The Mechanism of Asymmetric Homogeneous Hydrogenation. Rhodium Complexes formed by Dehydroamino-acids Co-complexed with *trans*-4,5-Bisdiphenylphosphino-2,2-dimethyldioxolan and Achiral Models [1]

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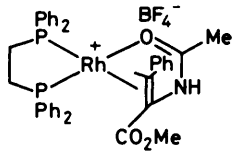
Enamiderhodium complexes formed by six- and seven-ring chelate-forming biphosphines have been investigated by ^{31}P and ^{13}C n.m.r. spectroscopy. Compared with five-ring chelate complexes discussed earlier, these generally undergo much readier dynamic exchange and possess lower binding constants. Their structure has been determined by observing chemical shifts and coupling constants in the ^{13}C n.m.r. spectrum of suitably labelled dehydroamino-acids. Derivatives of *Z*-dehydroamino-acids are co-ordinated to rhodium through olefin and amide (with possible intervention of the carboxylate group at low temperatures) whereas derivatives of *E*-dehydroamino-acids are co-ordinated to rhodium through olefin and carboxylate groups. Two anomalous complexes have been observed. With an excess of *Z*-acetamidocinnamic acid complexes of 2:1 olefin:rhodium were observed, particularly at low temperatures with the rhodium solvate of 1,3-bisdiphenylphosphinopropane. *E*-Benzamidocinnamic acid in deficiency to the rhodium solvate of 1,4-bisdiphenylphosphinobutane forms a binuclear complex where the enamide may act as a bridging ligand.

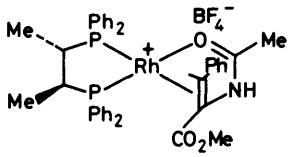
HOMOGENEOUS organometallic catalysis usually requires a sequence of reactions in which co-ordinatively saturated and unsaturated intermediates are linked by relatively low energy barriers. These intermediates are only rarely present in sufficient concentration for their solution structure to be defined by spectroscopic methods. For example, in homogeneous hydrogenation of olefins catalysed by tristriphenylphosphinerhodium(I) chloride [2] there is no definitive observation of an intermediate with bound substrate although a transient species has been observed by stopped-flow spectrophotometry in the hydrogenation of acrylonitrile.[3] Further information has come from n.m.r., particularly on the structure and dynamic behaviour of triphenylphosphinerhodium hydrides [4] but the major contribution to our understanding of the catalytic cycle has come from careful kinetic studies [5] which are consistent only with a reaction pathway involving sequential co-ordination of hydrogen and olefin followed by intracomplex hydride migration and elimination of hydrocarbon from the resulting alkylmetal hydride.

Kinetic studies alone cannot provide an adequate understanding of asymmetric homogeneous catalysis, since rate constants provide no information on the structural origins of stereospecificity. The most effective example is hydrogenation of dehydroamino-acids catalysed by cationic chelating biphosphine complexes of rhodium, where optical yields of better than 95% may be obtained with a range of catalysts.[6] Two types of experiments may help to define the cause of such striking asymmetric induction. First, *X*-ray crystal structure analysis of isolable species may help to determine the molecular interactions responsible for selectivity.[7] The commonest catalytic precursor is a cyclo-octa-1,5-diene- or bicyclo[2.2.1]heptadienerhodium biphosphine salt and numerous structures are now available. Hydrogenation of this complex in methanol and addition of an appropriate *Z*-dehydroamino-acid produces an enamide complex and in two cases these have been isolated and their crystal structures determined.[8] For complex (1) derived from bisdiphenylphosphinoethane, this demonstrates that only the olefin and amide are co-ordinated, and that the biphosphine assumes a chiral conformation with approximately C_2 symmetry by distortion of the five-membered chelate ring. The corresponding asymmetric complex (2) derived from (*SS*)-2,3-bisdiphenylphosphinobutane has a very similar structure, with the methyl groups of the chelate ring in a pseudoequatorial conformation. There are two possible diastereoisomers of (2) related by binding the opposite olefin prochiral faces to rhodium, and the one which is isolated is of opposite configuration to the product of hydrogenation assuming *cis*-delivery of hydrogen from rhodium.[9] It is assumed, although unproved, that stereoselectivity in substrate binding arises from H–H and H–X non-bonded interactions between *P*-phenyl rings and the substituents of the olefin. In almost all the examples studied,[7,8] the chelate ring assumes a conformation with one pair of axial and one pair of equatorial *P*-phenyl rings, and an *ortho*-hydrogen of each of the axial rings is in proximity to the rhodium at a pseudo-octahedral site orthogonal to the co-ordination plane as in (3).

Phosphorus-31 and carbon-13 n.m.r. studies have clearly shown that structures (1) and (2) are maintained in solution. In the case of (*RR*)-bis-[*o*-methoxyphenyl(phenyl)phosphino]ethane they additionally demonstrate that both rhodium enamide complexes (4a and b) are present in solution and that they are co-ordinated in the same fashion.[10] At low temperatures a transient alkylrhodium (5) has been observed [11] and it was conclusively shown that it arises by hydrogen addition to the minor enamide complex (4b) and that (4a) is essentially unreactive to hydrogen at −45 °C. The main flux of the catalytic cycle therefore involves the enamide complex which is thermodynamically disfavoured and intrinsically inaccessible to *X*-ray structural studies. Attempts are being made to determine the structure of (4) [and possibly (5)] in solution by the application of



(1)



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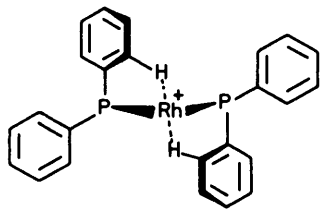

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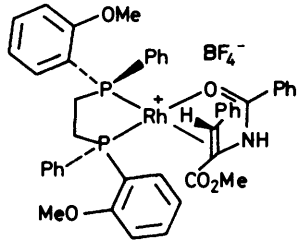
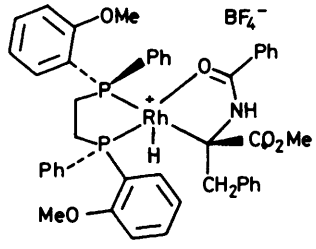


(4a)

(4b) diastereoisomer involving binding of opposite olefin face.

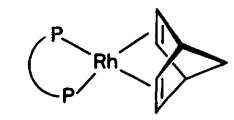


(5)

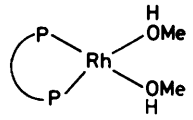
difference n.O.e. spectroscopy.[12] Since n.m.r. permits the observation of both diastereoisomeric species derived from a given chiral biphosphine complex and dehydroamino-acid, the rate and mechanism of their interconversion may be determined. In the cases examined,[13] it seems that this occurs much more rapidly than catalytic turnover, so that the complexation step is normally a pre-equilibrium rather than the rate-determining stage. This is in accord with kinetic experiments which show that the reaction is normally first order in hydrogen, although complexation, or the equilibration between diastereoisomers is probably important at high pressure.[8,14]

It seems clear that an understanding of the stable complexes formed in solution under the conditions of asymmetric hydrogenation is pertinent to an understanding of the reaction mechanism. In the present study, we report on the n.m.r. spectra of enamide complexes formed by the first [15] effective chiral chelating ligand (*RR*)-*trans*-4,5-bisdiphenylphosphino-2,2-dimethyldioxolan (DIOP) and the corresponding achiral analogues 1,3-bisdiphenylphosphinopropane and 1,4-bisdiphenylphosphinobutane.[1] Properties which are rather distinct from those of the corresponding five-ring chelate complexes are observed.

Complexes with Z-Dehydroamino-acids.—The bicyclo-[2.2.1]heptadiene complexes (6a)—(8a) may be prepared



(6)-(8) a



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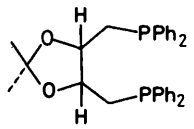
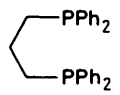


(6)



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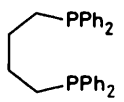

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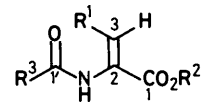
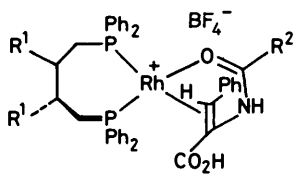


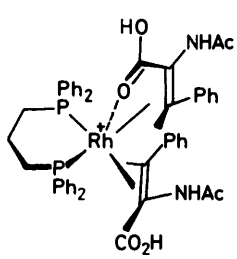
(9)

	R^1	R^2	R^3
a;	Ph	H	Ph
b;	Ph	Me	Ph
c;	Ph	H	Me
d;	Ph	Me	Me
e;	Ph	Pr^i	Me
f;	Ph	Et	Me



(10) R^1,R^1 =  R^2 = Ph

(11) R^1 = H, R^2 = Me



(12)

by previously described methods [10,16,17] and all give rise to solvate adducts (6b)—(8b) on hydrogenation in methanol solution.[17] The resulting solution is easily air-oxidised but otherwise stable. With the DIOP complex, addition of excess *Z*-benzamidocinnamic acid (9a) and sealing under argon gave rise to a scarlet solution with a rather broad phosphorus-31 n.m.r. spectrum at room temperature. Cooling to 274 K or below gave a sharp eight-line spectrum (Table 1) corresponding to a single diastereoisomeric species (10) with non-equivalent mutually coupled phosphines. Similar spectra were obtained from methyl *Z*-benzamidocinnamate (9b), *Z*-acetamidocinnamic acid (9c), and its methyl ester (9d). In the latter two cases dynamic exchange was more evident and it was necessary to cool the sample to 241 K or below in order to obtain sharp spectra. The complex prepared from an excess of (9a) showed no evidence of solvate (6b) at equilibrium but when the initial solution was 0.04M in (6b) and 0.05M in (9a) then solvate was still present at 270 K although it had disappeared at 230 K, suggesting that the equilibrium constant increases with decreasing temperature. For 0.11M-*Z*-α-methyl acetamidocinnamate (9d) in the presence of 0.025M-solvate (6b) formation of the enamide complex is incomplete at all temperatures. The complexation constant is *ca.* 120 l mol^{-1} at 230 K in this case and *ca.* 90 l mol^{-1} for *Z*-α-benzamidocinnamic acid at 270 K. These values are an order of magnitude less than those observed for related five-ring chelate complexes [8,18] but comparable to data obtained for enamide complexes of *trans*-1,2-bisdiphenylphosphinomethylcyclobutane.[19] Since the dynamic exchange process observed involves concomitant broadening of solvate resonances (and therefore relates to a dissociative breakdown of the complex) it is probable that the lower binding constant of the seven-ring chelate (10) reveals a faster reversion to reactants than obtains for five-ring chelate enamides, and complexation rates are comparable in the two cases. Only *Z*-α-isopropyl acetamidocinnamate (9e) shows two diastereoisomeric enamide complexes (Table 1) its spectrum being otherwise similar to the methyl ester derived species.

The closest achiral model for DIOP is 1,4-bisdiphenylphosphinobutane. Its rhodium solvate (7b) reacts with *Z*-acids and esters in the expected manner, although dynamic broadening is less evident and the enamide from (9b) is fairly sharp at room temperature. The mechanism by which dynamic broadening occurs was tested in a series of experiments with solvate (7b) and *Z*-α-acetamidocinnamic acid (9c) at varying concentrations. The width of signals in the resulting ^{31}P n.m.r. spectra is shown in Figure 1. Three possible sequences might be responsible for line broadening.

The first involves an intramolecular process such as rotation of the enamide ligand with respect to the P–Rh–P plane so that P(1) and P(2) are interchanged. This can be ruled out because signals due to solvate (7b) are broadened concomitantly. Similarly, a rate-determining attack of substrate (9c) on the complex would lead to a line width strongly dependent on the respective concentrations of (9c) and enamide complex (11), again at variance with observation. A dissociative mechanism is entirely consistent with the strong dependence of line width on concentration for solvate (7b) and the similar, albeit less pronounced dependence for (11).

The complexes derived from 1,3-bisdiphenylphosphinopropane *via* solvate (8b) are similar at room temperature. With *Z*-α-benzamidocinnamic acid the ^{31}P n.m.r. spectrum is sharp at room temperature whereas the complex derived from *Z*-α-acetamidocinnamic acid

TABLE 1

^{31}P N.m.r. spectra of rhodium phosphine complexes of *Z*-enamides

Phosphine	S : Rh	Substrate	*T*/K	$W_{1/2}$/Hz	%	δ P(1) (p.p.m.)	δ P(2) (p.p.m.)	J_{RhP}-(1)/Hz	J_{RhP}-(1))Hz	$J_{P(1)P(2)}$/Hz
$Ph_2P(CH_2)_4PPh_2$	5 : 1	(9b)	300	7		40.3	27.5	156	157	54
	5 : 1	(9a)	300	90						
			263	10		42.2	30.0	157	159	54
	4.8 : 1	(9c)	241	7		48.1	22.6	159	154	53
$Ph_2P(CH_2)_3PPh_2$	4 : 1	(9b)	300	5		30.2	9.5	154	146	65
	4 : 1	(9d)	276	3		31.5	10.2	154	146	65
	4 : 1	(9a)	274	4	88 [a]	30.7	10.2	154	145	65
			241	3	85	30.8	10.4	155	145	66
				3	15	20.5	16.0	124	131	44
			213	3	72 [b]	30.9	10.9	153	145	65
	4.8 : 1	(9c)	274	3	60	31.5	10.4	156	147	65
					40	19.4	16.7	126	131	44
			241		30	31.8	10.4	154	146	65
					70	19.9	16.5	124	130	44
DIOP	6 : 1	(9b)	274	3		34.6	11.0	152	157	53
	4.8 : 1	(9d)	241	3	*c*	35.5	10.8	150	152	52
	4.2 : 1	(9f)	241	3	*d*	35.1	10.3	152	153	52
	4.4 : 1	(9e)	241	3	69	35.0	10.0	152	153	52
					18 [e]	28.6	10.3	159	159	47
	4.5 : 1	(9a)	274	3		34.8	10.1	153	154	53
	5 : 1	(9c)	229	3		35.7	10.0	151	150	52

[a] 12% 2 : 1 complex present. [b] 28% 2 : 1 complex, broadened. [c] 7.5% MeOH complex. [d] 10% MeOH complex. [e] 13% MeOH complex.

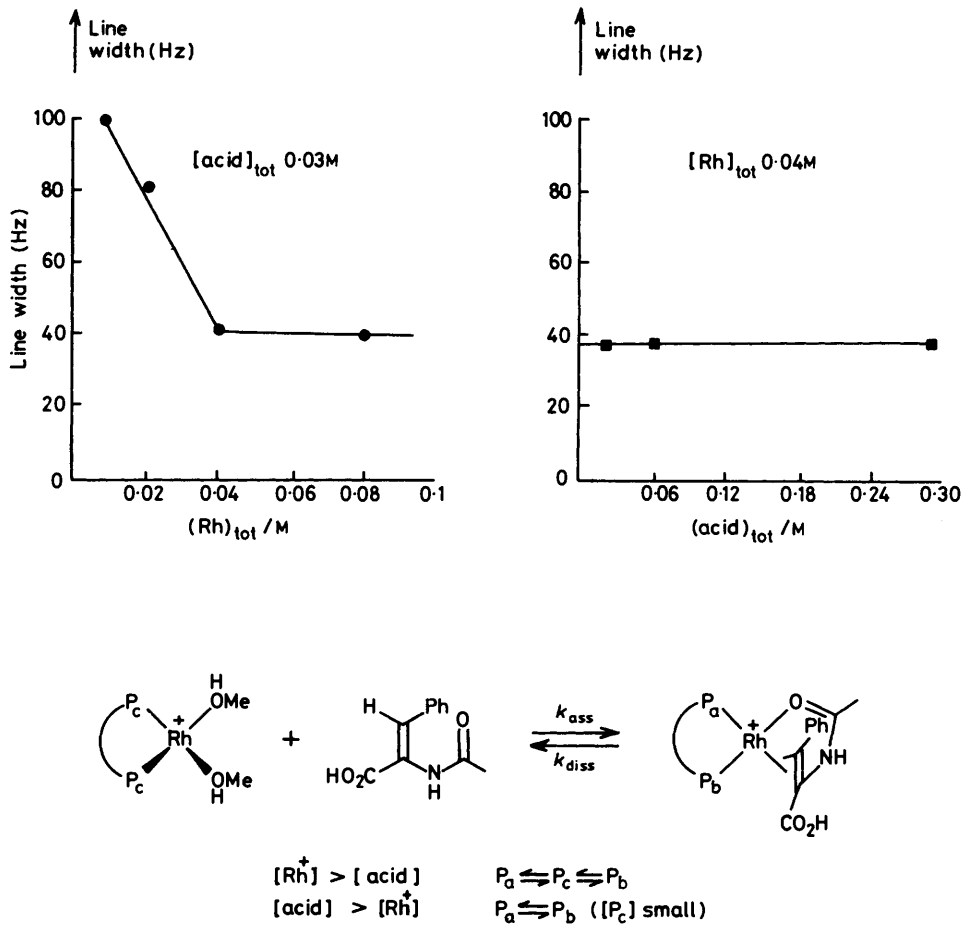


FIGURE 1 Phosphorus-31 n.m.r. line widths for enamide complex (11) at varying concentrations for *Z*-α-acetamidocinnamic acid and solvate (7b) at ambient temperature

exhibits a line width of 20 Hz at 300 K. At lower temperatures a second complex is evident particularly in the latter case, and a series of experiments with differing concentrations of solvate (8b) and acid (9c) demonstrate that it is a 2 : 1 complex (Figure 2), similar to those observed with propenoic, 2-methylpropenoic, and 2-methylenebutanedioic acids with rhodium solvates of seven-ring chelate biphosphines.[20,21] The chemical shifts of P(1) and P(2) are closely spaced and the smaller coupling constants observed (Table 1) suggest that it is five- or six-co-ordinate, a possible structure being (12). At low temperatures, with an excess of acid (9c) this can be the dominant product with almost complete exclusion of the conventional enamide complex.

Experiments with Carbon-13 Labelled Enamides.—The synthesis of dehydrophenylalanine derivatives (13a—c) containing a single site of ^{13}C enrichment has been described earlier.[10] Application of these labelled enamides made it clear that only the olefin and amide groups are bound to rhodium in DIPHOS and DIPAMP complexes and that the diastereomeric enamide complexes observed in the latter case are of similar structure, but with opposite prochiral faces of olefin bound to rhodium. The results obtained with labelled *Z*-enamides derived from solvates (6b)—(8b) demonstrate the generality of this structure [Supplementary Publication No. SUP 23275 (5 pp.)*], and the similarity of ^{13}C chemical shifts and coupling constants for different phosphine complexes. The major variant is the chemical shift of olefinic C(3), which will be expected to be very sensitive to the extent of back-bonding induced by the *trans*-related phosphine ligand.[22] One striking divergence from the behaviour of five-ring chelate complexes is apparent. The latter have ^{13}C spectra which are only sensitive to a small extent to changes in temperature. By contrast those derived from (6b)—(8b) exhibit interesting changes with decreasing temperature which point to structural modification (Figure 3). In all three cases the carboxy-carbon shifts to lower field whereas the chemical shift of free (13a) is effectively unaltered between 180 and 260 K. The amide carbon concomitantly shifts to higher field over the same temperature range whilst the free substrate (13b) is unaffected, and the olefinic carbon in complex shifts by up to 20 p.p.m. upfield. Entirely similar changes take place in

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.

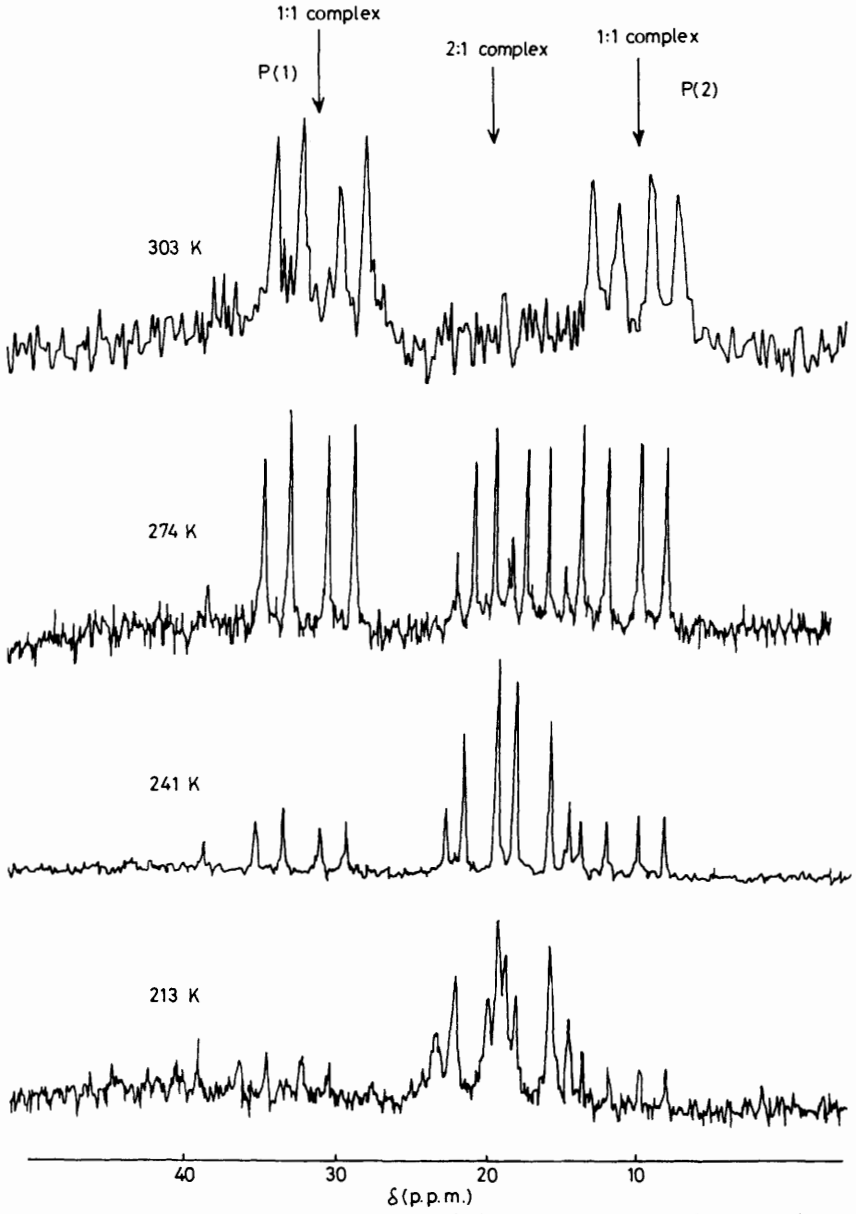


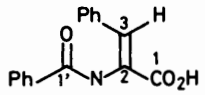
FIGURE 2 Phosphorus-31 n.m.r. spectra of 2 : 1 complexes derived from *Z*-α-acetamidocinnamic acid and solvate (8b)

the spectra of ^{13}C enriched esters (14a—c), and it is noteworthy that enamide complexes from these ligands form scarlet solutions at room temperature which lighten considerably to orange at dry-ice bath temperatures. The observation is consistent either with formation of a tridentate enamide complex (15) or incorporation of a solvent molecule (16) with support for the first structure arising from the deshielding observed in (13a) with decreasing temperature. Complexes with formally trico-ordinate structure have been proposed on similar criteria elsewhere.[23,24]

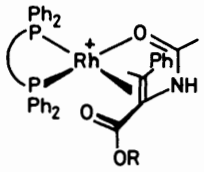
Labelled enamide (14d) was not available when the preliminary communication [1] was submitted but its bisdiphenylphosphinobutane complex has now been prepared. Its ^{13}C chemical shift is temperature dependent like that of (14c), but ^{13}C coupling constants both to rhodium and phosphorus are markedly different. The higher value of J_{CP} is consistent with unsymmetrical complexation of the olefin so that C(2) is closer to collinearity with the *trans*-P(1)–Rh bond, as is observed in *X*-ray crystal structures of enamides. This coupling constant increases markedly with decreasing temperature, reflecting increased σ-bonding as the trico-ordinate structure makes a greater contribution.

Small amounts of the 2 : 1 complex described above are visible in the ^{13}C spectra of (13) and the 1,3-bisdiphenylphosphinopropane solvate (8b) but they are insufficiently sharp to provide useful information.

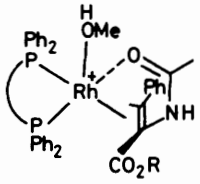
A 2 : 1 complex with different spectral characteristics has been reported in the course of a study of catalysis by



(13) R = H
(14) R = Me
a; ^{13}C-1
b; ^{13}C-1′
c; ^{13}C-3
d; ^{13}C-2



(15)



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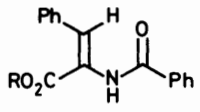
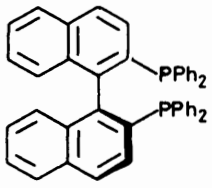


(17) a; R = H
b; R = Me



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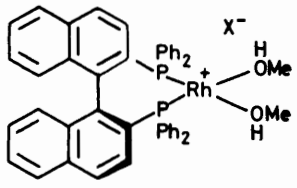

(19)

the atropisomeric biphosphine (18).[6a] The rhodium solvate (19) in the presence of a large excess of *Z*-α-benzamidocinnamic acid (9a) gives rise to a ^{31}P n.m.r. spectrum with a doublet at δ 50.0 p.p.m. (*J* 165 Hz) and a singlet at 41.8 p.p.m. The chemical shift of the latter resonance is rather close to that of related phosphine oxides and it is possible that a part-oxidised species is responsible rather than the rapidly equilibrating 1 : 2 co-ordination complex suggested.

Complexes derived from E-*Benzamidocinnamic Acid.*— In the preliminary communication,[1] the ^{31}P n.m.r. spectrum of DIOP solvate (6b) co-ordinated to *E*-benzamidocinnamic acid (17a) was reported. The spectrum showed two diastereoisomers in approximately equal proportions with phosphorus–rhodium coupling constants rather larger than those obtained for the comparable complex of *Z*-benzamidocinnamic acid (9a). Similar spectra, but showing only one diastereoisomeric complex as expected, were observed with acid (17a) and achiral solvates (7b) and (8b) (SUP 23275). All these complexes exhibit sharp spectra at room temperature and negligible amounts of uncomplexed solvate in the presence of excess of substrate (17a). Corresponding experiments with methyl *E*-benzamidocinnamate (17b) produced no initial complexation but a rapid isomerisation to the corresponding complexed *Z*-isomer was observed over 1 h at room temperature with both (6b) and (8b). Isomerisation in competition with hydrogenation has frequently been observed with *E*-enamides.[25]

The structure of complexes (20) derived from *E*-benzamidocinnamic acid was determined by observing the ^{13}C n.m.r. spectra of isotopically enriched substrates (SUP 23275). Using the criteria previously established these demonstrate that they are olefin-carboxylate complexes with the amide unbound, and probably an ionised carboxy-group so that the overall result is a neutral species. The phosphorus–phosphorus and phosphorus–rhodium coupling constants are very similar to those obtained with the salts of αβ-unsaturated acids and (6b) or with αβ-unsaturated amides and (6b).[20]

Where a choice of chelate structure pertains, as in complexation of dehydroalanines, the amide group is co-ordinated and the carboxylate group remains unbound. This is the main type of complex observed with *Z*-dehydrophenylalanines and a very wide variety of

TABLE 2

Monomeric and dimeric complexes of bisdiphenylphosphinobutanerhodium with *E*-α-benzamidocinnamic acid

^{31}P N.m.r.

Rh : S	*T*/K	%	δ P(1) (p.p.m.)	δ P(2) (p.p.m.)	$J_{RhP(1)}$/Hz	$J_{RhP(2)}$/Hz	$J_{P(1)P(2)}$/Hz
3.3	300	100	57.8	11.7	181	165	54
	241	100	60.8	10.3	182	165	54
1.2	272	80% A	60.0	11.1	179	165	53
		20% B	60.0	45.6	177	136	52
			43.4	7.9	133	163	41.5
0.6	272	45% A					
		55% B					
	260	25% A					
		75% B					

^{13}C N.m.r. of 2 : 1 complex

Position of label	*T*/K	
C(1)	260	177.6
C(1′)	241	169.9
C(3)	300	89.09 (J_{CRh}10/Hz)

A and B. respectively refer to mononuclear and dinuclear complexes. [a] Signal appears as a triplet and P(1) and P(2′) are broadened in the ^{31}P n.m.r. spectrum.

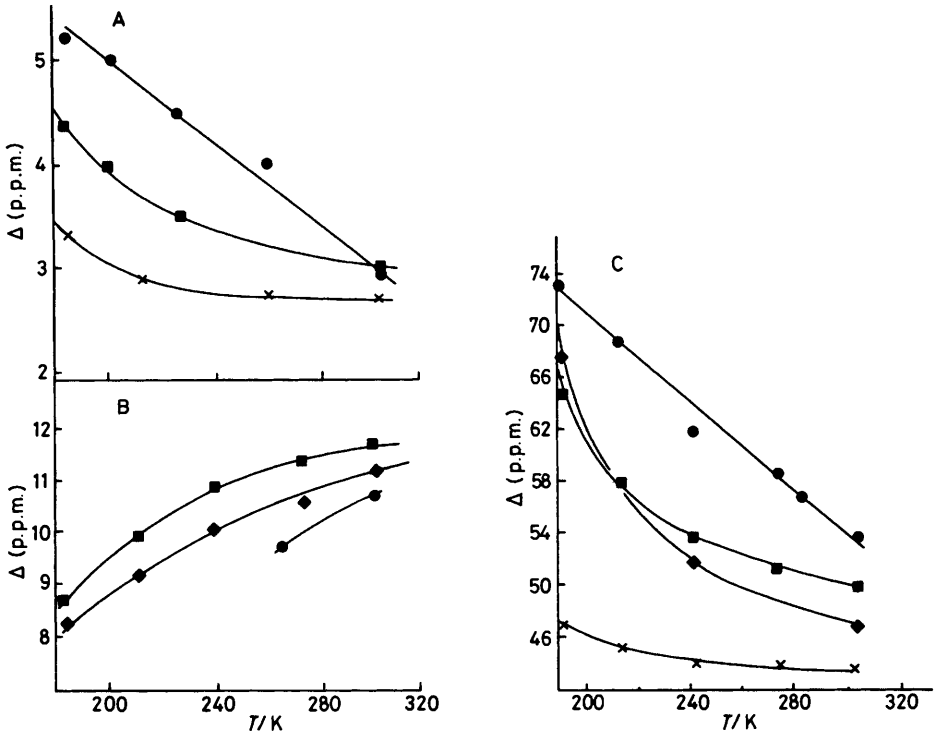

FIGURE 3 Temperature effects in carbon-13 n.m.r. chemical shifts of enamide complexes. Ordinate is complexation; chemical shift Δ (downfield in A and B, upfield in C) and abscissa is corrected probe temperature: ×, $Ph_2PCH{=}CHPPh_2$ ●, (6); ◆, (7); ■, (8); A, $^{13}C(1)$; B, $^{13}C(1')$; C, $^{13}C(3)$

chelating biphosphine rhodium cations. The divergent behaviour of *E*-dehydrophenylalanines is presumably caused by steric repulsion in the amido-olefin chelate. Molecular models demonstrate that the β-phenyl ring of (17a) in its biphosphinerhodium complexes is in a much more open environment when carboxylate is the second bound group as in (20) (Figure 4). This arrangement is generally inferior to the conventional enamide complex in effecting stereoselection, leading to lower optical yields in hydrogenation of *E*-amides [26] than in hydrogenation of *Z*-isomers under similar experimental conditions.

An anomalous ^{31}P n.m.r. spectrum was observed when acid (17a) was reacted with an excess of the bisphosphinobutane solvate (7b). The resulting species showed four distinct resonances (Table 2) and none of the complex observed when (17a) was present in excess. None of the experiments conducted formally distinguish between a single complex and a pair of complexes, one of which gives rise to P(1) and P(4) in the observed spectrum and the other gives rise to P(2) and P(3). All the signals are present in equivalent intensity however,

(20) R, R =

(21) R = H

(22)

(23)

FIGURE 4 Complexation of *E*- and *Z*-dehydroamino-acids; steric effects

so that a single species containing two biphosphine-rhodium moieties and one molecule of (17a) is most likely. Experiments with ^{13}C-labelled analogues of (17a) demonstrate that the carboxylate is bound, but the amide is not, chemical shifts being rather similar to those observed for complex (21). There is insufficient evidence to postulate a structure with any confidence, but (22) and (23) are possibilities which accord with the data available. There is some precedent for bridging binuclear rhodium complexes with bisdiphenylphosphinobutane ligands.[27]

EXPERIMENTAL

All manipulations involving air-sensitive species were carried out in a Schlenck apparatus under an atmosphere of dry argon and solvents were thoroughly degassed before use. ^{31}P N.m.r. spectra were recorded on a Brüker WH90 spectrometer and chemical shifts are reported relative to external H_3PO_4. Microanalyses were performed by Dr. F. B. Strauss, Oxford. All solvents were dried and distilled before use.

Bicyclo[2.2.1]*heptadienebiphosphinerhodium*(I) *Tetrafluoroborate Complexes*.—These were prepared by the methods previously described,[10, 17] as in the following example.

Bicyclo[2.2.1]*heptadiene*-1,4-*bisdiphenylphosphinobutanerhodium*(I) *tetrafluoroborate*. Bicyclo[2.2.1]heptadienerhodium(I) acetylacetonate (142 mg, 0.48 mmol) was dissolved in THF (3 ml) and fluoroboric acid (40% solution; 0.3 ml) added. 1,4-Bisdiphenylphosphinobutane (206 mg, 0.48 mmol) was added as a solid in one portion; the solution became deep red and addition of ether (20 ml) caused precipitation of the complex which was collected by filtration, washed with ether, and dried *in vacuo* (313 mg, 92%). Material thus obtained could be used without further purification. Recrystallisation (MeOH) gave orange needles, m.p. 210—215° (decomp.) (Calc. for $C_{35}H_{36}P_2RhBF_4$: C, 59.35; H, 5.1; P, 8.75; F, 10.75. Found: C, 59.1; H, 5.3; P, 8.45; F, 10.45%), δ_P (CH_3OH) 28.6 (J_{RhP} 153 Hz).

(Z)-α-*Benzamidocinnamic Acid and* (Z)-*Methyl* α-*Benzamido*[2-^{13}C]*cinnamate*.—To a solution of [2-^{13}C]glycine (90 atom %) (100 mg, 1.33 mmol) and sodium hydroxide (60 mg, 1.5 mmol) in water (1.5 ml) were added in turn portions of benzoyl chloride (0.16 ml, 1.38 mmol) and a solution of sodium hydroxide (106 mg, 2.6 mmol) in water (0.5 ml) over 0.5 h at such a rate that the solution remained alkaline. The mixture was stirred for a further 0.5 h then poured into concentrated hydrochloric acid (1 ml). The precipitate was filtered, washed with cold water, and dried *in vacuo* (210 mg). This was then boiled in CCl_4 (3 ml) for 10 min. The remaining solid was collected, dried, and recrystallised (boiling water) to give [2-^{13}C]hippuric acid (175 mg, 75%), m.p. 189—192° (lit.,[28] 191—192°). A suspension of [2-^{13}C]hippuric acid (175 mg, 1 mmol), freshly fused sodium acetate (118 mg, 1.44 mmol), and benzaldehyde (0.2 ml, 2 mmol) in acetic anhydride (2 ml) was heated at a carefully maintained temperature (85—95 °C) for 1 h. Methanol (2 ml) and water (2 ml) were cautiously added and the mixture poured into water (25 ml) causing the precipitation of (Z)-2-phenyl-4-benzylidene[4-^{13}C]oxazol-5(4*H*)-one which washed and dried *in vacuo* (203 mg, 84%), m.p. 164—166° (lit.,[29] 166—167°), δ_C (CD_2Cl_2) 133.74 p.p.m. The labelled (Z)-azlactone (0.2 g, 0.8 mmol) was added to a mixture of methanol (4 ml) and aqueous sodium hydroxide (M, 2 ml) and stirred until dissolved. Methanol was removed under reduced pressure and the solution extracted with ether (3 × 5 ml). The ether extract was washed ($NaHCO_3$ solution), dried (Na_2SO_4), and the solvent removed under reduced pressure to give a solid. Recrystallisation (aqueous methanol) gave (Z)-methyl α-benzamido[2-^{13}C]cinnamate (155 mg, 65%), m.p. 132—135° (lit.,[30] 142—143°), δ_C (CD_3OD) 126.84 p.p.m. Concentrated hydrochloric acid was added to the aqueous layer until the pH was 2. The precipitate was collected, washed with water, and dried *in vacuo* to give (Z)-α-benzamido[2-^{13}C]cinnamic acid (48 mg, 22%), m.p. 225—230° (decomp.) (lit.,[29] 223—226 °C), δ_C (CD_3OD) 129.7 p.p.m.

We thank Johnson-Matthey Ltd., for generous loans of rhodium salts and the E. P. Abraham Trust for a fellowship (to P. A. C.).

[1/1608 *Received*, 15*th October*, 1981]

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