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THE MECHANISM OF ASYMMETRIC HYDROGENATION CATALYSED BY RHODIUM COMPLEXES OF CHIRAL PYRROLIDINOBIPHOSPHINES *

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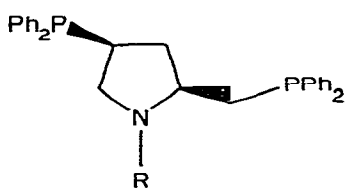
Summary

A wide range of modes of coordination of dehydroamino acids and itaconic acid derivatives to rhodium complexes of pyrrolidinobiphosphines may be discerned by an examination of their ^{31}P NMR spectra. Bidentate complexes may involve amide or carboxyl coordination and tridentate and bis(olefin) complexes are also important. The relevance of these observations to the mechanism of asymmetric hydrogenation is discussed.

Chiral pyrrolidinobiphosphines of general structure I have proved to be extremely successful ligands for the rhodium-catalysed hydrogenation of dehydroamino acid derivatives [1], unsaturated acids [2] and α-keto-esters [3] and



(Ia, R = H, PPM;
Ib, R = Co_2t-Bu, BPPM;
Ic, R = ^{13}COPh, BZPPM)

-lactones [4]. Extended studies on the effect of hydrogen pressure and of added bases have recently been published by Ojima [5], together with spectro-

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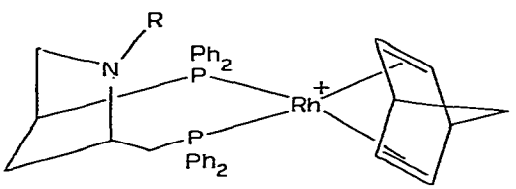
scopic data on intermediate complexes, prompting us to report our studies in this area.

Results and discussion

1. Biphosphine rhodium diene complexes

The rhodium bicyclo[2.2.1]heptadiene complexes IIa—IIc of Ia—Ic were prepared by previously described methods [6] and their ^{31}P NMR spectra are recorded in Table 1. It has been suggested that the doubling of the signals observed at low temperature for IIb arises from two diastereomers inequivalent by virtue of restricted rotation about the N—C—O bond [5]. Careful monitoring of the ^{31}P spectrum of IIb gives a coalescence temperature of 276 K. In the ^{1}H



(II)

spectrum the major changes on cooling take place in the region of the t-butyl group; this signal is split into a broad unequal doublet below 273 K suggesting that the t-butyl group is in a different environment in the two species. IIc shows no such dynamic behaviour (200—300 K) suggesting either that the ^{31}P signals of the two complexes are isochronous or that the equilibrium is very

TABLE 1

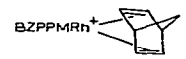
PHOSPHORUS-31 NMR SPECTRA OF PYRROLIDINOBIPHOSPHINE RHODIUM DIENE AND SOLVATE COMPLEXES [a]

Complex	δ_1 (ppm)	δ_2 (ppm)	J(RhP(1)) (Hz)	J(RhP(2)) (Hz)	J(P(1)P(2 (Hz)
S,S−BPPMRh$^+$ BF_4^-	42.2	18.0	156	150	35
S,S−BZPPMRh$^+$ BF_4^-	47.1	15.8	157	149	34
S,S−PPMRh$^+$ BF_4^-	46.8	39.9	127	122	23.5
S,S−PPMRh$^+$ BF_4^-	41.2	30.8	115	110	36
S,S−BPPMRh$^+$ $(MeOH)_n$ BF_4^- [b]	68.6	43.1	200	197	65
	69.2	43.1	200	197	67
S,S−BPPMRh$^+$ (MeO⌒OH)$_n$ BF_4^- [b,c]	66.5	41.3	203	200	68
	66.7	40.7	203	197	68
BZPPMRh$^+$ $(MeOH)_n$ BF_4^-	72.2	45.0	196	196	64

[a] Spectra were recorded at 300°K in methanol solution unless otherwise stated. [b] The two species were observed in approximately equal proportions. [c] Spectrum recorded in 2-methoxyethanol.

TABLE 2

^{13}C CHEMICAL SHIFTS OF COMPLEXES OF ^{13}C-LABELLED BZPPM Ic [a]

Complex		Temperature (°K)	^{13}C
BZPPM		300	171.6
		300	171.0
$BZPPMRh^+(MeOH)_n$	BF_4^-	300	170.0
$BZPPMRh^+$ (III)	BF_4^-	300	170.9 [b]
		228	170.5
$BZPPMRh^+$ (IV)	BF_4^-	300	170.8 [b]
$BZPPMRh^+$ (Va)	BF_4^-	300	170.7 [b]
$BZPPMRh^+$ (Va)	BF_4^- [c]	300	170.5
$BZPPMRh^+$ (Vb)	BF_4^- [c]	300	170.7 [b]
		228	170.4

[a] Spectra were recorded in CD_3OD solution at the stated temperatures. [b] Broadened signals. [c] Excess triethylamine was present.

biased or very fast. Interaction of the amide carbonyl group with rhodium or hydrogen bonding with a substrate might be invoked to explain conformational preferences in complexes of this type of ligand. ^{13}C BZPPM Ic was prepared from PPM and $^{13}C_1$ benzoyl chloride. The ^{13}C NMR of IIc shows a shift of <1 ppm on coordination to rhodium, and no spin-spin coupling to rhodium or phosphorus, indicating that direct interaction with the metal is absent (Table 2).

2- Biphosphinerhodium solvate complexes

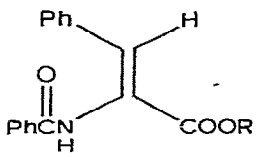
Attempts to hydrogenate IIa or its cyclooctadiene analogue (MeOH, 1 atm H_2) were unsuccessful, only starting material being observed in the ^{31}P NMR spectrum, even after 3 hours. A crystal structural determination of the cyclooctadiene complex indicated that the pyrrolidine nitrogen is coordinated to rhodium [7]. That this structure is maintained in solution is strongly suggested by the low phosphorus—rhodium, J(Rh—P) and phosphorus—phosphorus, J(P—P), coupling constants measured. These indicated a weakened rhodium—phosphorus σ-bond and an increased coordination number. J(P—P) is a very sensitive probe of complex geometry and coordination number [8—10]. The strong coordination of nitrogen presumably inhibits the oxidative addition of hydrogen. Hydrogenation of IIc (MeOH, $t_{1/2} \sim 2$ min) resulted in smooth conversion to a single methanol adduct whose ^{31}P NMR was temperature independent. Again the ^{13}C NMR showed no evidence of interaction between the amide and the metal. Under the same conditions IIb gave two solvent adducts (Table 1). At room temperature and above they were observed in approximately equal proportions but on cooling the higher field species predominated (2 : 1 at 230°K). The coalescence temperature was rather higher than for the diene complex and a value for $\Delta G^{\ddagger}$ was obtained in methanol ($\Delta G^{\ddagger} \sim 70$ kJ mol^{-1}, T_c = 333 K). This could not be measured with higher accuracy since the chemical shift difference between the two rotamers is small and temperature dependent.

The potential existence of two amide rotamers complicates further the interpretation of spectral data in substrate rhodium complexes of the pyrrolidinobi-

phosphine ligands. Since the two phosphorus atoms of the ligand are inherently distinct there may be two constitutional isomers on substrate coordination, which may occur through either prochiral face of the substrate. Thus there are eight possible complexes for a single mode of complexation.

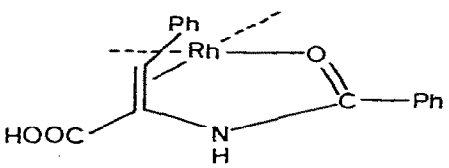
3. Complexes of dehydroamino acid derivatives

Extensive investigations have been conducted in Oxford on the ^{31}P and ^{13}C NMR spectra of rhodium enamide complexes, and we are now able to relate spectral features to specific modes of complexation with some confidence [11]. The binding of *Z*-α-benzamidocinnamic acid, III, to the BZPPM rhodium

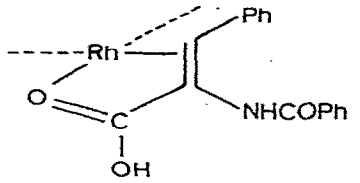


(III , R = H ;
IV R = Me)

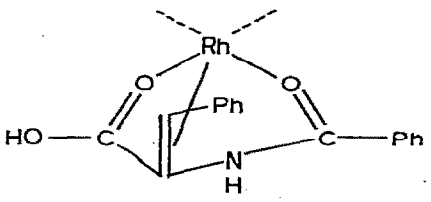
methanol complex is rather specific; a broad ^{31}P NMR spectrum is recorded at room temperature but a sharp eight line spectrum at 252 K (Table 3). The coupling constants suggest that the acid is bound to rhodium through the double bond and the amide carbonyl group (Type A, Fig. 1). It has been noted that the presence of triethylamine may considerably affect the optical efficiency of hydrogenation of these substrates [12], and this is also the case in the preparation of the enamide complex. Again a broadened spectrum is recorded at room temperature and on cooling a single species is observed, now with coupling constants characteristic of olefin carboxylate binding (Type B). *Z*-methyl-α-benzamidocinnamate is less strongly bound (binding constant $K \sim 15$ l mol^{-1} at 300, 10^3 at 228 K) and less selectively bound. Two rather similar enamide complexes are observed in the ratio of 2.3 : 1, both of Type A. Again there is no



A
Olefin — amide binding



B
Olefin — carboxyl binding



C
Tridentate binding

Fig. 1. Modes of enamide coordination to pyrrolidinobiphosphine rhodium complexes.

TABLE 3

^{31}P NMR SPECTRA OF DEHYDROAMINO ACID DERIVATIVE COMPLEXES [a]

Ligand	Substrate	Temperature (K)	% of diastereomer	δ(P(1)) (ppm)	δ(P(2)) (ppm)	J(RhP(1)) (Hz)	J(RhP(2)) (Hz)	J(P(1)P(2)) (Hz)	Complex type
BZPPM	III	252	100	59.5	14.2	166	150	49	A
BZPPM	III [b]	228	90	42.6	31.1	172	176	50	B
BZPPM	IV	228	63	58.7	15.0	163	150	50	A
			24	54.7	12.2	155	143	48	A
			13	71.7	44.6	199	196	65	[c]
BPPM	III	252	27	59.7	14.1	165	153	50	A
			13	58.6	16.7	168	152	50	A
			35	40.7	25.3	153	126	26	C
BPPM	III [b]	252	42	58.3	28.1	178	189	60	B
	initial		28	57.7	28.2	179	188	60	B
			12	40.1	26.0	180	165	44	B?
			12	39.9	26.1	179	164	45	B?
	final	300	50	41.2	31.1	172	175	50	B?
			50	40.7	31.1	172	175	50	B?
BPPM	IV	252	42	59.3	16.1	163	148	51	A
			28	57.8	13.6	164	146	50	A
			20	46.6	24.2	150	113	23	C

[a] Spectra were recorded in methanol solution at the temperatures stated. [b] Excess triethylamine was present. [c] Methanol complex.

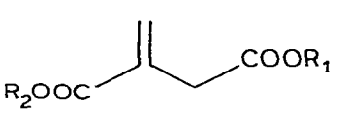
evidence for interaction of the amide carbonyl of the biphosphine with either the metal or the substrate.

The corresponding spectra of BPPM complexes were much more complex with several species evident in solution, whose relative proportions varied as a function of temperature (Table 3). In the case of the complex of IV some elucidation was provided by a study of the ^{13}C NMR spectrum of the enamide labelled with ^{13}C in the amide group [11]. Two species could be observed shifted to low field from the uncomplexed amide resonance. The more intense peak was shifted by 10.8 ppm and was split by a coupling of 7 Hz to the high-field phosphine (which is *trans* to the bound olefin) and a coupling of 2 Hz to the low-field phosphine. This is in accord with a structure of Type A. The minor resonance was shifted 5.8 ppm to lower field and only small phosphorus—carbon couplings were noted. This, together with the small values for J(Rh—P) and J(P—P) suggest a 1 : 1 tridentate complex of type C strongly reminiscent of those characterised from the sugar-derived phosphine DIOXOP [12]. For III, a similar range of complexes is obtained with presumably analogous structures.

In the presence of triethylamine, however, the position is more complex. Initially the spectrum, like its predecessors, shows dynamic behaviour at room temperature, while at 252 K four species may be discerned. The coupling constant data suggest that these are all of type B, possibly constitutional isomers. In this case the study of labelled enamides was less helpful; many resonances were observed but could not be assigned. After a period of several weeks at room temperature it was found that a further change had taken place to give two new species which did not give broadened spectra at 300 K. The possibility of isomerisation of the enamides was excluded by work up of the solution which led to their recovery unchanged and isomerically pure. Thus, despite the high optical yields obtained in asymmetric hydrogenation of enamides by BPPM complexes the coordination chemistry involved is rather complex and shows few useful trends.

4. Complexes of itaconic acid derivatives

Complexes of pyrrolidinobiphosphine ligands have been used in some of the most successful reductions of itaconic acid, V, and its derivatives [14]. This substrate affords the possibility of competitive or cooperative binding of α- and β-carboxylate groups. The β-methyl ester Vb and the dimethyl ester Vd



(Va , $R_1 = R_2 = H$;
Vb , $R_1 = Me$, $R_2 = H$;
Vc , $R_1 = H$, $R_2 = Me$;
Vd , $R_1 = R_2 = Me$)

were prepared by known methods [15,16], and the α-methyl ester Vc by acid hydrolysis of Vd. Itaconic acid is reduced in 84% (*S*) optical yield in the presence of BPPM rhodium cyclooctadiene perchlorate; this is increased to 92% in

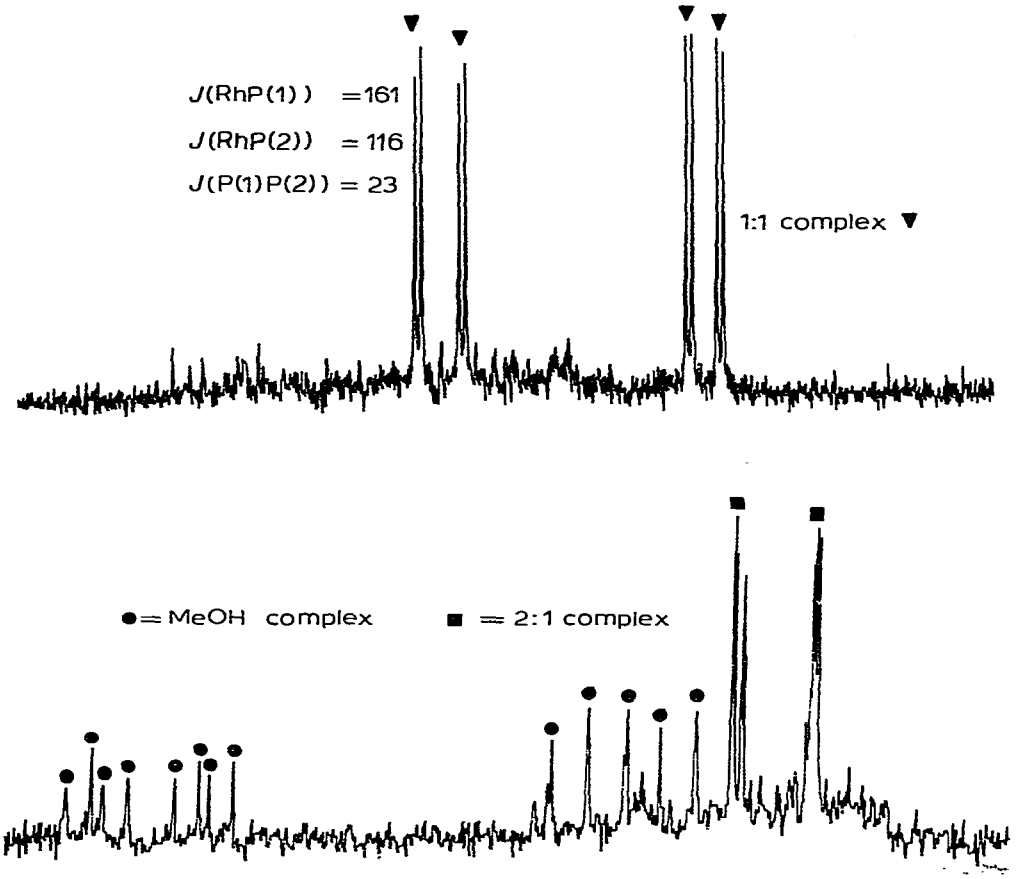


Fig. 2. Phosphorus-31 NMR spectra of complexes formed by the coordination of itaconic acid to BPPM rhodium solvate.

the presence of triethylamine [13]. The analogous values for BZPPM are 82% and 89% (*S*) [16]. The dimethyl ester Vd, which might be expected to coordinate less well, is reduced with lower optical efficiency (24% with BPPM) and gives the *R* enantiomer.

When itaconic acid (1.2 equivalents) is added to BPPM rhodium methanol complex and the reaction monitored by ^{31}P NMR at 228 K the spectrum initially observed is as shown in Fig. 2. The small values of J(Rh—P) and J(P—P) are consistent with a complex in which both α- and β-carboxyl groups are cooperatively bound. This may be represented as structure type D (Fig. 3) and has also been noted with several weakly basic dehydroamino acids bound to seven-ring chelate biphosphine rhodium complexes [18]. At room temperature the spectrum was exchange broadened and after 3 hours at or above 280 K it had changed irreversibly and revealed 50% methanol complex and 50% of a new species with changed coupling constants. The complexation sequence is shown in Fig. 3. The new complex was formed exclusively in the presence of excess itaconic acid, and its coupling constants and non-dynamic behaviour (200—

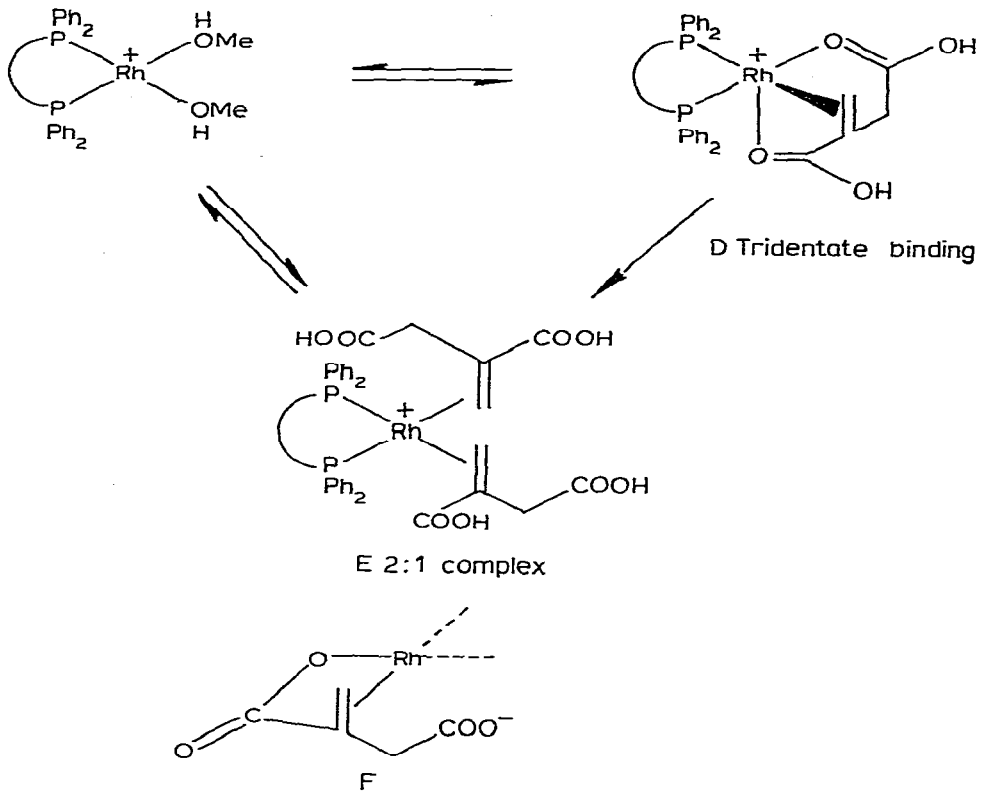


Fig. 3. Modes of complexation of itaconic acid to pyrrolidinobiphosphine rhodium complexes.

300 K) suggest that it is a 2 : 1 complex of type E. In this respect our conclusions differ from those of Ojima [5] who reports an apparently similar species in the presence of a large excess of substrate but assigns to it a 1 : 1 tridentate structure. It is of note that complexation is highly regio- and stereoselective in both types of complex and that only one carbamate rotamer is observed.

The complexation of the β-methyl ester Vb shows similar behaviour except that now two, very similar, diastereomeric bis(olefin) complexes are formed. Their relative proportions vary as a function of time and temperature; initially only one was observed below 252 K while at 300 K the ratio was 4 : 1. After two days equilibration at room temperature this ratio had been reduced to 2 : 1. The spectra obtained from complexes of the α-methyl ester are exchange broadened above 230° K but at lower temperature complexes of both type D and E were observed. Their relative proportions were time invariant, and the binding constant was low. Since an ester might be expected to bind less strongly than a free carboxylic acid this suggests that interaction with the α-carboxyl group is the more important in maintaining complex structure.

In the presence of excess triethylamine itaconic acid interacts with BPPM rhodium solvate to give two major species, their coupling constants suggesting that they are bidentate olefin carboxylate complexes. In this case the chemical

TABLE 4

^{31}P NMR SPECTRA OF COMPLEXES OF ITACONIC ACID DERIVATIVES [a]

Ligand	Substrate	S/Rh	Temperature (K)	% of diastereomer	δ(P(1)) (ppm)	δ(P(2)) (ppm)	J(RhP(1)) (Hz)	J(RhP(2)) (Hz)	J(P(1)P(2)) (Hz)	Complex type
BPPM	Va	1.1	228	100	47.2	20.2	161	116	23	D
BPPM	Va	6.0	303	100	37.4	35.3	150	136	36.5	E
BPPM	Va [b]	6.0	228	50	39.8	39.2	172	169	40	F
				50	39.9	33.0	180	164	56	F
BPPM	Vb	1.1	210	100	48.8	19.7	162	117	21	D
BPPM	Vb	6.0	303	80	42.5	31.6	157	132	37	E
				20	42.0	32.0	155	132	37	E
BPPM	Vb [b]	6.0	252	80	39.8	33.1	179	163	56	F
				20	71.7	23.6	169	160	51	F
BPPM	Vc	6.0	228	50	50.9	20.3	159	115	22	D
				50	43.1	35.6	145	146	36	E
BZPPM	Va [b]	9.0	203	100	41.6	38.8	178	169	57	F
BZPPM	Vb [b]	7.0	228	82	40.7	38.3	175	168	54	E
				18	71.8	18.5	172	166	50	F
BZPPM	Va [b]	9.0	228	[c]	71.9	18.3	173	169	49	F
					47.1	19.8	157	144	34	E?

[a] Spectra were recorded in methanol solution at the stated temperatures. [b] Excess triethylamine present. [c] Several other species noted.

shifts of P(1) and P(2) are very similar (Table 4). The β-methyl ester, Vb, gave a similar species and in one case the large chemical shift separation of P(1) and P(2) suggested that it might be a constitutional isomer. The similarity of the two species suggests that the favoured mode of coordination is F, involving the double bond and the α-carboxylate anion.

The results obtained with BZPPM complexes were less easy to interpret. Of the three substrates itaconic acid is the most efficiently bound, giving a broad spectrum of a bound complex (at all temperatures) in the presence of a large excess of acid. Neither Vb or Vc showed any significant binding, but broadening of the signals due to the methanol complex at 300 K suggested exchange with an unobserved species. Itaconic acid in the presence of triethylamine gave several complexes, the major of which was of type F; its spectrum showed dynamic behaviour above 230 K. Vb was similar giving two well defined species at 228 K in the ratio of 4.5 : 1 but gave broadened spectra and other complexes on warming. The spectra of the complexes of the anion of Vc were very complex below 230 K and dynamic at room temperature. Thus in this series it also seems that the α-carboxylate group is the more important binding to the metal centre. In no case was any significant change in the ^{13}C chemical shift of the labelled amide of the ligand noted, ruling out interaction with the metal or hydrogen bonding with the substrate.

5. Relevance to asymmetric catalysis

Complexes of the pyrrolidinobiphosphines have proved to be extremely versatile, reducing a wide range of substrates with good optical efficiency. However, their coordination chemistry presents problems not previously encountered with the simple C_2 symmetric phosphines DIOP [19] and DIPAMP [20]. This study suggests that the complexes of the two phosphines BPPM and BZPPM, while showing very close similarities in hydrogenation experiments seem to interact rather differently with unsaturated substrates. Enamides bind quite selectively to BZPPM complexes while itaconic acid derivatives bind weakly, the reverse being true for BPPM complexes. However, our own experiments with DIPAMP [21] and those of Halpern with CHIRAPHOS [22] have suggested that a minor stereoisomer must be the most significance species in the catalytic cycle. Additionally in this case the 2 : 1 complexes might be expected to have a lower affinity for hydrogen than the 1 : 1 species on steric and electronic grounds and addition to a 5-coordinate species will also be disfavoured. Thus while this study defines closely the modes for recognition of catalyst and substrate it does not give definitive information regarding the rate- or product-determining transition state.

Experimental

^1H NMR spectra were obtained on a Perkin Elmer R 32 spectrometer relative to internal TMS. ^{31}P and ^{13}C NMR spectra were obtained on a Bruker WH 90 spectrometer and their chemical shifts are expressed in ppm relative to external 85% H_3PO_4 and TMS, respectively. Melting points were determined on a Reichert Köfler block and are uncorrected. Microanalyses were performed by Dr. F.B. Strauss.

Bicyclo[2.2.1]hepta-2,5-diene-(2S,4S)-N-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine rhodium (I) tetrafluoroborate, IIb

This and other biphosphine rhodium diene complexes were prepared by the method of Glaser [6]. IIb was obtained in 95% yield, m.p. 238—241 (dec.) Analysis. Found: C, 58.9; H, 5.54; N, 1.87; P, 7.19; F, 8.86. $C_{41}H_{45}BF_4NP_2O_2Rh$ calcd.: C, 58.8; H, 5.75; N, 1.67; P, 7.41; F, 9.08%.

Bicyclo[2.2.1]hepta-2,5-diene-(2S,4S)-N-^{13}C-benzoyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine rhodium (I) tetrafluoroborate, IIc

$^{13}C_1$-benzoic acid (30 mg, 0.25 mmol) and thionyl chloride (0.05 ml) in benzene (5 ml, distilled from Na) was heated under reflux for 3 hours. After cooling a solution of 2*S*,4*S*-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine (90.6 mg, 0.2 mmol) and triethylamine (30 mg, 0.3 mmol) in benzene (5 ml) was added and the mixture stirred at room temperature (30 min). It was then poured into water (25 ml), extracted (benzene, 3 × 10 ml), the extract washed ($NaHCO_3$ solution), dried (Na_2SO_4) and the solvent removed under reduced pressure to give Ic as a white solid m.p. 159—161°C (lit. [22] 160—161°C). Bicyclo[2.2.1]hepta-2,5-diene (2,4-pentanedionato-*O,O*)rhodium (58 mg, 0.2 mmol) was dissolved in THF (2 ml) and 5 drops of tetrafluoroboric acid added. A solution of Ic (THF, 1 ml) was added and IIc was precipitated with ether, washed and dried (122 mg, 83% from $^{13}C_1$-benzoic acid).

Methyl hydrogen-2-methylenebutanedioate, Vc

To a solution of dimethyl-2-methylenebutanedioate (5 g, 0.032 mol) in formic acid (90%, 20 ml) was added methanesulfonic acid (2.5 ml). After 10 min at 100°C the mixture was poured into iced water (50 ml) and extracted with dichloromethane (3 × 50 ml). The organic layer was washed ($NaHCO_3$ solution, water), dried ($MgSO_4$) and the solvent removed under reduced pressure to give a viscous colourless liquid (2.25 g, 55%). Chromatography (SiO_2, ethyl acetate : hexane, 1 : 2) and distillation under reduced pressure (b.p. 80—83°C, 0.13 mmHg) gave pure Vc (m.p. 8—10°C). Analysis. Found: C, 50.2; H, 5.59. $C_6H_4O_3$ calcd.: C, 50.0; H, 5.55%. NMR (^{1}H, $CDCl_3$) 3.38 (2 H, br.s, CH_2); 3.78 (3 H, s, OMe); 5.74 (1 H, br. s, H_E); 6.34 (1 H, s, H_Z); 12.4 (1 H, s COOH). Mass spec. (*m/e*; rel int.) 144 (M^+, 20); 126(27); 113(80); 100(35); 85(100); 68(59). Solvate and substrate complexes for NMR spectroscopy were prepared under argon as previously described [11].

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