The Mechanism of Asymmetric Hydrogenation. Chiral Bis(diphenylphosphino)-α-phenylalkane Complexes in Catalytic and Structural Studies

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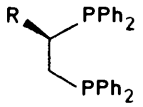
(*R*)-1,2-Bis(diphenylphosphino)phenylethane has been synthesised in good overall yield from (*S*)-mandelic acid [hydroxy(phenyl)acetic acid]; its cationic rhodium(I) solvated complex has been shown to be effective in catalytic asymmetric hydrogenation with optical yields of up to 88% having been observed. The n.m.r. spectra of complexes of this phosphine are discussed. Racemic (*R**,*R**)-1,3-bis(diphenylphosphino)-1,3-diphenylpropane and (*R**,*R**)-1,4-bis(diphenylphosphino)-1,4-diphenylbutane have been prepared. These form a range of rhodium complexes with dehydroamino-acids whose structures may be assigned on the basis of characteristic n.m.r. P–Rh and P–P coupling constants.

ASYMMETRIC hydrogenation of dehydroamino-acids by cationic rhodium complexes is well established.[1] A number of chiral biphosphines, most of which form 5-membered ring metal chelates, have proved particularly effective in producing high optical yields. Since other examples form 7-membered ring chelates, and as there are characteristic differences between the catalytic behaviour of the two types, it was felt that a systematic study of complexation and reactivity as a function of ring size would be desirable.



(1)

a ; R = Ph
b ; R = Me
c ; R = cyclo-C_6H_{11}
d ; CD_2 isotopomer of (1a)

For this reason the phosphines (1a)—(4) have been synthesised by conventional methods, the first as the (*R*)-enantiomer and the remainder as racemates. Complexes of compound (1a) are comparable in their effectiveness in catalysing asymmetric hydrogenation to the methyl analogue (1b)[2] or the cyclohexyl analogue (1c);[3] typical results from hydrogenation experiments are recorded in Table 1. Taken together with the work of King, Marko, and their co-workers[4] on catalysis by complexes of the ligand (1a) these results adequately demonstrate that a single asymmetric centre may control the stereochemical course of catalysis when it is contained in a 5-membered chelate ring. In all cases complexes derived from the (*R*)-enantiomers of compound (1a) give rise to (*S*)-α-amino-acid or (*S*)-α-hydroxy-acid derivatives, but (*R*)-enantiomers should be equally readily available from the (*S*)-enantiomer of compound (1a) since both stereoisomers of mandelic acid can be obtained.†

Synthesis of Biphosphines.—The preparative route to the phosphine (1a) is shown in Scheme 1. An improved yield of (*S*)-(+)-1-phenylethane-1,2-diol (6) was obtained by reducing (*S*)-(+)-mandelic acid [hydroxy(phenyl)-acetic acid] (5) in refluxing tetrahydrofuran rather than in diethyl ether.[5] The critical phosphination step was first attempted with its bistoluene-*p*-sulphonate (7a) and

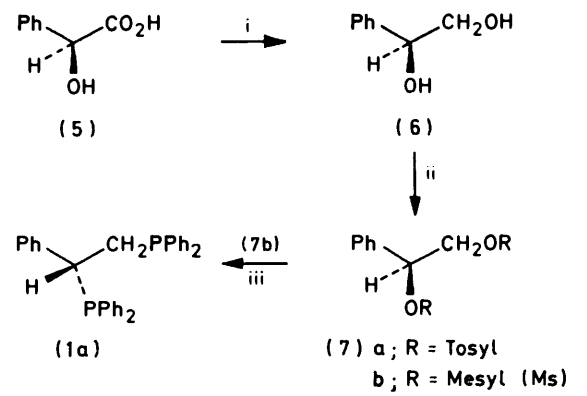
† Both (*R*)- and (*S*)-mandelic acid are available commercially in ≥99% optical purity, approximate prices being £2.20 and £0.50 per g respectively (February 1982).

TABLE 1

Hydrogenations catalysed by ligand (1a)–rhodium complexes

Reactant	Enantiomeric excess (1a)	(1a) [4]	(1b)	(1c)
(18a)	— [a]	84	88	90
(18c)	85 [b]	85	83.5	88
(18d)	88 [c]			
(18f)	79 [c]	78	83	84
(20a)	82 [c]		90 (EtOH)	93
(20b)	78 [c]			
(21)	72 [d]		81	

Catalyst prepared *in situ* from compounds (1a) (4.7 mg) and (14) (3.8 mg) in methanol (*ca.* 5 ml); catalyst:substrate normally 1 : 50 [1 : 25 in the case of compound (21)]; solutions stirred under hydrogen to complete loss of the red–orange enamide chromophore. [a] No reduction observed under our conditions. [b] Determined by rotation, (*S*)-*N*-benzoylphenylalanine methyl ester $[\alpha]_D^{20}$ −45.3° (*c* 1.3 in EtOH); G. Gelbard, H. B. Kagan, and R. Stern, *Tetrahedron*, 1976, **32**, 233. [c] Determined by g.l.c. on a 3 m column of (*S*)-*N*-docosanoylvaline-t-butylamide.[18] [d] Determined by n.m.r. spectroscopy in the presence of the chiral shift reagent europium trisheptafluorobutyrylcamphorate in CCl_4.

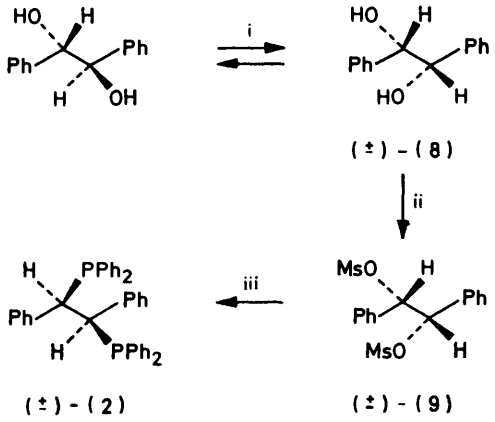


(5) (6) (7a) (7b) (1a)

(7) a ; R = Tosyl
b ; R = Mesyl (Ms)

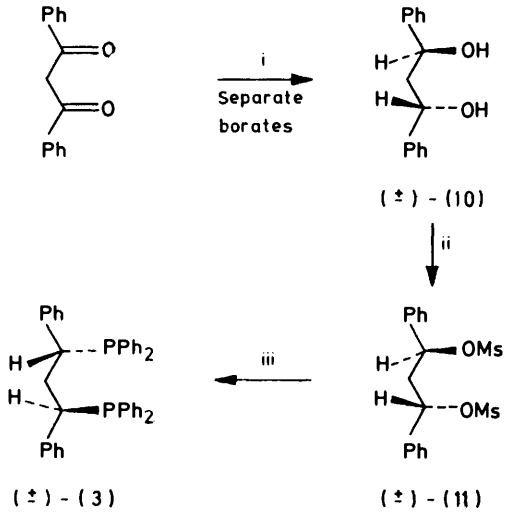
SCHEME 1 Synthesis of ligand (1a). *Reagents*: i, $LiAlH_4$; ii, pryidine, RCl; iii, $LiPPh_2$

potassium diphenylphosphide (prepared by the cleavage of triphenylphosphine with sodium–potassium alloy) in dioxan [6] but the product (1a) was never formed in more than 15% yield. Allowing the corresponding bismethanesulphonate (7b) to react with lithium diphenylphosphide in tetrahydrofuran at −78 °C gave up to 87% of the phosphine (1a) which was readily isolated from the reaction mixture by removal of the solvent and the addition of methanol. The product proved to be unstable to oxidation in solution and was therefore recrystallised from dichloromethane–methanol under argon. In the solid state it is stable for several months at −30 °C. The deuteriated analogue (1d) was prepared in a similar manner by employing lithium aluminium deuteride for the reduction of the acid (5) and was shown, by its mass and ^{1}H n.m.r. spectra, to be fully and specifically labelled.



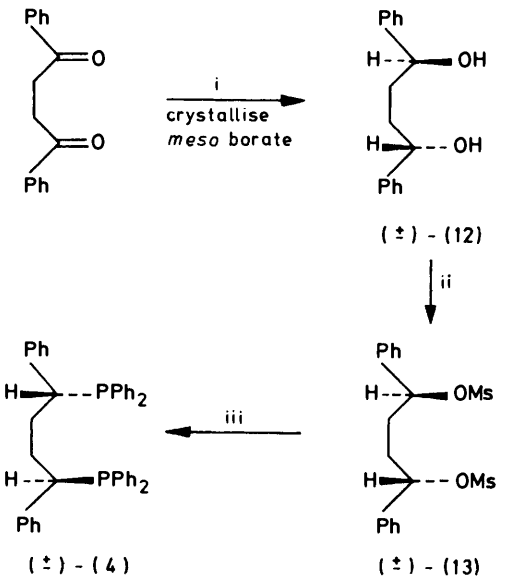
SCHEME 2 Synthesis of ligand (2). *Reagents*: i, KOH; ii, pyridine, MsCl; iii, $LiPPh_2$

(±)-1,2-Bis(diphenylphosphino)-1,2-diphenylethane (2) was prepared by a similar route (Scheme 2) which required (±)-1,2-diphenylethane-1,2-diol (8). This was prepared from the more readily available *meso*-isomer by heating the latter at 190 °C with anhydrous potassium hydroxide [7] and recrystallising the residue from ethyl acetate–cyclohexane. In one preparation large crystals were produced which were shown to have undergone partial spontaneous resolution, $[\alpha]_D^{20}$ 1.26°, and which melted 20 °C higher than the racemic material. The product was similarly prepared *via* the bismethanesulphonate derivative (9) and was found to be rather more air-sensitive than similar ligands. Its homologue (±)-1,3-bis(diphenylphosphino)-1,3-diphenylpropane (3) was readily synthesised by taking advantage of the separation of the *meso*- and (±)-borate esters produced in the reduction of dibenzoylmethane by sodium borohydride (Scheme 3); the optically active ester, which has one axial phenyl group in a chair conformation, is more readily hydrolysed and the diol (10) [8] may be cleanly separated by extraction into chloroform. The corresponding bismethanesulphonate ester (11) is very unstable and must be used immediately after preparation otherwise it rapidly decomposes to a black tar. The final



SCHEME 3 Synthesis of ligand (3). *Reagents*: i, $NaBH_4$; ii, pyridine, MsCl; iii, $LiPPh_2$

member of the series, (±)-1,4-bis(diphenylphosphino)-1,4-diphenylbutane (4), was prepared from dibenzoylethane *via* sodium borohydride reduction (Scheme 4). In this case the (±)-isomer of the diol (12) was separated by fractional crystallisation.[9] Its bismethanesulphonate

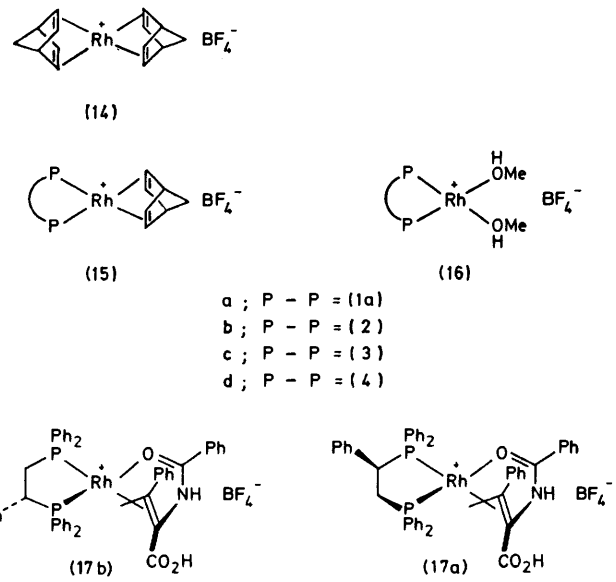


SCHEME 4 Synthesis of ligand (4). *Reagents*: i, $NaBH_4$; ii, pyridine, MsCl; iii, $LiPPh_2$

(13) likewise proved to be thermally unstable and was treated with lithium diphenylphosphide immediately after preparation. The phosphine (4) was insoluble in cold organic solvents and even after recrystallisation from hot tetrahydrofuran contained 5% of its dioxide (^{31}P n.m.r. spectrum).

^{31}P *N.m.r. Studies on Dehydroamino-acid Complexes.*—(a) *With* (R)-1,2-*bis*(*diphenylphosphino*)*phenylethane* (1a). Chelating biphosphines react quantitatively with bis(bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) tetrafluoro-

borate (14) to give the corresponding biphosphine complex (15) with displacement of one olefin molecule. The complex (15a) derived from the phosphine (1a) eluded isolation but ^{31}P n.m.r. spectroscopy indicated that the reaction had proceeded satisfactorily. Hydrogenation of the resulting solution gave a mixture of monomeric and



dimeric methanol solvates whose structures have been discussed elsewhere [10] and which may be represented as compound (16a) for present purposes. This solution reacted with (*Z*)-α-benzamidocinnamic acid (18a) to give a red solution, the ^{31}P n.m.r. spectrum of which is shown in Figure 1. In previous work [11] it has been shown that dehydroamino-acids form rhodium enamide complexes (17) which give a distinct eight-line multiplet for each diastereoisomer present in solution. Since the phosphine (1a) has no symmetry elements four such complexes are possible. The fact that both DIPAMP * and CHIRAPHOS * form one strongly predominant complex with a stereochemistry which is the reverse of that of the hydrogenation product [12] suggests that the two complexes observed are the regioisomers (17a) and (17b). Some support for this interpretation was provided by two further experiments. With ^{13}C-labelled (*Z*)-α-benzamidocinnamic acid (18b) [11] a P–C coupling of 6 Hz was observed (indicated by ◑ in Figure 1) caused by the nucleus *cis* to the amide group.[13] The complex formed from the deuteriated phosphine (1d) shows deuterium coupling to the two low-field nuclei (indicated by ● in Figure 1). In the series of compounds (15a), (16a), (17a), and (17b) it is always the low-field signals which

* DIPAMP is (*R,R*)-bis-(*o*-methoxyphenylphenylphosphino)-ethane; B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachmann, and D. J. Weinkauff, *J. Am. Chem. Soc.*, 1977, **99**, 5946; CHIRAPHOS is (*S,S*)-2,3-bis(diphenylphosphino)-butane; M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, 1977, **99**, 6262.

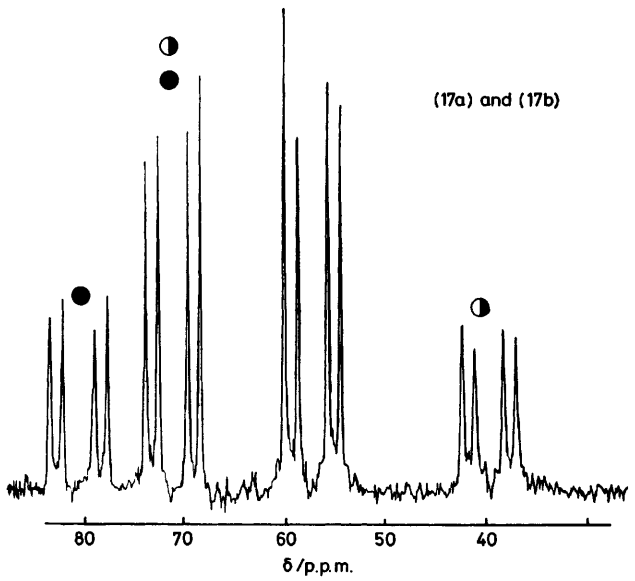
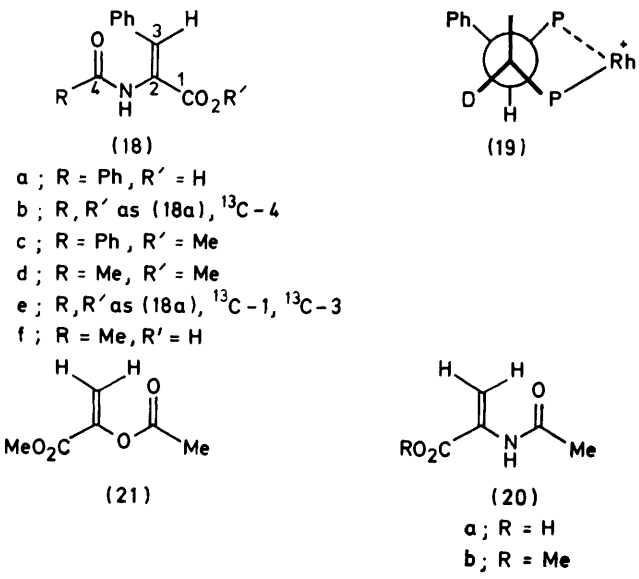


FIGURE 1 The ^{31}P n.m.r. spectrum of complex (17), derived from ligand (1a) and (*Z*)-α-benzamidocinnamic acid, at 300 K. ● refers to peaks broadened in the analogue prepared from the deuteriated ligand and ◑ refers to peaks exhibiting coupling in the ^{13}C-enriched amide complex

exhibit broadening due to deuterium coupling. Since the ^{31}P n.m.r. spectrum of the free phosphine showed no significant broadening it is considered that the effect is due to a *trans–vicinal* coupling [indicated in structure



(19)] for which there is a good literature precedent.[13] Taken together these two labelling experiments demonstrate that the two complexes are regioisomers with the same prochiral face of the olefin bound to rhodium.

The spectra of the enamide complexes derived from dehydrophenylalanine derivatives are sharp at room temperature (Table 2) whilst those derived from the secondary amides (20) or methyl α-acetoxyacrylate (21)

TABLE 2

^{31}P N.m.r. spectra of complexes derived from ligand (1a) [a]

Olefin	Temperature (K)	Diastereoisomer ratio [c]	δ (P-1)	δ (P-2)	$J_{P-1,P-2}$ (Hz)	$J_{P-1,Rh}$ (Hz)	$J_{P-2,Rh}$ (Hz)
(18a)	298	2 : 1	73.1	57.5	49	158	141
			81.7	42.1	47	165	157
(18d)	298	1 : 1	73.0	58.2	47	156	157
			81.3	40.4	49	162	153
(18f)	298	3 : 1	72.6	58.1	47	157	159
			81.4	40.1	50	165	154
			71.4	42.2	34	137	143
(20a)	215 [b]	41 : 25 : 17 : 17	76.8	41.9	35	146	131
			80.0	34.0	43	140	143
			74.4	45.0	35	134	149
(20b)	215 [b]		79.9	34.0	43	150	142
(21)	215 [b]		82.0	34.9	43	153	137

[a] Chemical shifts are quoted in p.p.m. relative to external H_3PO_4; [Rh] = 0.04M and [enamide] = 0.12M in MeOH. [b] Broad at higher temperatures. [c] Major isomer first.

require cooling before dynamic broadening becomes insignificant. The proportion of isomers is variable but both compounds (20b) and (21) give a single species. The spectrum derived from (*Z*)-α-acetamidoacrylic acid (20a) is anomalous in that four species are formed. Since their relative proportions are concentration dependent they may include complexes of stoicheiometries other than 1 : 1 (*vide infra*).

(b) *With* (R*,R*)-1,2-*bis*(*diphenylphosphino*)-1,2-*diphenylethane* (2). Attempts to prepare the phosphine complex (15b) as described above led to the formation of an orange, crystalline solid which was insoluble in methanol. The ^{31}P n.m.r. of this product consisted of a symmetrical, ' deceptively simple ' multiplet centred at 26.9 p.p.m., suggesting an oligomeric species. In dimethoxyethanol there was no change in the spectrum of this species after two hours agitation under hydrogen, and thus it cannot be a precursor to catalytically active species.

(c) *With* (R*,R*)-1,3-*bis*(*diphenylphosphino*)-1,3-*diphenylpropane* (3). Formation of the bicycloheptadiene complex (15c) and its hydrogenation to give the solvate (16c) proceed normally (Table 3). The enamide complexes were prepared in the usual fashion by the transfer of a solution of the enamide in methanol (normally 2 equiv. per Rh) into a solution of the methanol complex (16c) with strict exclusion of air, followed by sealing of the n.m.r. tube under an argon atmosphere. With (*Z*)-α-benzamidocinnamic acid (18a) the spectrum is broad at room temperature but well defined on cooling to −45 °C. Since the ligand has a C_2 symmetry axis there are two possible enamide complexes and one of these is predominant (*ca.* 5 : 1). With the esters (18c) and (18d) the proportions of these diastereoisomers are comparable (Table 3). These complexes were bright red, as expected, but those derived from α-acetamidoacrylic acid or its methyl ester were pale yellow and had a totally different type of ^{31}P n.m.r. spectrum. The single diastereoisomer observed was characterised by a very low P-2–Rh coupling (Table 3) suggestive of a 5- or 6-co-ordinate species. The complex was formed quantitatively with exactly one equivalent of the ester (20b) and therefore has 1 : 1 stoicheiometry. At rather higher concentrations of substrate (3 : 1 excess) a second type of complex is observed to which 2 : 1 stoicheiometry is ascribed. This new species showed two four-line multiplets at low-field, corresponding to P-1 in the separate diastereoisomers, and a complex multiplet at 38.4 p.p.m. Changes in the ^{1}H n.m.r. spectrum of the complex (16c) on addition of the acrylate (20b), monitoring the 2.1 (NHCOMe) and 3.8 (CO_2Me) p.p.m. regions, are also consistent with the predominant formation of one complex with a small proportion of the acrylate (20b) and of another with a higher proportion. Complexes with 2 : 1 stoicheiometry have also been observed with the amide (20a) and the rhodium solvate derived from

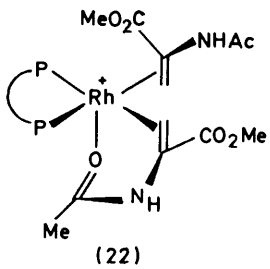
TABLE 3

^{31}P N.m.r. spectra of complexes derived from ligand (3) [a]

Olefin	Temperature (K)	Diastereoisomer ratio	δ (P-1)	δ (P-2)	$J_{P-1,P-2}$ (Hz)	$J_{P-1,Rh}$ (Hz)	$J_{P-2,Rh}$ (Hz)
(18c)	298	1 : 1	38.3	22.5	59	154	144
			41.8	20.4	62	157	153
(18d)	240	3 : 2	35.6	22.8	59	152	144
			40.3	19.0	59	160	151
(18f)	230	9 : 1	36.2	22.7	59	153	146
			39.9	19.4	64		151
(20a)	298		55.0	10.5	44	138	84
(20b) [b]	298		54.6	12.8	41	138	82
(20b) [c]	298	*c*	70.1	38.4	38	166	*c*
			66.5	38.4	34	155	*c*

[a] [Rh] = 0.04M and [olefin] = 0.12M unless otherwise stated; chemical shifts are given in p.p.m. relative to external H_3PO_4. [b] Equivalent concentration of methyl α-acetamidoacrylate. [c] Large excess of methyl α-acetamidoacrylate used; ratio of complexes obtained was concentration dependent; high-field phosphorus was observed as a complex multiplet.

1,3-bis(diphenylphosphino)propane and with carboxylic acids and a variety of the rhodium solvates.[14] In the present case a tentative structure is (22).



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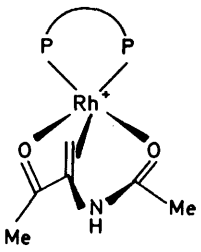


(23)

(d) *With* (R,R)-1,4-*bis*(*diphenylphosphino*)-1,4-*diphenylbutane* (4). Despite the insolubility of the ligand formation of the bicycloheptadiene complex (15d) and its hydrogenation to the methanol solvate (16d) proceeded smoothly although the latter reaction was moderately slow. With methyl (*Z*)-α-benzamidocinnamate (18c) two species are observed (Table 4) and both the chemical shifts and the coupling constants suggest that these are conventional enamide complexes (17) present in approximately equal proportions. Although this spectrum was sharp at room temperature that derived from (*Z*)-α-benzamidocinnamic acid (18a) was broad and required cooling to −22 °C. At this temperature two species were observed corresponding to one diastereoisomer of the normal enamide complex (20%) and one anomalous species (80%) of the type observed with the methanol solvate (16c) and acetamidoacrylates. The structure of this second species was shown to be the complex (23) by a series of experiments employing ^{13}C-labelled enamides. The enamide complex (17c) derived from amide-^{13}C-labelled benzamidocinnamic acid (18b) shows a 6 Hz P–C coupling, to the *low-field* phosphine P-1, in its ^{31}P n.m.r. spectrum (Table 4) whilst the major complex (23) exhibits a 10 Hz P–C coupling to the *high-field* phosphine P-2. The same couplings are observed in the ^{13}C n.m.r. spectrum and both complexes have amide carbons chemically shifted to low-field as expected. A sample of the doubly labelled enamide (18e) was available [12] and the corresponding complex thus prepared from the methanol solvate (16d). No coupling information was discernible from the ^{31}P n.m.r. spectrum of the resulting enamide complex (17d) and its ^{13}C resonance was displaced by 2.4 p.p.m. to low-field relative to the free enamide as observed in previous experiments. The second complex (23) showed coupling between P-2 and the carboxylate-C together with a substantial deshielding of the carboxylate ^{13}C signal. This strongly suggests that both the amide and carboxylate groups are rhodium-bound in the anomalous complex in accord with its representation as the structure (23). Species of this type were the only complexes observed in the ^{31}P n.m.r. spectra on treating the methanol solvate (16d) with acrylic acid derivatives (20a) and (20b). Methyl (*Z*)-α-acetamidocinnamate (18d) gives rise to a ^{31}P n.m.r. spectrum with signals from two normal enamide complexes and one anomalous one.

Summary and Conclusions.—The work initially formed part of an attempt to correlate catalytic efficiency in asymmetric hydrogenation with the structure of stable species formed in solution under catalytic conditions. This was to some extent undermined by observations made on other systems, since it has now been demonstrated [12] that the enamide complex favoured at equilibrium is the one which is stable to hydrogen, the catalytic cycle being sustained by the minor enamide complex. It was additionally felt that chiral biphosphines forming 5- and 7-membered ring chelates would be intrinsically more effective as asymmetric catalysts than those forming a 6-membered chelate ring.[15] This precept was based on the ability of 6-membered ring chelates to adopt a chair conformation in which the PPh_2 moieties are related by mirror symmetry with possible local distortion by α-substituents (Figure 2). This contrasts with the alternating *axial/equatorial* phenyl groups in a non-planar 5- or 7-membered chelate. There is, however, a related twist conformation available to a 6-membered chelate which is comparable and has overall C_2 symmetry.

Recent results from Bosnich [16] and Kagan [17] and their respective co-workers clarifies the course of asymmetric hydrogenation with 6-membered ring chelate biphosphines. Whilst complex (24) with a single asymmetric centre gives low optical yields in the hydrogenation of

TABLE 4

^{31}P N.m.r. spectra of complexes derived from ligand (4) [a]

Olefin	Temperature (K)	Diastereoisomer ratio	δ (P-1)	δ (P-2)	$J_{P-1,P-2}$ (Hz)	$J_{P-1,Rh}$ (Hz)	$J_{P-2,Rh}$ (Hz)
(18a)	250	4 : 1	40.9	40.2	46	160	162
			58.8	23.2	37	143	93
(18c)	298	1 : 1	48.0	41.2	45	159	163
			58.2	29.2	47	163	156
(18d)	250	3 : 3 : 1	47.3	44.5	44	156	163
			61.0	29.2	47	163	149
			59.0	22.4	35	150	91
(18f) [b]	250		58.6	22.9	32	141	91
(20a)	298		59.8	21.4	34	144	90
(20b)	298		60.8	21.3	34	144	88

[a] [Rh] = 0.04M and [olefin] = 0.12M in MeOH. Chemical shifts are given in p.p.m. relative to external H_3PO_4. [b] A second species is observed below 225 K which has the characteristic closely spaced multiplet of a 2 : 1 complex.[14]

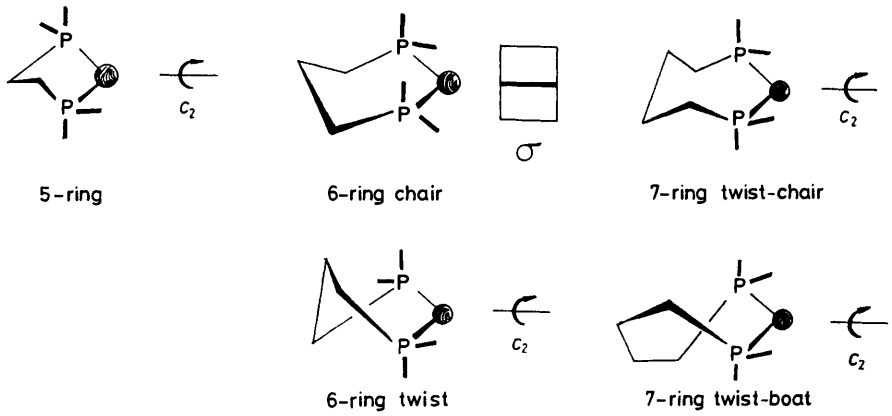
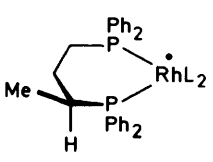


FIGURE 2 Orientation of diphenylphosphine groups in symmetrical conformations of 5-, 6-, and 7-membered ring chelate biphosphine complexes

dehydroamino-acids, complex (25) is a most effective catalyst. Evidence has been presented which suggests that the former exists in chair-form and the latter in a C_2-twist conformation.

The enamide complexes formed by the ligands (3) and (4) include a type which has not been observed elsewhere and which appears, on the basis of spectroscopic results with ^{13}C-enriched dehydroamino-acids, to have the tridentate structure (23). Since this is co-ordinatively



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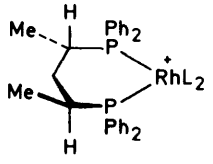

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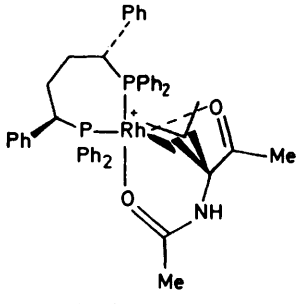

(26)

saturated it is unlikely to react readily with hydrogen and therefore cannot act as a catalyst. The α-phenyl groups of the interphosphine chain of the ligands (3) and (4) are electron-withdrawing and render the rhodium atom more acidic in their complexes. This will increase the tendency for the co-ordination of a second σ-donor carbonyl group from the dehydroamino-acid. Only the high-field phosphorus-nucleus shows an anomalous P–Rh coupling constant suggesting a structure in which the low-field phosphine is *trans* to an amide, in the normal way, and the high-field phosphine is influenced by the carboxy-group and olefin in an orientation such as (26).

EXPERIMENTAL

M.p.s were determined on a Reichert Köfler block and are uncorrected. ^1H N.m.r. spectra were recorded on Perkin-Elmer R32 (90 MHz) or Perkin-Elmer R24 (60 MHz) spectrometers with tetramethylsilane as internal standard. ^{31}P and ^{13}C N.m.r. spectra were recorded on a Bruker WH90 spectrometer (36.43 and 22.62 MHz respectively). ^{31}P Chemical shifts are quoted relative to external phosphoric acid (85%) and ^{13}C chemical shifts relative to external tetramethylsilane. I.r. spectra were recorded on a Unicam SP 1000 spectrometer. Optical rotations were measured with a Perkin-Elmer 141 polarimeter. Chiral g.l.c. separations were achieved with a Perkin-Elmer F11 chromatograph using columns described previously.[18] Microanalyses were performed by Dr. F. B. Strauss and staff (Oxford) and mass spectra were run by Dr. R. T. Aplin and staff on a V G Micromass 16F instrument. Reagent grade solvents were purified according to standard procedures before use.[19] Manipulations involving air-sensitive species were carried out in a Schlenk apparatus under an atmosphere of dry argon and the solvents were thoroughly degassed before use according to standard vacuum line techniques.

Samples for ^{31}P n.m.r. spectroscopy were prepared as described in previous papers of this series.

(+)-(S)-*Phenylethane*-1,2-*diol* (6).—A solution of (+)-(*S*)-mandelic acid (Aldrich, 22.8 g, 150 mmol) in dry tetrahydrofuran (500 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (6.0 g, 150 mmol) in tetrahydofuran (150 ml) over a period of *ca.* 2 h. The mixture was heated under reflux (4 h) and stirred overnight at room temperature. Water (15 ml) was then cautiously added to the stirred solution and the resulting suspension filtered through Celite. The precipitate was washed with diethyl ether (100 ml) and the solvent removed under reduced pressure to give (+)-(*S*)-phenylethane-1,2-diol (7.4 g). Extraction of the inorganic precipitate with diethyl ether in a Soxhlet apparatus gave a further 7.0 g of product, total yield 14.4 g (71%) (lit.,[5] 43%). Recrystallisation from toluene–hexane gave colourless plates, m.p. 65—66 °C (lit., 65 °C); $[\alpha]_D^{20}$ +38.8° (*c* 1.1 in H_2O) [lit.,[20] 40.4 °C (*c* 3.34 in H_2O)]. Further recrystallisation gave a sample with m.p. 66—66.5 °C; $[\alpha]_D^{20}$ +44.3° (*c* 3.34 in H_2O); δ 3.6 (2 H, m, CH_2), 4.75 (1 H, q, CH), 5.2 (2 H, br s, OH), and 7.25 (5 H, s, ArH).

(+)-(S)-*Phenylethylene Bismethanesulphonate* (7).—A solution of (+)-(*S*)-phenylethane-1,2-diol (6) (3 g, 21.7 mmol) in dry pyridine was cooled to −5 °C and stirred

mechanically. Methanesulphonyl chloride (3.83 ml, 5.63 g, 48.7 mmol) was added by syringe during 1 h whilst the temperature was maintained below 0 °C. The thick white suspension was stirred for 4 h at 0 °C then poured on to ice (50 g), mixed well, and acidified to pH 3 with concentrated hydrochloric acid. The solid was filtered off, washed with water (2 × 10 ml), and transferred to a separating funnel whilst still wet. Dichloromethane (20 ml) was added, the organic phase was collected, and the aqueous layer extracted with further dichloromethane (2 × 5 ml). The combined extracts were dried ($MgSO_4$), filtered, and hexane (25 ml) added. Recrystallisation at 5 °C gave (+)-(*S*)-phenylethylene bismethanesulphonate (5.5 g, 86%), m.p. 108—110 °C; $[\alpha]_D^{20}$ +89.85° (*c* 1 in $CHCl_3$) (Found: C, 40.9; H, 4.7; S, 21.7. $C_{10}H_{14}S_2O_6$ requires C, 40.8; H, 4.8; S, 21.8%); δ 2.85 (3 H, s, OMs), 3.0 (3 H, s, OMs), 4.4 (2 H, m, CH_2), 5.8 (1 H, q, CH), and 7.4 (5 H, s, ArH); *m/e* 199 (18%) (M^+ − OMs), 198 (20), 185 (70), 107 (100), 91 (65), and 79 (65).

(−)-(R)-1,2-*Bis*(*diphenylphosphino*)*phenylethane* (1a).—Finely cut lithium metal (813 mg, 116 mg atom) was added, under a flow of argon, to a degassed solution of triphenylphosphine (7.61 g, 29.04 mmol) in dry tetrahydrofuran (20 ml) contained in a Schlenk tube. The red solution was stirred under argon (4 h) and the resulting solution of lithium diphenylphosphide was transferred to an argon-filled Schlenk tube *via* a stainless steel capillary. 2-Chloro-2-methylpropane (3.15 ml, 2.60 g, 29.04 mmol) was added by syringe, the solution refluxed (5 min) and then cooled to −78 °C. (+)-(*S*)-Phenylethylene bismethanesulphonate (4.27 g, 14.52 mmol) was then added, the mixture degassed at −78 °C, and allowed to warm to room temperature with vigorous stirring. The solvent was removed under reduced pressure to give a yellow oil. Addition of degassed methanol (40 ml) gave a white solid. Recrystallisation under argon from degassed dichloromethane–methanol gave (−)-(R)-1,2-*bis*(*diphenylphosphino*)*phenylethane* as fine, white needles (5.99 g, 87%), m.p. 165—175 °C (decomp.); $[\alpha]_D^{20}$ −33.2° (*c* 0.762 in $CHCl_3$) (Found: C, 80.9; H, 6.0; P, 12.9. $C_{32}H_{28}P_2$ requires C, 81.0; H, 5.9; P, 13.1%); δ 2.55 (2 H, m, CH_2), 3.3 (1 H, m, CH), and 6.4—8.2 (25 H, m, ArH); δ(^{31}P) ($CHCl_3$) 9.2 and −15.4 p.p.m. (J_{pp} 18 Hz); $\nu_{max.}$ (Nujol) 750 (s), 740 (m), and 700 cm^{-1} (s).

(+)-(S)-1-*Phenyl*[2,2-$^2H_2$]*ethane*-1,2-*diol*.—The method described for the undeuteriated analogue, with (+)-(*S*)-mandelic acid (3.7 g, 24.3 mmol) and lithium aluminium [$^2H_4$]hydride (1 g, 24.3 mmol), was used to give (+)-(S)-1-*phenyl*[2,2-$^2H_2$]*ethane*-1,2-*diol*, recrystallised from toluene–hexane as colourless plates (1.1 g, 32%), m.p. 66—67 °C; $[\alpha]_D^{20}$ +39.6° (*c* 0.59 in H_2O).

(+)-(S)-1-*Phenyl*[2,2-$^2H_2$]*ethylene Bismethanesulphonate*.—The method described for the undeuteriated analogue, with (+)-(*S*)-1-phenyl[2,2-$^2H_2$]ethane-1,2-diol (0.76 g, 5.43 mmol) and methanesulphonyl chloride (0.7 ml, 1.04 g, 10.88 mmol), was used to give (+)-(S)-1-*phenyl*[2,2-$^2H_2$]-*ethylene bismethanesulphonate* (1.22 g, 76%), m.p. 105—107 °C; $[\alpha]_D^{20}$ +79.9° (*c* 1 in $CHCl_3$); *m/e* 201 (18%) (M^+ − OMs), 200 (20), 185 (70), 107 (100), and 79 (50).

(+)-(S)-1,2-*Bis*(*diphenylphosphino*)-1-*phenyl*[2,2-$^2H_2$]-*ethane*.—The method described for the undeuteriated analogue, with (+)-(*S*)-1-phenyl[2,2-$^2H_2$]ethylene bismethanesulphonate (0.84 g, 2.87 mmol) and lithium diphenylphosphide (5.75 mmol), was used to give (+)-(S)-1,2-*bis*(*diphenylphosphino*)-1-*phenyl*[2,2-$^2H_2$]*ethane* (0.543 g, 40%), m.p. 165—175 °C (decomp.); $[\alpha]_D^{20}$ −39.02° (*c* 0.82 in $CHCl_3$); δ 3.3 (1 H, m, CH) and 6.4—8.2 (25 H, m, ArH).

(+)-(S)-1,2-*Bis*(*diphenylphosphino*)*phenylethane* PP'-*Dioxide*.—(+)-(S)-1,2-*Bis*(*diphenylphosphino*)*phenylethane* (100 mg, 0.21 mmol) in chloroform (5 ml) was stirred with 30% aqueous hydrogen peroxide (1 ml) for 1 h. The organic layer was washed with water (2 × 5 ml), dried ($MgSO_4$) and hexane added to give (+)-(S)-1,2-*bis*(*diphenylphosphino*)*phenylethane* PP'-*dioxide* (73 mg, 68%) as hygroscopic, white needles, m.p. 315—316 °C (sublimed at 220 °C) (Found: C, 74.2; H, 5.8; P, 12.0. $C_{32}H_{28}P_2O_2 \cdot 0.5H_2O$ requires C, 74.5; H, 5.8; P, 12.0%); $[\alpha]_D^{20}$ −177.7° (*c* 0.28 in $CHCl_3$); δ(^{31}P) (benzene) 41.7 and 36.4 p.p.m. (J_{PP} 47.6 Hz); $\nu_{max.}$ (Nujol) 3 600—2 800br (m), 1 190 (s), 1 125 (m), 750 (m), 730 (m), and 700 cm^{-1} (m).

The racemic compound was prepared on the same scale as above from (±)-1,2-bis(diphenylphosphino)phenylethane, m.p. 290—291 °C (sublimed at 220 °C).

(±)-1,2-*Diphenylethane*-1,2-*diol* (8).—*meso*-1,2-Diphenylethane-1,2-diol (6 g, 28 mmol) and potassium hydroxide (50 g) were dissolved in methanol (100 ml) and the solvent removed under reduced pressure. The resulting solid was placed in a 2-necked 250-ml flask equipped with a thermometer and connected to a water pump. The flask was heated under reduced pressure (15 mmHg), until the internal temperature reached 110 °C, and then kept at this temperature for 15 min. The temperature was then raised to 190 °C and the melt kept at this temperature under reduced pressure for 15 min. The flask was then allowed to cool under reduced pressure. Water (150 ml) and diethyl ether (100 ml) were added and the ether layer was washed with water (2 × 50 ml) and dilute hydrochloric acid (50 ml), dried ($MgSO_4$), and the solvent removed under reduced pressure. Recrystallisation from ethyl acetate–cyclohexane gave (±)-1,2-diphenylethane-1,2-diol (1.4 g, 23%), m.p. 142—143 °C (lit.,[7] 121 °C). The compound was shown to have undergone partial spontaneous resolution on crystallisation, thus explaining the high m.p. A single crystal, weight 24.5 mg, had $[\alpha]_D^{20}$ +1.26° (*c* 1.2 in EtOH). Another preparation gave a yield of 3.1 g, 51% (m.p. 123—124 °C); δ 3.0 (2 H, s, OH), 4.45 (2 H, s, CH), and 7.1 (10 H, s, ArH).

(±)-1,2-*Diphenylethylene Bistoluene*-p-*sulphonate*.—Purified toluene-*p*-sulphonyl chloride (2.86 g, 15 mmol) was added to a solution of (±)-1,2-diphenylethane-1,2-diol (1.4 g, 6.54 mmol) in dry pyridine (10 ml) at 0 °C and the solution was kept at 0 °C for 4 d. The mixture was then poured on to ice (100 g), extracted with dichloromethane (3 × 50 ml), the combined organic extracts washed with water (2 × 50 ml) and 6M-hydrochloric acid (2 × 50 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure until a residue of *ca.* 20 ml remained. Addition of hexane (50 ml) and cooling to 0 °C gave (±)-1,2-diphenylethylene bistoluene-*p*-sulphonate (1.4 g, 44.6%), m.p. 112—115 °C (decomp.) (lit.,[20] 121 °C); δ 2.35 (6 H, s, Me), 5.6 (2 H, s, CH), and 6.7—7.7 (18 H, m, ArH).

(±)-1,2-*Diphenylethylene Bismethanesulphonate* (9).—Methanesulphonyl chloride (5.07 ml, 7.5 g, 32.1 mmol) was added dropwise during 20 min to a stirred solution of (+)-1,2-diphenylethane-1,2-diol (2.45 g, 11.5 mmol) in dry pyridine (30 ml) at 0 °C. The mixture was kept at 0 °C for 4 d, then poured on to ice (100 g), extracted with dichloromethane (3 × 50 ml) and the combined organic extracts washed with water (2 × 50 ml) and 6M-hydrochloric acid (50 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure until a residue of *ca.* 20 ml remained.

Addition of hexane (50 ml) and cooling to 0 °C gave (±)-1,2-*diphenylethylene bismethanesulphonate* as white needles (3.96 g, 92.5%), m.p. 113—114 °C (decomp.) (Found: C, 52.1; H, 4.9; S, 17.5. $C_{16}H_{18}O_6S_2$ requires C, 51.9; H, 4.86; S, 17.3%); δ 2.55 (3 H, s, OMs), 5.5 (2 H, s, CH), and 7.0 (10 H, br s, ArH), $\nu_{max.}$ (Nujol) 1 175 (m), 960 (w), 890 (w), and 820 cm^{-1} (w).

(±)-1,2-*Bis*(*diphenylphosphino*)-1,2-*diphenylethane*(2).—(±)-1,2-Diphenylethylene bismethanesulphonate (1.06 g, 2.86 mmol) was added to a solution of lithium diphenylphosphide (5.75 mmol) under argon, prepared as previously described [from triphenylphosphine (1.5 g, 5.75 mmol), lithium (400 mg), tetrahydrofuran, 4 h], in tetrahydrofuran (10 ml) at −78 °C. The mixture was allowed to warm to room temperature, the solvent removed under reduced pressure and degassed methanol (20 ml) added by syringe to give a white solid. Recrystallisation from degassed dichloromethane–methanol under argon gave (±)-1,2-*bis*-(*diphenylphosphino*)-1,2-*diphenylethane* as an air-sensitive, white solid (0.82 g, 52%), m.p. 108—110 °C; δ 2.7 (2 H, m, CH), and 6.8—8.4 (30 H, m, ArH); δ(^{31}P) ($CHCl_3$) 22.4 p.p.m.; $\nu_{max.}$ (Nujol) 755 (m), 740 (s) and 700 cm (s).

(±)-1,3-*Diphenylpropane*-1,3-*diol* (10).—A solution of sodium borohydride (1 g, 26.5 mmol) and sodium hydroxide (35 mg) in methanol (15 ml) was added dropwise to a stirred solution of dibenzoylmethane (Aldrich, 4.5 g, 20 mmol) in dry methanol (50 ml). The resulting clear, colourless solution was evaporated under reduced pressure and the resulting white solid extracted with diethyl ether (2 × 50 ml). Removal of the ether under reduced pressure and recrystallisation from aqueous methanol gave (±)-1,3-diphenylpropane-1,3-diol as white needles (1.35 g, 30%); m.p. 128—130 °C (lit.,[8] 128—130 °C); δ 2.1 (2 H, t, *J* 6 Hz, CH_2), 3.05 (2 H, br s, OH), 4.9 (2 H, t, *J* 6 Hz, CH), and 7.25 (10 H, s, ArH).

(±)-1,3-*Diphenyltrimethylene Bismethanesulphonate* (11).—Methanesulphonyl chloride (0.9 ml, 1.33 g, 11.6 mmol) was added dropwise by syringe to a stirred solution of (±)-1,3-diphenylpropane-1,3-diol (1.33 g, 5.83 mmol) and triethylamine (1.62 ml, 1.18 g, 11.6 mmol) in dry diethyl ether (50 ml) at 0 °C. Stirring was continued for 3 h at 0 °C. The solvent was removed under reduced pressure at 0 °C and the resulting white solid dissolved in diethyl ether (50 ml) and water (50 ml). The ether layer was washed with water (2 × 50 ml), saturated aqueous sodium chloride (50 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure at 0 °C. Crystallisation of the colourless oil from methanol gave (±)-1,3-*diphenyltrimethylene bismethanesulphonate* as white needles (1.53 g, 40%), decomp. 64—65 °C (the compound decomposed within *ca.* 1 h at room temperature to give a black tar); δ 2.5 (2 H, t, *J* 6 Hz, CH_2), 2.7 (6 H, s, OMs), 5.65 (2 H, t, *J* 6 Hz, CH), and 7.3 (10 H, s, ArH); *m/e* 384 (2%) (M^+), 96 (100), and 79 (100).

(±)-1,3-*Bis*(*diphenylphosphino*)-1,3-*diphenylpropane* (3).—(±)-1,3-Diphenyltrimethylene bismethanesulphonate (0.96 g, 2.5 mmol) was added under argon to an air-free solution of lithium diphenylphosphide (5.5 mmol) [from triphenylphosphine (1.44 g, 5.5 mmol) and lithium (200 mg) in tetrahydrofuran, 4 h; then 2-chloro-2-methylpropane (0.64 ml, 0.5 g, 5.5 mmol)] in tetrahydrofuran (10 ml) at −78 °C. The solution was degassed at −78 °C, allowed to warm, with stirring, to room temperature and the solvent removed under reduced pressure. Addition of degassed methanol (10 ml), filtration, and recrystallisation from degassed dichloromethane–methanol gave (±)-1,3-*bis*(*diphenylphosphino*)-1,3-*diphenylpropane* as white needles (0.718 g, 51%); m.p. 132—133 °C (decomp.) (Found: C, 83.1; H, 6.2; P, 10.8. $C_{39}H_{34}P_2$ requires C, 83.0; H, 6.0; P, 11.0%); δ 2.2 (2 H, m, CH_2), 3.2 (2 H, m, CH), and 6.5—7.8 (30 H, m, ArH); δ (^{31}P) (CH_2Cl_2) 4.4 p.p.m.; $\nu_{max.}$ (Nujol) 740 (m) and 700 cm^{-1} (s).

1,2-*Dibenzoylethane*.[9]—A suspension of *trans*-1,2-dibenzoylethene (Aldrich, 20 g, 80.6 mmol) in ethanol (100 ml) was added rapidly with stirring to a suspension of tin(II) chloride (20 g, 105.4 mmol) in 8M-aqueous hydrochloric acid (30 ml) and ethanol (10 ml) at 70 °C. When the addition was complete water (10 ml) was added and the mixture allowed to cool to room temperature. The solid was collected and recrystallised from chloroform–methanol to give 1,2-dibenzoylethane as white needles (12.9 g, 64%); m.p. 145—147 °C (lit.,[9] 145—147 °C).

(±)-1,4-*Diphenylbutane*-1,4-*diol* (12).—A solution of sodium borohydride (3 g, 79 mmol) in methanol (20 ml) was added dropwise to a stirred suspension of dibenzoylethane (10 g, 40 mmol) in dry methanol (100 ml) over *ca.* 15 min. Stirring was continued for 30 min and the solvent then removed under reduced pressure. The resulting oil was dissolved in diethyl ether (100 ml) and, in time, the borate complex of *meso*-1,4-diphenylbutane-1,4-diol was deposited as a white solid. This was filtered off and washed with diethyl ether (100 ml). The combined ether solutions were evaporated under reduced pressure. The resulting solid was dissolved in hot aqueous methanol (100 ml) and acidified with concentrated hydrochloric acid to hydrolyse any remaining borate complex. On cooling white needles (5 g), m.p. 82—85 °C were deposited. Two recrystallisations from chloroform–hexane gave pure (±)-1,4-diphenylbutane-1,4-diol (3.1 g, 31%) as white needles, m.p. 90—91 °C (lit.,[9] 91 °C); δ 1.75 (4 H, m, CH_2), 2.65 (2 H, s, OH), 4.6 (2 H, m, CH), and 7.2 (10 H, s, ArH).

(±)-1,4-*Diphenyltetramethylene Bismethanesulphonate* (13).—Methanesulphonyl chloride (0.62 ml, 0.91 g, 8 mmol) was added dropwise by syringe to a stirred solution of (±)-1,4-diphenylbutane-1,4-diol (1.0 g, 4 mmol) and triethylamine (1.1 ml, 0.8 g, 8 mmol) in dry diethyl ether (20 ml) at 0 °C. The mixture was kept at 0 °C overnight and then the solvent was removed under reduced pressure. The resulting white solid was dissolved in diethyl ether (50 ml) and water (50 ml) and the ether layer was washed with water (2 × 50 ml), saturated aqueous sodium chloride (50 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure until a residue of *ca.* 10 ml remained. At 0 °C after addition of hexane (10 ml) (±)-1,4-*diphenyltetramethylene dimethanesulphonate* (1.34 g, 84%) was obtained as white needles, m.p. 61—63 °C (decomp.); δ 2.1 (4 H, m, CH_2), 2.65 (6 H, s, OMs), 5.6 (2 H, m, CH), and 7.4 (10 H, s, ArH); *m/e* 398 (24) (M^+), 206 (100), 205 (55), 203 (38), 98 (30), 95 (50), 91 (20), and 89 (30).

This compound was found to decompose overnight, even at −30 °C. Accordingly it was used as soon as prepared.

(±)-1,4-*Bis*(*diphenylphosphino*)-1,4-*diphenylbutane* (4).—Freshly prepared (±)-1,4-diphenyltetramethylene bismethanesulphonate (0.98 g, 2.5 mmol) was added under argon with vigorous stirring to an air-free solution of lithium diphenylphosphide (5 mmol) [from triphenylphosphine (1.31 g, 5 mmol) and lithium (175 mg, 25 mg atom)] in tetrahydrofuran, stirred 4 h; then 2-chloro-2-methylpropane (0.64 ml, 0.5 g, 5.5 mmol)] in tetrahydrofuran (5 ml) at −78 °C. The solution was degassed at −78 °C and allowed to warm, with stirring, to room temperature and the solvent

was removed under reduced pressure. Addition of degassed methanol (10 ml), filtration of the resulting white solid and recrystallisation from hot tetrahydrofuran gave (±)-1,4-*bis*(*diphenylphosphino*)-1,4-*diphenylbutane* as white needles, decomp. >200 °C (480 mg, 30%), together with *ca.* 5% of the phosphine dioxide (estimated by ^{31}P n.m.r.), which could not be removed by repeated recrystallisation; δ (^{31}P) ($CHCl_3$) 5.9 (phosphine) and 33.7 p.p.m. (phosphine dioxide); the compound was not sufficiently soluble for ^1H n.m.r. spectroscopy; $\nu_{max.}$ (Nujol) 750 (m), 740 (s), 730 (m), and 700 cm^{-1} (s).

Hydrogenation Procedures.—The required biphosphine (1 equiv., typically 1×10^{-2} mmol) and bis(bicyclo[2.2.1]-hepta-2,5-diene)rhodium(I) tetrafluoroborate (1—1.2 equiv., 1—1.2×10^{-2} mmol, 3.74—4.49 mg) were stirred together in air-free methanol under argon in a Schlenk tube attached to a vacuum line until a homogeneous orange solution was obtained (5—30 min). The substrate (1.25—100 equiv., see text) was then added, the solution degassed with 3 freeze–pump–thaw cycles and the argon atmosphere replaced by a hydrogen atmosphere. The Schlenk tube was then evacuated and filled with hydrogen (×3) at −78 °C and allowed to warm to room temperature. The hydrogen flow was then turned off and the Schlenk vessel and gas line sealed in a hydrogen atmosphere. The solution was vigorously stirred until hydrogenation was complete (15 min—48 h, see text), this being indicated by the change in colour of the solution from orange or deep red (enamide complex) to pale yellow (methanol complex). Hydrogenation of substrates other than dehydroamino-acids was allowed to proceed for 24 h giving, in all cases, complete reduction.

Isolation Procedures.—(a) *In the hydrogenation of dehydroamino-acids.* The reaction mixture was evacuated and the complete conversion checked by ^1H n.m.r. spectroscopy. Rhodium complexes were removed by chromatography on a short column of silica (*ca.* 10 g), packed with diethyl ether, with ethyl acetate as eluant. The optical purity of *N*-benzoylamino-acids and esters was measured by rotation. The optical purity of *N*-acetylamino-acid esters was measured by g.l.c. using (*S*)-*N*-docosanoylvaline-t-butylamide (4% on Chromosorb G AW DCMS) as stationary phase. Chromatographed *N*-acetylamino-acids were converted into the methyl esters before optical purity determination by g.l.c. A typical procedure is given below.

N-*Acetyl*-β-*phenylalanine Methyl Ester.*—*N*-Acetyl-β-phenylalanine (5 mg, 2.4×10^{-2} mmol) was dissolved in methanol (1 ml) and placed in the ' bucket ' of a trap-to-bucket distillation apparatus. The outer tube of the apparatus was placed in an ice–salt bath and ' Diazald ' (*N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide) (20 mg, 9.6×10^{-2} mmol) in methanol (0.5 ml) followed by sodium hydroxide (*ca.* 50 mg) in water (0.5 ml). The ' bucket ' was immediately put in place, cooled with solid carbon dioxide–isopropyl alcohol and the ice-bath allowed to melt. This was then replaced by a water-bath at 60 °C and the apparatus left for 1 h during which time no more solid carbon dioxide was added to the cold finger. This procedure caused the evaporation of diazomethane and methanol on to the cold finger and the consequent reaction with the amino-acid. The resulting *N*-acetyl-β-phenylalanine methyl ester was used without further purification for enantiomer excess determination by g.l.c.

In all cases the (*R*)-amino-acid derivative was eluted first from the g.l.c. column, with $\Delta t_{ref.}$ for (*R*)- and (*S*)-alanine derivatives at 120 °C of *ca.* 30 s, and *ca.* 3 min for (*R*)- and (*S*)-phenylalanine derivatives at 160 °C. Traces were analysed by tracing on to graph paper and finding the area under each peak which gave an estimated precision of ±2% in the optical yield.

(b) *For hydrogenation of other substrates.* Compounds hydrogenated were methyl 2-acetoxypropenoate, methyl 2-phenylpropenoate, and dimethyl itaconate (dimethyl methylenesuccinate). Hydrogenation was carried out by the method described above for dehydroamino-acids. After 24 h of hydrogenation the solvent was removed under reduced pressure (0 °C; *ca.* 0.2 Torr), the complete hydrogenation checked by n.m.r. spectroscopy and the product chromatographed on a silica (10 g) column with diethyl ether as eluant. The ether was removed under reduced pressure (0 °C; 20 Torr) and the residue distilled (30 °C; 0.05 Torr) in a short-path distillation apparatus. Optical purity was determined by ^1H n.m.r. spectroscopy using the chiral shift reagent $Eu(hfc)_3$.*

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* $Eu(hfc)_3$ is europium bisheptafluorobutyrylcamphorate.

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