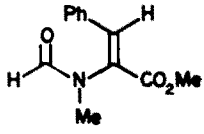


7R



8R



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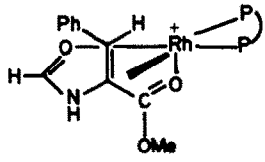


10

enamide, as in **10**. It seems to be the case that reduced coupling constants are characteristic of 5-or 6-coordination[9,10] and in such cases the enamide complex solutions tend to be yellow or orange rather than the normal scarlet colour.

(c) *Variation of ester residue in Z-alkyl-α-acetamidocinnamates*

Spectral parameters obtained for this series are recorded in Table 3 and permit several generalisations to be made. All the complexes exhibit broad ^{31}P NMR spectra at 305 K and have similar line-widths at 274 K, so that their dynamic character is essentially independent of the nature of the alkyl group. The equilibrium constant K does depend on the nature of R however, and both 11-Bu^t and 11-CH_2CF_3 have ~ 10% of methanol complexes in equilibrium at 274 K although none is observed in the case of 11-Me. All the complexes have chemical shifts and coupling constants consistent with amide/olefin bidentate binding, although one of the diastereomers of 11-CH_2CF_3 has an abnormally low field P1 resonance.

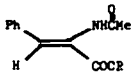
The most striking aspect of this set is the variation in diastereomer ratio between 11-Me and 11-Bu^t (Fig. 2). It is the latter which is anomalous based on the chemical shifts of the resonances of the major isomer in comparison to the rest of this and other series. As will be discussed later, the correlation between these observed diastereomer ratios and optical yields in hydrogenation of the corresponding enamides is quite variable, and 11-Me and 11-Bu^t give quite similar optical yields.

(d) *Variation of Z-β-alkyl substituent in methyl-α-formamidoacrylates*

The complexes of a range of compounds of general structure **12** have been studied and their spectral parameters are recorded in Table 4. A common characteristic is that metal binding is appreciably poorer and intermolecular exchange processes more pronounced than in the cases previously discussed, there being broadened spectra in all cases excepting 12-CF_3 down to 240 K (Fig. 3). This is in part due to the weaker binding of formamides when compared to acetamides or benzamides made evident by the presence of methanol complex in equilibrium which increases with the bulk of the alkyl substituent. The complex derived from 12-Bu^t is not observed although broadening of the methanol complex resonance suggests that it is exchanging with an undetected species.

The spectrum of the enamide complex derived from '12-CF_3 shows an absence of methanol complex and no exchange broadening, even at room temperature. The high-field P nucleus is coupled to fluorine in both diastereomers ($^4J_{P-F} = 12$ Hz). Through-space coupling mechanisms are rather common in fluorine-containing organometallic complexes.[11] The dynamic behaviour of 12-CF_3 is quite different to that of other alkyl-enamide complexes. On lowering the temperature the P1 signal selectively broadens and eventually becomes indistinct. The complex, in common with the major diastereomer

Table 3. ^{31}P NMR spectra of complexes of alkyl-*Z*-α-acetamidocinnamates



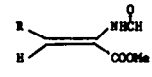
R	Temp °K	Diastereomer 1 δ_{P_1}	J_{RhP_1}	δ_{P_2}	J_{RhP_2}	$J_{P_1P_2}$	Diastereomer 2 δ_{P_1}	J_{RhP_1}	δ_{P_2}	J_{RhP_2}	$J_{P_1P_2}$	Line-width at half height	Ratio of diastereomers	% of methanol complex	enantiomer excess in hydrogenation[a]
Me	305	b										30	b	c	71R (44R)
	274	38.4	153	14.7	154	51	b					9	91:9	0	
	241	39.5	152	13.6	150	50	31.3	160	14.7	159	45	3	93:7	0	
tBu	305	b										30	b	b	52R (40R)
	274	39.2	160	10.7	150	46	28.5	162	15.1	166	43	9	23:77	13	
	241	39.7	158	b	b	46	29.1	159	14.3	163	43	variable	21:79	6	
CH_2CF_3	305	b										43	b	b	c
	274	38.3	152	14.8	154	51	37.7	150	15.2	154	51	8	20:80	11	
d	241	39.3	151	14.0	150	50	38.5	149	15.0	150	50	3	13:87	2	

(a) Values from present work using isolated cationic complexes as catalysts. Values in parentheses refer to hydrogenations using neutral chlororhodium complexes, Ref. 5.

(b) Could not be observed accurately due to low intensity or line-broadening. (c) Not determined.

(d) A small amount of another, unidentified species is also observed; this represents less than 5% of the total signal.

Table 4. ^{31}P NMR spectra of *Z*-β-alkyl-α-formamidoacrylate methyl esters



R	Temp °K	Diastereomer 1 δ_{P_1}	J_{RhP_1}	δ_{P_2}	J_{RhP_2}	$J_{P_1P_2}$	Diastereomer 2 δ_{P_1}	J_{RhP_1}	δ_{P_2}	J_{RhP_2}	$J_{P_1P_2}$	Line-width at half height	Ratio of diastereomers	% of methanol complex	enantiomer excess in hydrogenation[a]
Ph	241	43.9	153	8.1	128	40	No second species observed					10		17	55% R
	274	b										25		60	
Me	241	40.0	154	14.0	147	49	36.1	154	11.2	147	46	10	41:59	17	37% R
	274	b										very br.	b	50	
Et	241	40.6	153	14.4	144	49	36.4	152	10.7	144	46	7	48:52	6	30% R
	274	b										very br.	b	40	
i-Pr	241	45.5	159	4.3	122	34	32.6	162	12.7	154	43	9	67:33	31	11% S
t-Bu	241	None observed										15		100	24%[e]
CF_3	305	40.3	144	b	b	35	32.4	141	b	b	37	10	74:26	0	33[e]
	274	41.8	144	9.2	123	37[d]	33.9	140	11.6	124	38[d]	10	65:35	0	
	241	b										74 or P_1	b	0	
	213	b										300 for P_1	b	0	

(a) Ref. 17 (b) The signals were too broad or too weak for accurate observation. (c) Not determined. (d) J_{P_2F} = 12 Hz.

(e) Absolute configuration not known.

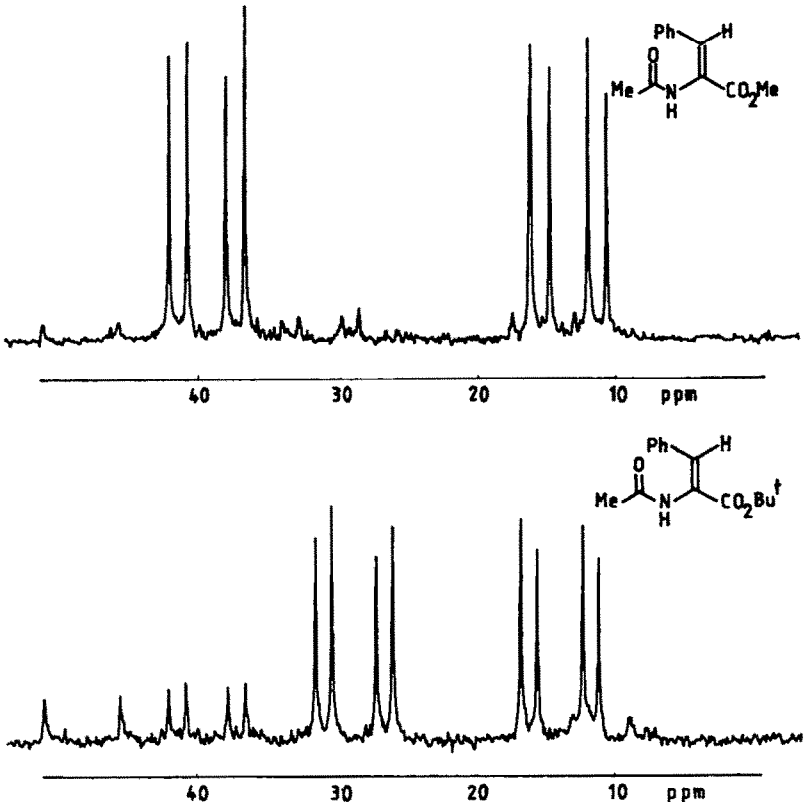


Fig. 2. ^{31}P NMR spectra of enamide complexes derived from (a) 11-Me and (b) 11-Bu^t observed at 241 K.

derived from 12-Me or 12-Ph, has small P2-Rh coupling and also a small P1-P2 coupling. These factors have previously been associated with tridentate enamide binding and this inference is further supported by the fact that solutions of the rhodium complex of 12-CF_3 are pale yellow over the whole temperature range. A 5-coordinate complex may be conformationally labile with respect to pseudorotation processes.[12] In this case it is necessary to equivalence two states without interchanging the two phosphine sites, and one possible mechanism for this is represented by 13→14. The olefin acts as a pivot about which the bound amide and ester CO groups interchange between axial and equatorial sites. There is no comparable process in 12-Me or 12-Ph, however, and the true explanation may be more complex.

There are pronounced differences in the selectivity of binding which are not readily rationalised. Thus 12-Ph gives rise to a 90% predominance of one diastereomer, but in the case of 12-*i*Pr and 12-CF_3 the proportions are more nearly equal. Both 12-Me and 12-Et, which form scarlet bidentate complexes do so with little stereoselectivity.

(e) *Complexes derived from E-α-Benzamidocinnamic acid*

Previous work has established[6] that 15 forms complexes in which both olefin and carboxylate, but not amide, bind to the metal. The alteration presumably arises from the Ph-Ph steric compression engendered in the normal mode of complexation. In the present case (Fig. 4) two diastereomers are observed which are tightly bound since little line-broadening is observed at room temperature, and the methanol complex is undetectable. The ratio of diastereomers is 40:60 at room temperature but 25:75 at 241 K, and both isomers have large P-Rh coupling constants, particularly to the lower-field phosphine. This is also the case with the corresponding complex derived from 1[6] although the present phosphine tends to give rise to *E*-acid complexes more cleanly. The optical yield in hydrogenation of the corresponding *E*-benzamidocinnamic acid is very low as expected.[6]

(f) *Relationship of these results to asymmetric hydrogenations catalysed by complexes of* 2

Most of the substrates studied here have been hydrogenated in the presence of 2 and appropriate rhodium complexes, and optical yields determined. The enantiomer excess thus obtained is plotted against the enamide diastereomer excess at 240–260 K in Fig. 5. Whilst there are a number of discrepancies between the two sets of experiments (for example, the temperature difference, change of solvent, generation of catalyst *in situ* for hydrogenation) comparison of the data does allow us to make some useful general conclusions. Firstly the degree of scatter is quite large, and there is no obvious and direct correlation between optical yield and diastereomer excess, although a rough general trend is observed. Secondly methyl esters tend to complex more selectively than acids, although they give inferior optical yields in hydrogenation. Thirdly, the greatest discrepency occurs for t-butyl ester 11-Bu^t where a large excess of the diastereomer which corresponds to the minor isomer in 11-Me is observed. Nevertheless, 11-Bu^t gives a higher optical yield (52% *R*, both at 4.5:1 and 40:1 substrate/catalyst ratio in methanol) than does 11-Me (35% *R* at 17:1 sub-

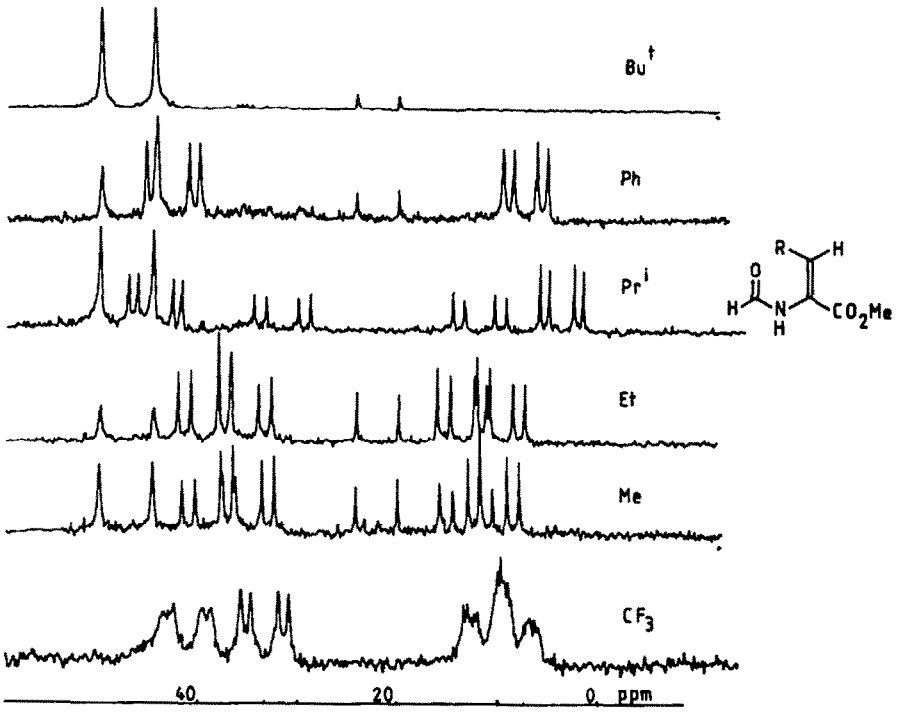


Fig. 3. (a) ^{31}P NMR spectra of enamide complexes derived from 12, under the conditions stated.

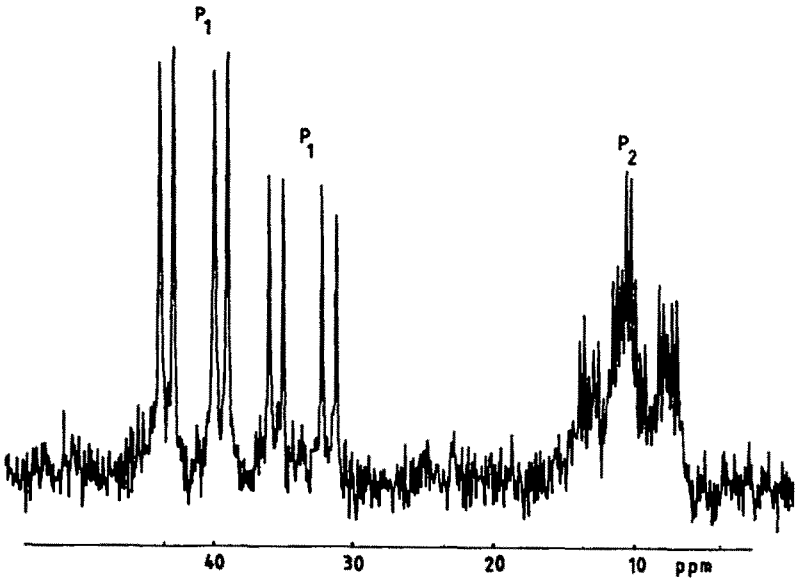


Fig. 3(b). Spectrum of 12-CF$_3$ recorded at 274 K.

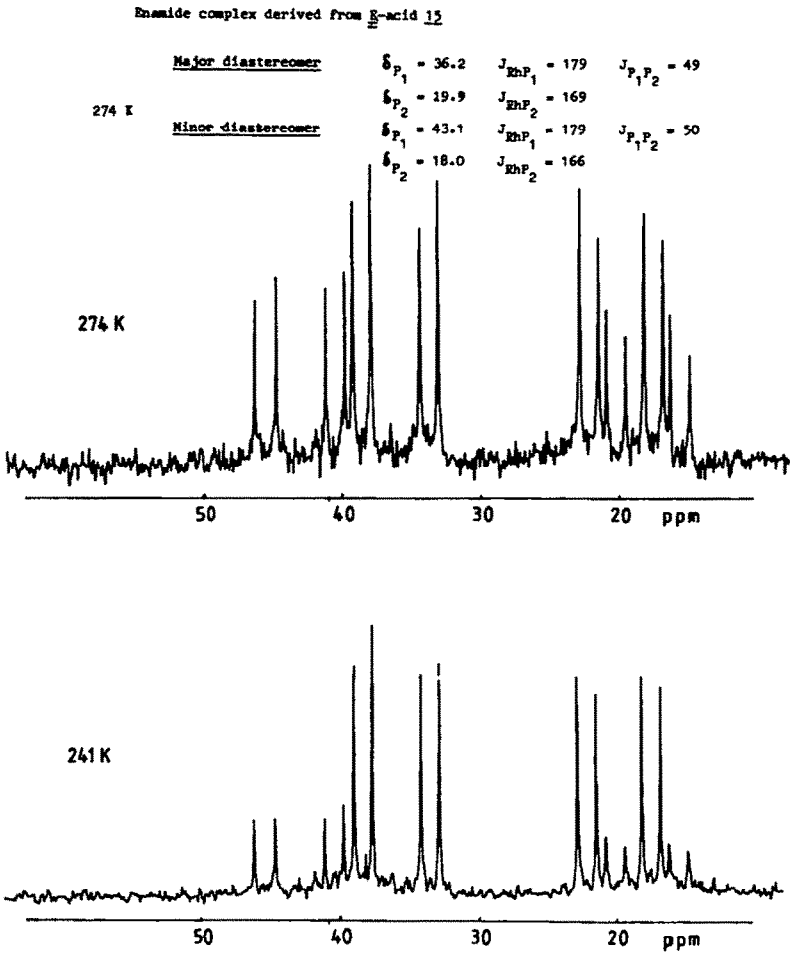


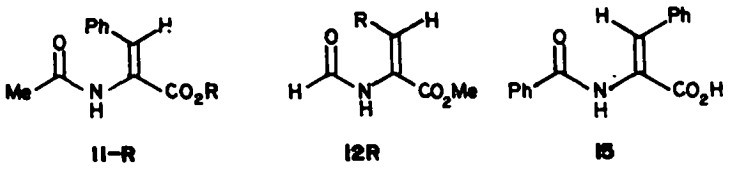
Fig. 4. ^{31}P NMR spectra of enamide complexes derived from E-acid **15**.

state/catalyst ratio under the same conditions). This must mean that steric effects are operative in enamide binding equilibria which are unimportant at the rate-determining transition state for hydrogenation.

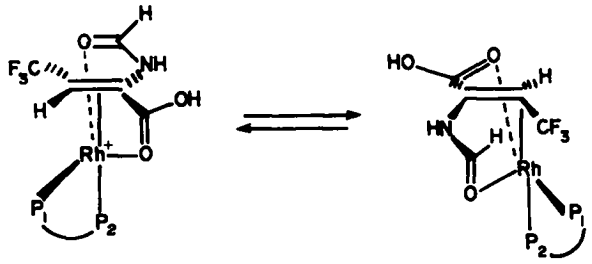
We have previously suggested[3] that 7-ring chelate complexes derived from **1** may exist in two conformations which are related to the chair and twist-boat geometries of cycloheptane.[13] The chair conformation has C_2 symmetry and the twist-boat conformation may attain this through a low-energy pseudorotation process. The structures may be represented in idealised form by **16a** and **16b**. A *trans*-ring fusion across C4 and C5 produces a chiral molecule in which each P-phenyl group is diasteromeric with respect to its partner and symmetry-related to one of the opposing pair. For the 4*R*,5*R*-enantiomer of **2** it is the pro-*R* phenyl groups which are axial in the chair conformation **16a** but the pro-*S* phenyl groups which are axial in boat conformation **16b**. Stereoselection in ligand binding arises from steric interactions between hydrogens on the equatorial phenyl rings and substituents on the bound olefin. Inspection of molecular models suggests that a dehydromino acid ester with non-bulky substituents such as 11-Me will bind preferentially through its *re-si* face to the complex of *RR*-**2** in chair conformation leading to *S*-amino acid ester on hydrogenation. Correspondingly, 11-Me will bind to the same complex in twist-boat conformation through its *si-re* face (Fig. 6) leading to *R*-amino acid ester on hysrogenation. The latter product is observed (35–40% enantiomer excess, depending on conditions) and we therefore presume that the major diastereomer of enamide complex derived from 11-Me is bonded through the *si-re* face of the olefin with the ligand in the twist-boat conformation. *Trans*-fusion of a 4-membered ring to the chelate will be expected to favour this geometry over the chair conformation, by analogy with simple carbobicyclic systems.[14] Thus enamide complex **17a** is energetically preferred.

It is reasonable to presume that the ester group in **17** has the preferred *trans*-conformation.[15] A bulky O-alkyl group will then interfere with the *pro-S* axial phenyl ring and destabilise this conformation with respect to the chair alternative. The t-butyl ester therefore prefers to be bound as indicated in **17b**. Clearly the t-Bu group does not exert so importance a steric effect at the rate-determining transition-state for hydrogenation. This is consistent with its structure being close to **18** in which the amide has rotated to an axial site and the carboxyl group is involved in the stabilisation of an incipient metal hydride.

Since the correlation between optical yield in hydrogenations catalysed by rhodium complexes of **2** and the diastereomer ratio in enamide binding is poor, it was of interest to see whether this is connected with the con-

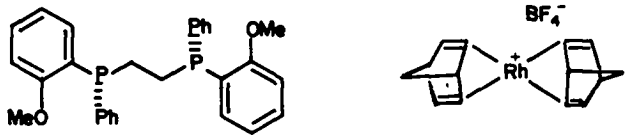


11–R 12R 15



13 14

16A 16B



19 20

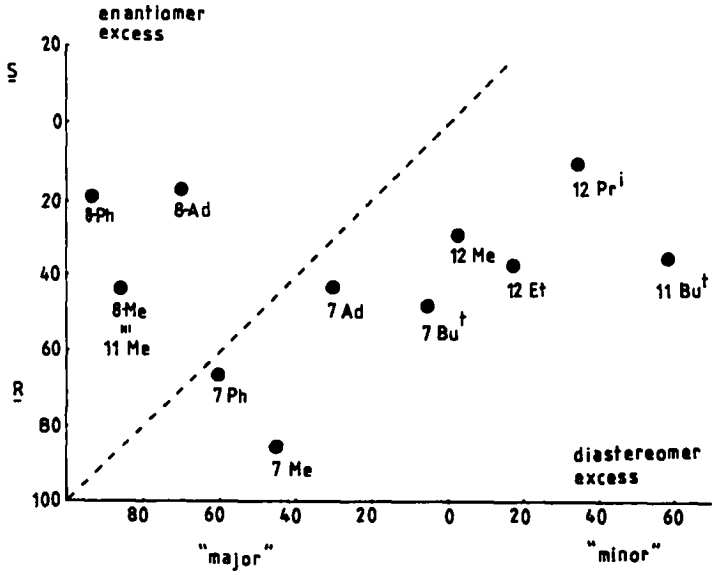
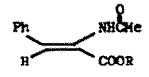


Fig. 5. The relationship between enantiomer excess obtained on hydrogenation in the presence of catalytic quantities of rhodium complexes derived from 2 (conditions described in Ref. 5) and diastereomer excess observed by ^{31}P NMR at 240–260 K.

Table 5. Asymmetric Hydrogenation of α-acetamidocinnamic acid esters with bicyclo[2.2.1] heptadiene S,S-DIPAMP rhodium (I) tetrafluoroborate



R	Temp °K	Diastereomer 1 δ_{P_1}	J_{RhP_1}	δ_{P_2}	J_{RhP_2}	$J_{P_1P_2}$	Diastereomer 2 δ_{P_1}	J_{RhP_1}	δ_{P_2}	J_{RhP_2}	$J_{P_1P_2}$	Ratio of diastereomers	Enantiomer excess in hydrogenation
Me	305	71.7	162	48.3	.50	40	69.6	157	58.1	160	38	93:7	95% S
	274	72.2	160	48.2	150	40	a					95:5	
	241	72.3	159	47.9	149	38	a					98:2	
t-Bu	305	71.5	162	48.2	150	40	69.6	153	55.1	160	35	80:20	92% S
b	274	72.0	162	48.0	150	40	70.4	152	54.9	160	35	84:16	
	241	72.1	160	47.6	149	40	70.7	149	54.5	159	35	87:13	

(a) Signals were too weak for an accurate estimate of the chemical shifts.

(b) After standing for 24 hours at room temperature a new species accounting for approximately 12% of the total intensity could be seen δ_{P_1} = 66.0 J_{RhP_1} = 137, δ_{P_2} = 53.6 J_{RhP_2} = 153, $J_{P_1P_2}$ = 20 Hz. After heating the proportion of this species had increased. It is presumed to be a decomposition of the initially formed enamide complex and is unlikely to be significant in the catalytic process.

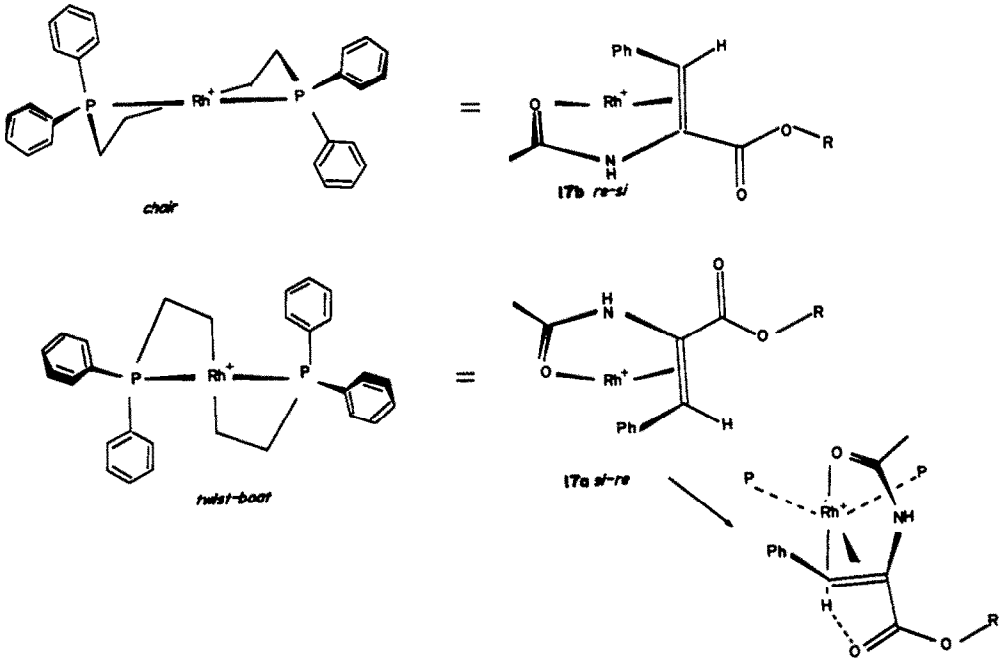


Fig. 6. Possible conformations of the enamide complexes derived from 11. The stereochemical sense is reversed if axial P-phenyl rings are disposed edge-on.

formational flexibility of 7-ring chelates. It is not the case with the rigid 5-ring chelate formed by the chiral diphosphine DIPAMP **19** which gives very high yields in enamide hydrogenation.[4] Hydrogenation of 11-Me and 11-Bu^t by the complex formed *in situ* from **19** and *bis* (bicyclo[2.2.1] heptadiene) rhodium tetrafluoroborate **20** in methanol gave very similar optical yields of amino acid ester (Table 5). What is more significant, however, is that the diastereomer ratios in complexes formed from **19** and 11-Me or 11-Bu^t are similar. This clearly suggests that stereochemical control of the overall hydrogenation pathway is rather more readily obtained when rigid 5-ring chelates are employed.

EXPERIMENTAL

Samples of dehydroamino acid derivatives were prepared as described previously[14] and have the reported physical properties. Optical purities of hydrogenation products were determined by glc[16] (4% N-behenylvaline t-butylamide on Chromasorb W, prepared by B. A. Murrer). M.ps were determined on a Reichert Kofler block and are uncorrected. Microanalyses were carried out by Dr. F. B. Strauss, Oxford. Optical rotations were measured with a Perkin-Elmer 141 polarimeter. PMR spectra were recorded on a Perkin-Elmer R32 spectrometer relative to TMS as internal standard. P and C NMR spectra were recorded on a Bruker WH90 spectrometer, P chemical shifts quoted relative to external 85% phosphoric acid and carbon chemical shifts relative to external TMS. All manipulations involving air-sensitive species were car-

ried out in Schlenck tubes under an atmosphere of dry argon and solvents were purified and thoroughly degassed before use according to standard vacuum line techniques.

Bicyclo [2.2.1] *heptadiene* 1R,2R-trans-1,2-bis (*diphenylphosphinomethyl*) *cyclobutane rhodium* (*I*) *tetrafluoroborate.* To a soln of bicyclo [2.2.1] heptadiene rhodium (I) acetylacetonate (72.2 mg, 0.25 mmol) in THF (3 ml) was added tetrafluoroboric acid (40%, 0.15 ml). To the stirred soln was added solid 1*R*,2*R*-*trans*-1,2-*bis*(diphenylphosphinomethyl) cyclobutane (113.2 mg, 0.25 mmol), a deep red colour being immediately generated. To this was added dropwise dry ether (20 ml) with vigorous stirring to give a red-orange powder. This was collected by Craig filtration, thoroughly washed with dry ether and dried under vacuum to give bicyclo[heptadiene 1*R*,2*R*-*trans*-1,2-*bis* (diphenylphosphinomethyl) cyclobutane rhodium (I) tetrafluoroborate (171 mg, 95%). This was indefinitely stable at 0° under argon and was used without further purification for the preparation of enamide complexes. Further purification could be effected by recrystallisation from warm MeOH to give orange needles, m.p. 215–225°, dec. (Found: C, 60.37; H, 5.45; P, 8.21; F, 10.38. Calc. for $C_{37}H_{38}P_2RhBF_4$: C, 60.52; H, 5.22; P, 8.43; F, 10.34). $[\alpha]_D$ (0.25, $CHCl_3$) + 34.3°.

Preparation and NMR analysis of enamide complexes. A sample of the bicyclo [2.2.1] heptadiene complex (22.5 mg, 30.6 μ mol) was dissolved in MeOH (0.5 ml) and transferred to an 8 mm NMR tube having a constricted neck. The sample was degassed and blanketed with argon three times and then the inert atmosphere replaced by H_2. The tube was agitated (Whirlimix, Fison's Ltd.) for 10 min during which time the soln changed from light orange to yellow-brown in colour. A soln of the substrate (124 μmol) in MeOH (0.7 ml) was transferred to the sample by a steel tube, both solns being kept at −78° with rigorous exclusion of O_2. The tube was sealed, this being facilitated by very slight evacuation, and allowed to warm to room temp. This caused a colour change from light brown to scarlet (excepting those complexes thought to be 5-coordinate, which were orange to yellow). The ^{31}P NMR spectrum was recorded immediately (10mm external tube, D_2O or CD_3OD lock) with cooling if necessary.

Hydrogenation of enamides. The following procedure is typical: t-Butyl-*Z*-α-acetamidocinnamate (15.4 mg, 59 μmol) and bicyclo [2.2.1] heptadiene 1*R*,2*R*-*trans*-1,2-*bis* (diphenylphosphinomethyl) cyclobutane rhodium (I) tetrafluoroborate (1.06 mg, 1.44 μmol) were dissolved in dry MeOH (1.35 ml) in a Schlenk tube and thoroughly degassed under argon. The argon was then removed, hydrogen admitted and the soln stirred under a H_2 for 2 h. The initial colour was orange and the soln became pale yellow as the reaction proceded. The solvent was then removed under reduced pressure and the oil chromatographed on silica to remove traces of catalyst. Glc analysis of the eluate indicated (on the basis of an average of three traces) 52% *R* enantiomer excess.

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