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THE MECHANISM OF ASYMMETRIC HOMOGENEOUS HYDROGENATION. SOLVENT COMPLEXES AND DIHYDRIDES FROM RHODIUM DIPHOSPHINE PRECURSORS

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Summary

Bicyclo[2,2,1]hepta-2,5-diene and cycloocta-1,5 diene(biphosphine)rhodium tetrafluoroborates react with hydrogen at 1 atmosphere in methanol or other polar solvents. The initial product may be either a solvated dihydride or a solvate; depending on phosphine structure the equilibrium between these two species varies widely. Dihydrides are normally the stable product when the ligand is a monophosphine although (*o*-methoxyphenyl)methylphenylphosphine is an exception. *cis*-Chelating biphosphines normally form solvate complexes with no affinity for hydrogen. *R*-Phenyl bis-diphenylphosphinoethane falls into this category, but the ^{31}P NMR spectra of its complexes demonstrate an equilibrium between monomeric and dimeric species, and addition of triethylamine gives rise to a trimer. *trans*-Chelating biphosphines show more variable behaviour, and in the case of bis-1,5-diphenylphosphinopentane, a number of complexes, including one requiring C—H activation, are observed.

Numerous examples [1] now exist of the asymmetric hydrogenation of prochiral olefins by rhodium bisphosphine complexes. The most effective cases require chelating biphosphines and employ cationic complexes in methanol or ethanol solution. Several workers have made observations on the initial hydrogenation products of complexes of type a [2—6]. Both solvates and dihydrides have been characterised, depending on the structure of the phosphine. This paper summarises the results of our own studies, carried out as part of a more general survey of the mechanism of asymmetric hydrogenation.

Monophosphines

Prior work by Schrock and Osborn [2] and more recently by Halpern [3] and coworkers has established that the normal species formed by reduction of com-

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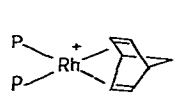
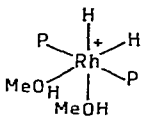
plex **1a** in coordinating solvents is a disolvate dihydride, of which numerous examples have been reported, particularly by Schrock and Osborn [2]. In some cases this intermediate has been isolated and fully characterised. Our own studies, limited to methanol solution, have demonstrated more varied behaviour (Table 1). We first reduced **1a** at $p(H_2) = 1$ atm and observed only hydride **1b** in the ^{31}P NMR spectrum. At a concentration of 0.01 *M* in methanol,

Complexes



a



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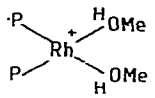

c

all BF_4^-

Phosphines

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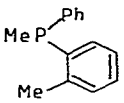

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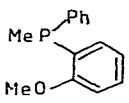

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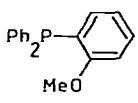

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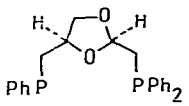

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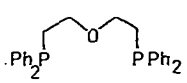

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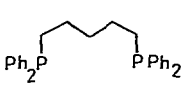

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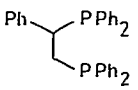

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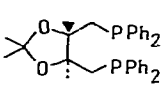

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the spectrum did not change over several hours, even in an argon atmosphere. Similar observations were made at 0.025 *M*, but after protracted pumping

TABLE 1

^{31}P NMR SPECTRA OF MONOPHOSPHINERHODIUM(I) COMPLEXES IN METHANOL. CHEMICAL SHIFTS ARE REPORTED IN ppm RELATIVE TO H_3PO_4

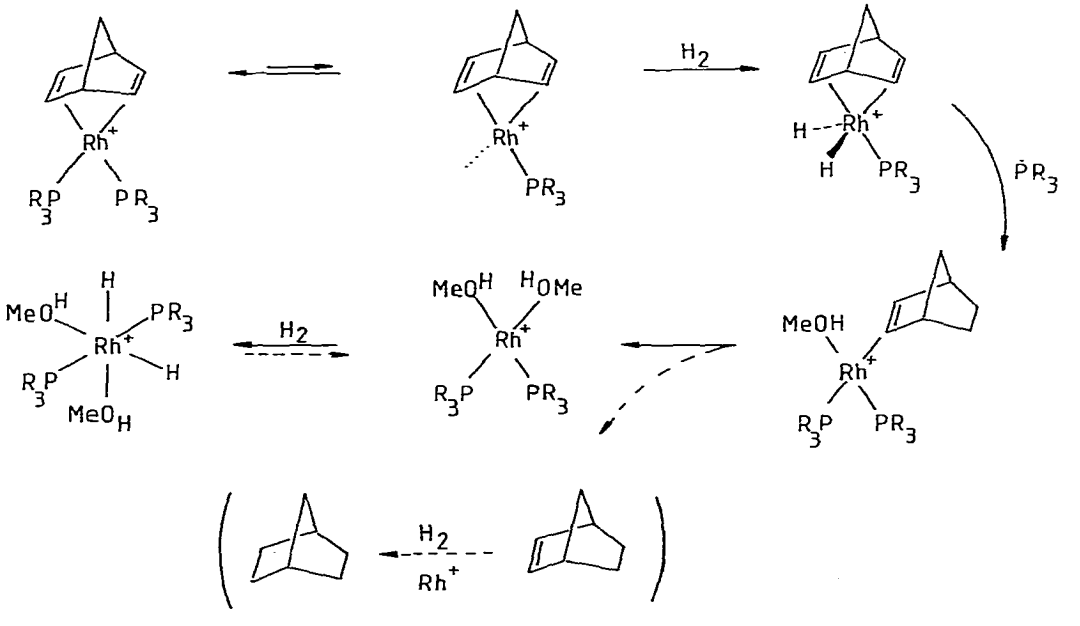
Phosphine	Olefin complex [a]		Dihydride		Methanol solvate	
	δ	*J*(RhP) (Hz)	δ	*J*(RhP) (Hz)	δ	*J*(RhP) (Hz)
PPh_3 (1)	27.6	156	41.8	121	57.2	207
Ph_2PCH_3 (2)	3.5	140	23.8	118	—	—
$Ph(o\text{-}C_6H_4CH_3)PCH_3$ (3)	9.3	153	22.2	118	35.9	201
	8.4	153	21.7	116	34.4	201
$Ph(o\text{-}C_6H_4OCH_3)PCH_3$ (4)	9.8	156	19.6	118	38.5	206
	12.0	157	19.3	119		
$Ph_2P(o\text{-}C_6H_4OCH_3)$ (5)	24.8	156	41.3	121	—	—

[a] Bicyclo[2.2.1]heptadiene.

traces of a second species, presumed to be **1c**, were observed. When a solution 0.05 *M* in **1a** was hydrogenated the second species was evident in the initial hydrogenation product, and on standing under argon at room temperature it became the exclusive species, although exposure to hydrogen led to reformation of **1b**. This suggests that the solvent adduct **1c** is oligomeric and its formation thus favoured by high concentrations of complex.

In the case of **2a** hydrogenation occurred more slowly and the only species observed was **2b**. Methylphenyl-*o*-tolylphosphine is chiral, and the racemic ligand gives rise to two diastereomeric norbornadienerhodium tetrafluoroborates **3a** in near equal proportions. In methanol hydrogenation occurs rapidly and if reaction is monitored by ^{31}P NMR after 10 s then both **3b** and **3c** may be observed. Further hydrogenation leads to complete conversion into **3b** but if the solution is evacuated for a period of time below room temperature some reversion to **3c** occurs. In one experiment with a very short hydrogenation time (<5 s) only **3c** was present, thereby demonstrating that it is the initial product of hydrogenation. Reaction is inhibited if excess of the parent phosphine is first added, suggesting the suppression of an initial dissociative step. This is supported by the observation of site exchange between free phosphine and **3a**, even at 270 K with a small amount of added phosphine. On this basis we favour the mechanism of Scheme 1, which is similar to the dissociative addition proposed for hydrogen addition to tris(triphenylphosphine)rhodium-(I) chloride [7] in the first step of catalysis.

SCHEME 1



R-*o*-Anisylmethylphenylphosphine is one of the most effective non-chelating ligands in asymmetric homogeneous hydrogenation [8]. Its complex **4a** on treatment with hydrogen in methanol gives rise only to the solvate complex **4c** but not the corresponding dihydride. The corresponding racemic complex

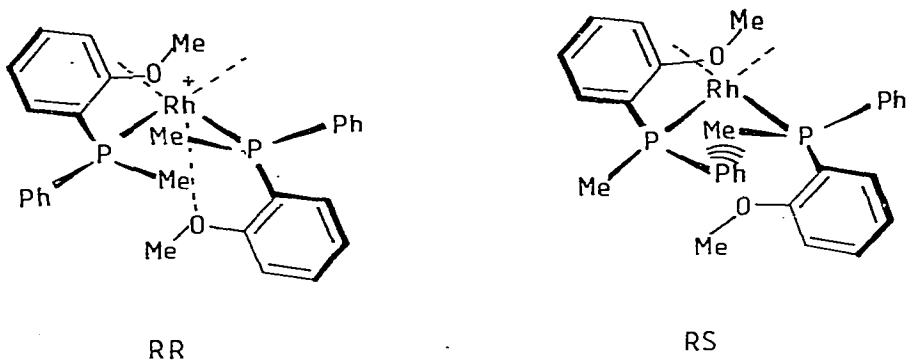


Fig. 1. Steric interactions in *cis*-chelated square-planar complexes of *RR*-4 and *RS*-4.

was prepared from unresolved phosphine and shows a slight preference for the R^*R^* diastereomeric form since the predominant species has an NMR spectrum identical to 4a. On hydrogenation in methanol, only the R^*R^*-isomer of 4c is observed, since the two line spectrum is identical to that obtained from the optically pure phosphine complex. A very small amount of 4b, apparent as two diastereomers, was evident after hydrogen had been bubbled through the solution for several minutes. A solution of 4c in methanol, derived from racemic phosphine, was reacted with excess norbornadiene at 195 K, followed by immediate monitoring of the NMR spectrum at 260 K. This showed both isomers of racemic 4a to be present at their equilibrium proportions. Intercomplex exchange therefore equilibrated the R^*R^* and *RS* diastereomers of 4a very rapidly.

The stereoselectivity observed in formation of 4c may result from a conformational preference of the methoxy groups, either by electrostatic bonding to rhodium or through H-bonding to coordinated methanol molecules. Ether bonding in cationic rhodium complexes is well described [9]. In either case, (Fig. 1) the *RS* isomer may possess a serious inter-ligand Ph—Ph repulsive interaction carrying a destabilising effect relative to the R^*R^* isomer. Any balance between steric and electronic factors in favouring the methanol complex over a dihydride is rather finely tuned since the *o*-anisylphosphine complex 5a gives only dihydride 5b under similar conditions. A case for methoxyl—metal binding may be made by reference to an unpublished study of rhodium complex-catalysed hydrogenation and isomerisation of methyl linoleate [10]. Thus *o*-anisyldiethylphosphine complexes are different in relative hydrogenation/isomerisation reactivity from diethylphenylphosphine complexes in dichloromethane, but the two species behave similarly in iso-propanol. This implies that the methoxy group may exert a similar role to that of a coordinating solvent.

Chelating biphosphines

Halpern and coworkers [4] have already reported that 6a reacts with two moles of hydrogen in methanol solution, giving a solvent complex with no tendency to coordinate hydrogen. Similar results with a range of chelating biphosphines have been reported by Baird and coworkers [4], demonstrating

the general principle that hydrides are quite disfavoured in these cases. Our own results are recorded in Table 2 and broadly support this conclusion.

cis-Chelation supports the formation of solvates, and conversely a 6-coordinate dihydride requires a *trans*-biphosphine arrangement inaccessible to smaller ring chelates. We have already demonstrated [11] that the sugar-derived biphosphine DIOXOP complex **7a** forms a *trans*-chelate rhodium dihydride on reduction. This slowly loses hydrogen in an argon atmosphere, giving rise to a solvent adduct of the type described above. The related complex **8a** gives rise to a dihydride which is stable. Comparison with the hydrocarbon analogue proved to be instructive. Phosphine $Ph_2P(CH_2)_5PPh_2$ forms a rhodium norbornadiene complex **9a** of the expected type, whose behaviour on hydrogenation in methanol solution is more complex. Two species are formed initially, one with a coupling constant *J*(PRh) characteristic of a solvent adduct **9c** and the second **9d** similar in some respects to a dihydride, save that the ^{31}P NMR signal is anomalously to low field and the coupling constant of 135 Hz is abnormally large. The two species are both formed in the early stages of reaction since they are both evident in partially hydrogenated samples even after 5 seconds at 0°C.

On further hydrogenation the proportion of **9c** decreases and a new species appears with chemical shift and rhodium—phosphorus coupling constant consistent with dihydride **9b**, although this is formed very slowly. The latter is the major species (70%) present after standing overnight under hydrogen, with 30% of **9d** as the only other complex observed. When hydrogenation is carried out and monitored by ^1H NMR a single high-field hydridic species is initially

TABLE 2

^{31}P NMR OF BIPHOSPHINE-RHODIUM COMPLEXES IN METHANOL

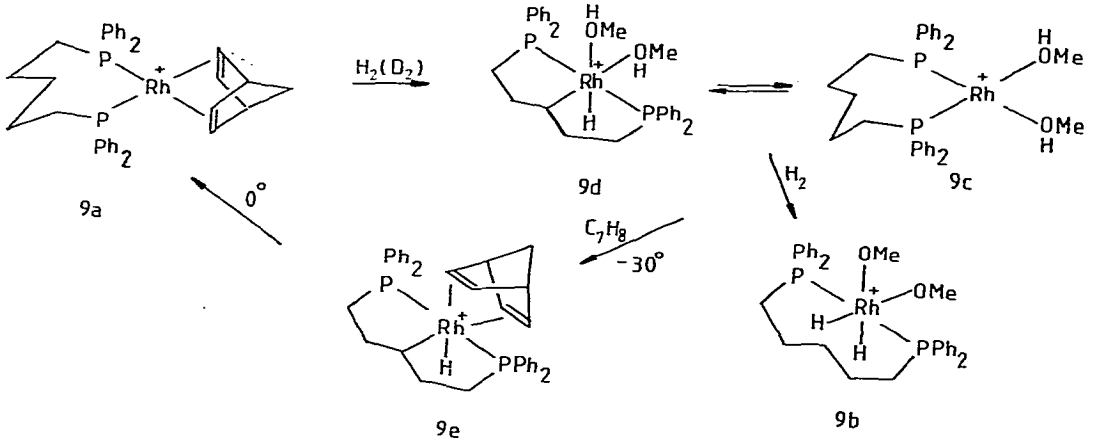
CHIRAPHOS is *SS*-2,3-bis(diphenylphosphino)butane DIPAMP is *RR*-bis(*o*-anisylphenylphosphino)-ethane; DIOP is *RR* 4,5-bis(diphenylphosphino)methyl-2,2-dimethyldioxolane.

Phosphine	Bicyclo[2.2.1]heptadiene complex		Methanol solvate	
	δ (ppm)*	*J*(RhP) (Hz)	δ (ppm)	*J*(RhP) (Hz)
$Ph_2P(CH_2)_2PPh_2$ (6)	56.9	156	81.2	203
CHIRAPHOS	58.4	154	83.9	200
DIPAMP	50.9	159	80.8	209
R-$Ph_2PCH_2CHPhPPh_2$ (13)	69.4	157	94.4	206
	41.3	154 (37)	64.9	200 (57)
			94.4	204
			64.7 [a]	200 (59)
			88.5	201
			56.2 [a]	197 (44)
rac-$Ph_2PCH_2CHPhPPh_2$			98.9	212
			66.8 [a]	197 (57)
			86.7	202
			58.1 [a]	197 (47)
$Ph_2P(CH_2)_3PPh_2$	15.4	149	40.2	190
$Ph_2P(CH_2)_4PPh_2$	28.6	153 [b]	53.6	199
DIOP	17.1	152	43.0	199
$(C_5H_4PPh_2)_2Fe$	28.2	162	55.3	215

[a] Dimeric species. [b] Analytical sample was of cycloocta-1,5-diene complex.

seen (Fig. 2), which on standing under a hydrogen atmosphere is slowly replaced by a second species at higher field. The latter has very similar P—H and Rh—H coupling constants to **1b**. If reduction is carried out with deuterium then the initial proton and phosphorus NMR spectra are similar, but the second species **9b** is not observed. This suggests that the initial complex **9d** is a CH insertion product formed from solvate **9c** *. The lack of protium incorporation in **9b** when **9a** is reduced with deuterium suggests that this insertion product does

SCHEME 2



not exchange its metal hydride, and that it forms and breaks down by a stereospecific process. There are precedents for simple alkane activation reactions of

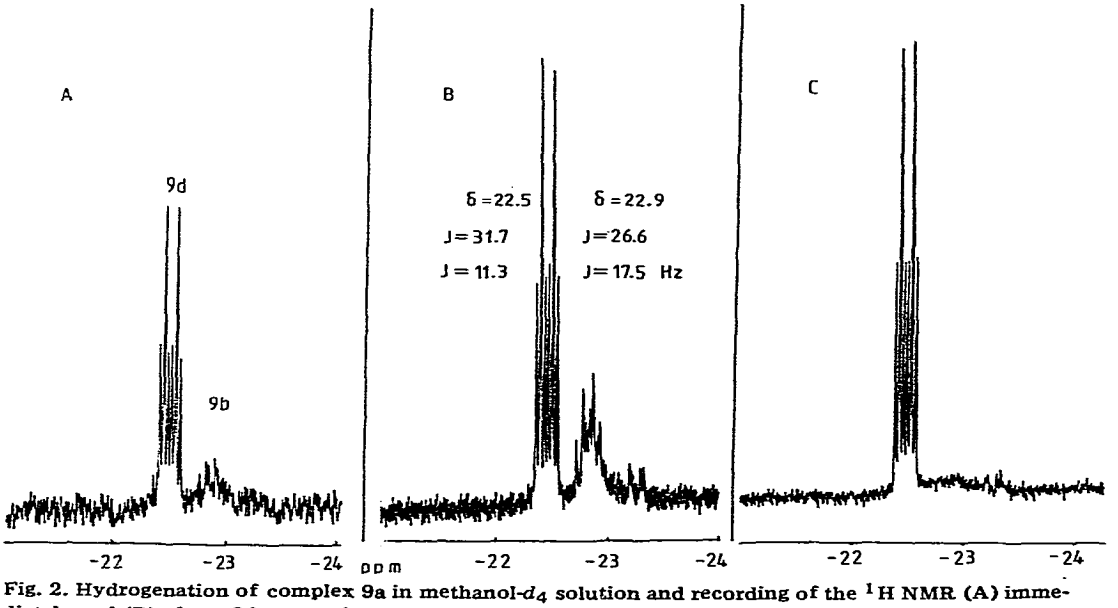
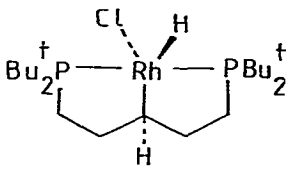


Fig. 2. Hydrogenation of complex **9a** in methanol-d_4 solution and recording of the ^{1}H NMR (A) immediately and (B) after 12 hours. After reduction with D_2 the spectrum is recorded (C). The changes observed are summarised in Scheme 2.

* *Note added in proof.* Professor J. Halpen [22] has independently observed formation of **9d** under similar conditions to those described.

the type, both in simple alkylphosphineplatinum complexes [12] and in rhodium and iridium complexes of $Bu^t_2P(CH_2)_5PBu^t_2$ [13] where insertion products such as **10** and **11** have been characterised. A number of related observations have been made by Bennett, Clark and coworkers [14,15] in which the formation of **12** from a saturated $Ph_2P(CH_2)_6PPh_2$ precursor is most pertinent.



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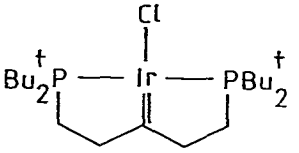

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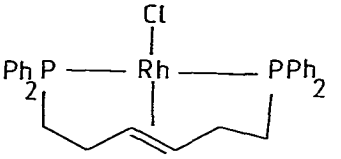

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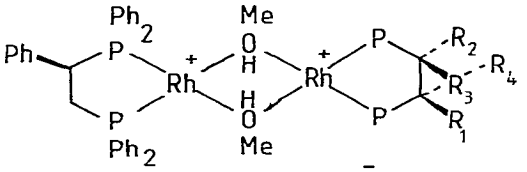


2 BF_4^-

14 a R_1 = Ph
14 b R_2 = Ph
14 c R_3 = Ph
14 d R_4 = Ph

else R H

Complex **9a** may be reformed by the addition of norbornadiene to hydrogenated samples in methanol. With excess norbornadiene added at −30°C, **9c** is immediately quenched but **9d** reacts much more slowly, although the olefin complex **9a** is the only species evident at equilibrium. With a deficiency of norbornadiene a further species **9e** is transiently formed at this temperature (Scheme 2) tentatively assigned the structure shown on the basis on proton and phosphorus NMR evidence. This decays at 0°C with formation of **9a**, but is more stable to this transformation than **9b** or **9c**.

Oligomeric solvates

Asymmetric hydrogenations catalysed by rhodium complexes of *R*-phenylbis(diphenylphosphino)ethane has been reported previously [16,17]. In our preliminary communication [17] we showed that the hydrogenation of *R*-**13a** in methanol gave rise to two species in solution, a monomer *R*-**13c** related to the solvates produced from other chelating biphosphine rhodium precursors, and a dimer existing in two diastereomeric forms (**14a** and **14b**). This was confirmed by the concentration dependence of the relative proportion of these two types of complex and further tested by examination of the racemic phosphine complex, *rac*-**13a**. This has an identical ^{31}P NMR spectrum to the pure enantiomer, but on hydrogenation two new dimeric species (**14c** and **14d**) are observed in similar proportions. Each of the four isomers is present at comparable concentration and their eight-line spectra suggest a C_2 symmetry axis in **14a** and **14b** but a mirror plane in **14c** and **14d**, so that all possess two pairs of magnetically equivalent phosphines.

Solvates from either the optically active or racemic precursor **14a** give rise to a common ^{31}P NMR spectrum with 32 lines (Fig. 3) following addition of triethylamine. This is consistent with the stereospecific formation of trimers **15a, b** for which analogies, including one defined by preliminary crystal-structure evidence [3], exist.

A sample of *R*-**13a** was hydrogenated in methanol and the ^{31}P NMR spectrum monitured during successive additions of triethylamine. It was observed that the original solvents were more than 50% depleted by addition of 0.33 equivalents of triethylamine per mole of rhodium and completely converted into **15** after addition of 0.66 equivalents of triethylamine. A field desorption mass spectrum of **15** (delivered to the probe as a methanol solution) showed an ion at *m/e* 1834 ± 10, which is consistent only with the indicated structure.

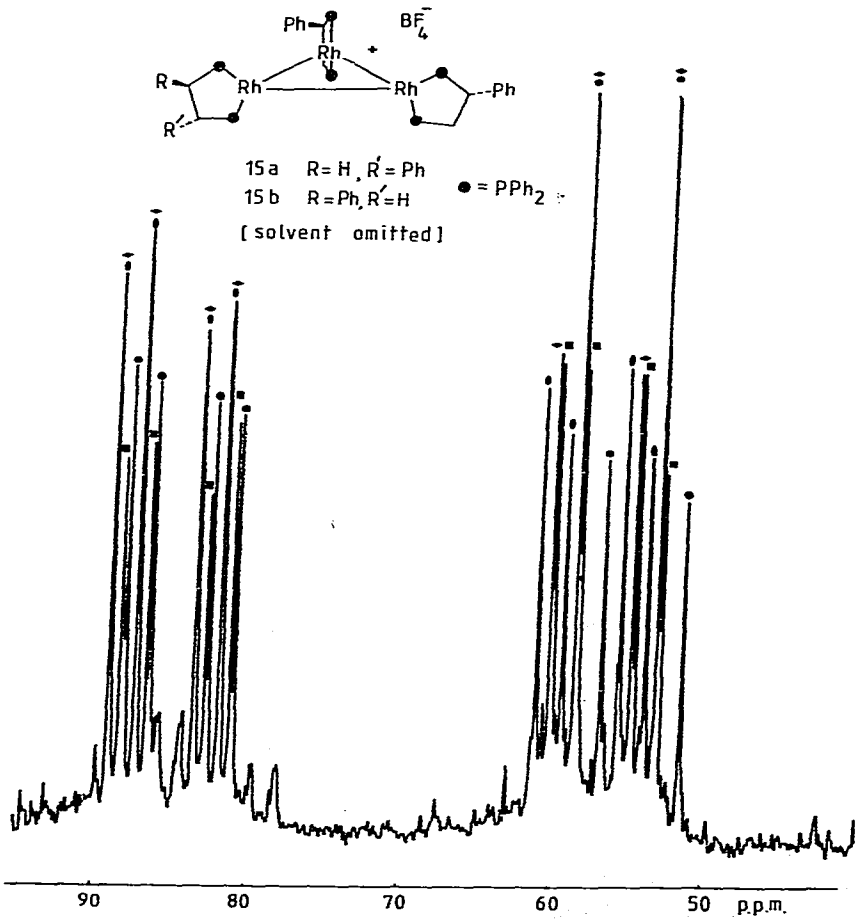


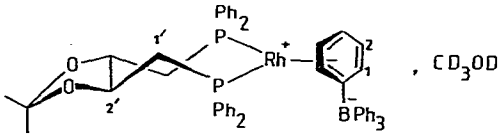
Fig. 3. ^{31}P NMR spectrum of trimers **15a** and **15b** in CH_3OH; ●, ●, ■, ◆, are 8-line multiplets.

TABLE 3

^{31}P NMR SPECTRA OF SOLVATE COMPLEXES AND RELATED SPECIES FORMED IN OTHER SOLVENTS

Phosphine	Solvent	δ (ppm)	J(RhP) (Hz)	J(PP) (Hz)
DIOP (16)	MeOH	43.0	199	
DIOP (16)	THF	42.2	200	
	(2 species)	29.4	203	
DIOP (16)	Benzene	29.7	203	
DIOP (16)	BPh_4^-/CH_2Cl_2	17.6	153	
R-$Ph_2PCH_2CHPhPPh_2$ (13)	$MeOCH_2CH_2OH$ [a]	93.5	208	60
		65.0	202	
R-$Ph_2PCH_2CHPhPPh_2$ (13)	BPh_4^-/CH_2Cl_2	69.3	155	35
		40.6	156	

[a] Only monomer observed.



(16 d)

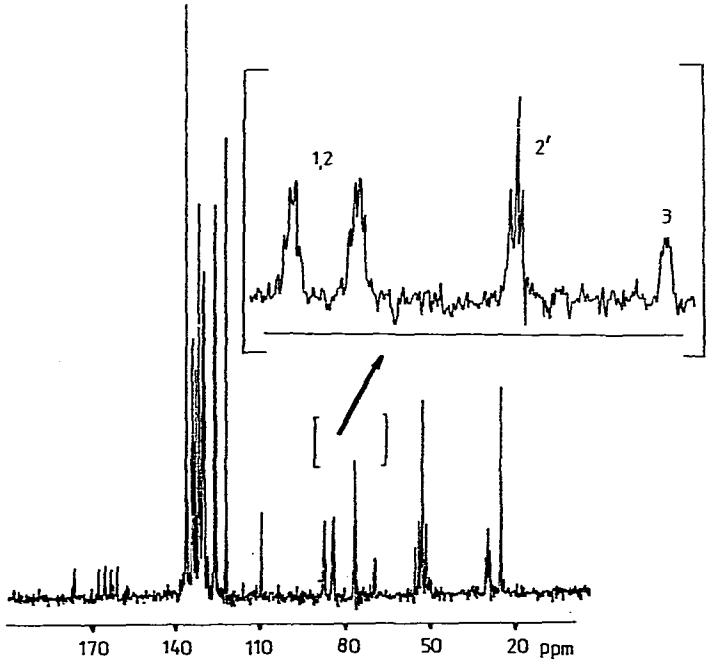


Fig. 4. ^{13}C NMR spectrum of complex 16d in CD_3OD solution, with the coordinated arene region expanded.

Hydrogenation in other solvents

A limited number of hydrogenation experiments have been carried out in 2-methoxyethanol, tetrahydrofuran and benzene (Table 3), mainly using **16a**. It is somewhat surprising that reduction can be carried out in benzene solution in the absence of donor molecules, although this has been observed in other cases [18]. The product structure is unknown, although it is unlikely to be an η^6-arene complex [3,19]. This structure was ruled out by adding $Na^+BPh_4^-$ to the solution of **16c** in methanol and showing that the coupling constant J(PRh) = 153 Hz resembled that of a bis-olefin adduct rather than that obtained on hydrogenation of **16a** in benzene. The ^{13}C NMR of **16d** clearly demonstrates that a single phenyl ring is coordinated (Fig. 4) since rhodium couplings to each ring carbon atom may be observed.

Experimental

All manipulations involving air-sensitive species were carried out in Schlenck apparatus under an atmosphere of dry argon and solvents were thoroughly degassed before use according to standard vacuum-line techniques. Melting points were recorded on a Reichert Köfler block and are uncorrected. ^{31}P NMR spectra were recorded on a Bruker WH 90 spectrometer and chemical shifts are reported relative to external H_3PO_4. ^1H NMR spectra were recorded on a Brüker WA 300 spectrometer. Microanalyses were recorded by Dr. F.B. Strauss, Oxford. All solvents employed were dried and distilled before use.

Bicyclo[2,2,1]heptadienerhodium(I) biphosphine tetrafluoroborate complexes

These were prepared by methods described below and the appropriate details of individual complexes are collected in Table 4.

Method A. Cycloocta-1,5-dienerhodium(I) acetylacetonate (0.155 g, 0.5 mmol) was dissolved in tetrahydrofuran (2 ml, freshly distilled from sodium benzophenone ketyl) under argon and fluoboric acid (40% in H_2O, 0.3 ml) added. Bis(diphenylphosphino)butane (0.213 g, 0.5 mmol) was added as a solid in one portion to give a dark orange solution. Addition of ether (20 ml) caused precipitation of the complex, which was collected by filtration, washed with ether and dried in vacuo, giving 0.330 g (91%) of cycloocta-1,5-diene(bis-diphenylphosphino)butanerhodium(I) tetrafluoroborate as orange needles: m.p. 215—20°C (dec).

Method B. A mixture of bis(bicyclo[2,2,1]heptadiene)chloro-μ-chlorodirhodium (0.095 g, 0.2 mmol) and silver tetrafluoroborate (0.080 g, 0.41 mmol) in acetone (2 ml) was agitated vigorously in a Craig tube under argon. Solid 1,5-bis(diphenylphosphino)pentane (0.180 g, 0.4 mmol) was added in one portion to give a red solution. The solution was filtered to remove precipitated silver chloride and poured into ether (25 ml), giving a yellow-orange solid. This was filtered, washed with ether and dried in vacuo to give 0.261 g (85%) of bicyclo[2,2,1]heptadiene-1,5-bis(diphenylphosphino)pentanerhodium(I) tetrafluoroborate. The product could be recrystallised from methanol as orange needles.

Method C. A mixture of bis(bicyclo[2,2,1]heptadiene)rhodium(I) tetrafluoro-

TABLE 4

ANALYTICAL DATA ON BICYCLO[2.2.1]HEPTADIENE(PHOSPHINE)RHODIUM(I) FLUOROBORATE COMPLEXES

Phosphine	Method of preparation	Analysis Found (calcd.) (%)			
		C	H	P	F
PPh_3	B, C			[a]	
PPh_2CH_3	B			[a]	
$Ph(o\text{-}C_6H_4CH_3)PCH_3$	B	59.1(59.1)	5.41(5.35)	8.53(8.73)	10.70(10.7)
$Ph(o\text{-}C_6H_4OCH_3)PCH_3$	B	56.3(56.6)	5.11(5.13)	8.17(8.36)	9.99(10.2)
$Ph_2P(o\text{-}C_6H_4OCH_3)$	C	61.7(62.3)	5.0(4.9)	6.8(7.15)	
$Ph_2P(CH_2)_2Ph_2$	A			[a]	
$Ph_2P(CH_2)_3PPh_2$	A	58.8(58.7)	4.94(5.20)	8.93(8.96)	10.95(11.14)
$Ph_2P(CH_2)_4PPh_2$	A [b]	59.2(59.5)	5.39(5.49)	8.72(8.53)	10.70(10.90)
$Ph_2P(CH_2)_5PPh_2$	B	59.6(59.8)	5.45(5.30)	8.60(8.58)	10.76(10.52)
CHIRAPHOS	A			[a] (ClO_4^-)	
DIPAMP	C, in situ	—			
DIOP	B			[a]	
$(C_5H_4PPh_2)_2Fe$	B	59.0(58.9)	4.54(5.34)	7.16(7.41)	
R-$Ph_2PCH_2CHPhPPh_2$	C, in situ			—	

[a] Known compound [21]. [b] Cycloocta-1,5-diene complex.

borate (0.080 g, 0.21 mmol) and *o*-anisyldiphenylphosphine (0.122 g, 0.42 mmol) were stirred in freshly distilled tetrahydrofuran (2 ml) for 10 minutes. The volume of the solution was reduced to 1 ml, and it was then poured into diethyl ether (Na-dried and distilled, 25 ml). The sample was isolated by filtration (Craig tube) and washed with ether, giving 0.151 g (82%) of bicyclo-[2,2,1]heptadienebis(*o*-anisyldiphenylphosphine)rhodium(I) tetrafluoroborate as a yellow solid m.p. 143—144°C; *m/e* (field desorption, M^+) 779.

Hydrogenation experiments

A solution of bicyclo[2,2,1]heptadiene-rhodium complex (typically 0.025 g, c 0.03 mmol) in methanol (1.3 ml) was transferred to an 8 mm NMR tube with constricted neck and thoroughly degassed by three freeze-thaw cycles on a vacuum line. A hydrogen atmosphere was established, and the tube then agitated vigorously (Whirlimix, Fisons) until the characteristic orange colour of the diene was discharged. The tube was then sealed under hydrogen, or alternatively this was removed by three cycles of evacuation at —80°C, and sealing carried out under argon. The ^{31}P NMR spectrum was accumulated with this tube contained in a 10 mm tube with lock solvent (D_2O or CD_3OD) in the interannular space.

Experiments involving $Ph_2P(CH_2)_5PPh_2$

(i) A sample of rhodium-norbornadiene complex **9a**, (0.020 g) in methanol (1.5 ml) was agitated under a hydrogen atmosphere for 10 minutes and then sealed under hydrogen. The ^{31}P NMR spectrum was taken immediately and showed two doublets at 51.6 ppm (J(PRH) = 131 Hz), A, and 39.4 ppm (J(PRh) = 202 Hz), B. After 5 hours the latter signal was much fainter and a new absorption at 33.0 ppm (J(PRh) = 116 Hz), C, was apparent. After stand-

ing the sample overnight C was the major species present.

(ii) A similar experiment was carried out but here hydrogen was removed by pumping before the tube was sealed under argon. After standing overnight a 50 : 50 mixture of A and B was observed.

(iii) A sample of **9a** (0.016 g) in methanol (1.5 ml) was hydrogenated for 5 seconds at 0°C. The ^{31}P NMR spectrum showed traces of starting material and a 3 : 2 mixture of A and B.

(iv) A sample of **9a** (0.010 g) in methanol-d_4 (0.4 ml) was hydrogenated in a 5 mm NMR tube and then capped under hydrogen. Changes in the hydride region of the proton NMR spectrum were recorded over a period of 14 hours and are displayed in Fig. 2. A similar experiment was carried out in which deuterium replaced hydrogen.

(v) A sample of **9a** (0.030 g) in methanol (1.5 ml) was hydrogenated as before and then bicyclo[2,2,1]heptadiene (2 μl) added to the solution at −78°C. The NMR spectrum was monitored at −30°C and showed a mixture of A, B and a new species D at 66.6 ppm (J(PRh) = 115 Hz). Frequent monitoring at this temperature showed that B rapidly disappeared with concomitant formation of **9a**, and D and A disappeared more slowly. Similar observations were made in an experiment where an excess of norbornadiene was employed, but here **9a** was the sole species present after prolonged standing at −30°C. The formation of D was associated with the appearance of a new peak at −8.0 ppm (J(RhH) = 18 Hz, J(PH) < 5 Hz) in the ^1H NMR spectrum.

Synthesis of R-phenylbis(diphenylphosphino)ethane

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 tetrahydrofuran (150 ml) over a period of about 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 ether (100 ml) and the solvent removed in vacuo to give (+)-(*S*)-1-phenylethane-1-2-diol (7.4 g). Extraction of the inorganic precipitate with ether in a Soxhlet apparatus gave a further 7.0 g of product, total yield 14.4 g (71%), (lit. [20] 43%). Recrystallisation from toluene/hexane gave colourless plates, m.p. 65—66°C (lit. 65°C); $[\alpha]_D^{20}$ + 38.8° (*c* 1.1, H_2O) lit. [20] 40.4° (*c* 3.34, H_2O). Further recrystallisation gave a sample m.p. 66—66.5°C, $[\alpha]_D^{20}$ + 44.3° (*c* 3.34, H_2O); δ 3.6 (2 H, m, CH_2), 4.75 (1 H, q, CH), 5.2 (2 H, bs, OH), 7.25 ppm (5 H, s, aromatic).

A solution of (+)-(*S*)-1-phenylethane-1,2-diol (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 over 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 collected and the aqueous layer extracted with further dichloromethane (2 × 5 ml). The combined extracts were dried (magnesium sulphate),

filtered and hexane (25 ml) added. Recrystallisation at 5°C gave (+)-(*S*)-1-phenylethane-1,2-diol dimethanesulphonate (5.5 g, 86%), m.p. 108—110°C; $[\alpha]_D^{20}$ + 89.85° (*c* 1, $CHCl_3$). Found: C, 40.9; H, 4.7; S, 21.7; $C_{10}H_{14}S_2O_6$ calcd.: 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), 7.4 ppm (5 H, s, aromatic); Mass spec. (*m/e*): 199(18) ($M^+ - OSO_2Me$), 198(20), 185(70), 107(100), 91(65), 79(65).

Finely cut lithium metal (813 mg, 116 mmol) 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 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 h) and then cooled to —78°C. (+)-(*S*)-1-phenylethane-1,2-diol dimethanesulphonate (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 in vacuo 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)1-phenylethane as fine white needles (5.99 g, 87%), m.p. 165—175°C (dec); $[\alpha]_D^{20}$ — 33.2°C (*c* 0.762, $CHCl_3$); found: C, 80.9; H, 6.0; P, 12.9. $C_{32}H_{28}P_2$ calcd.: C, 81.0; H, 5.9; P, 13.1%; δ 2.55 (2 H, m, CH_2), 3.3 (1 H, m, CH), 6.4—8.3 ppm (25 H, m, aromatic); ^{31}P NMR: δ ($CHCl_3$) 9.2, —15.4 ppm, *J*(PP) = 18 Hz; IR (Nujol): 750s, 740m, 700s.

Racemic biphosphine was similarly prepared from (±)1-phenylethanediol.

(—)-trans-4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyldioxolanrhodium(I) η^6-tetraphenylborate

Di-μ-chlorobis(bicyclo[2.2.1]hepta-2,5 diene)dirhodium(I) (92.2 mg, 0.2 mmol) and (—)-*trans*-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyldioxolan (175 mg, 0.35 mmol) were stirred together in dry methanol (7.5 ml) for 30 min. Excess phosphine was removed by filtration under argon and sodium tetraphenylborate (155 mg, 0.47 mmol) in methanol (2.5 ml) was added by syringe. After 1 h, the yellow precipitate was filtered, and washed with cold methanol (2 × 2 ml) before drying in vacuo 255 mg, (80%); m.p. 129—130°C (lit. [21] 129—131°C). Analysis: Found: C, 70.3; H, 6.03; P, 6.27. $C_{55}H_{52}BO_2P_2Rh \cdot MeOH$ calcd.: C, 70.6, H, 5.92; P, 6.50%. NMR (^1H, CD_2Cl_2) δ 1.16 (6 H, s, CH_3), 2.64 (4 H, m, CH_2P), 3.60 (2 H, brs, CH); 3.64 (1 H, m, *para*-coord. Ar); 4.20 (2 H, m, coord. Ar); 4.40 (2 H m coord. Ar); 6.8—7.7 ppm (40 H, m. Ar). (^{13}C, CD_2Cl_2) δ 26.6, 31.1, 53.7 (MeOH), 70.2 (coord. Ar, *para*), 77.4, 85.0 (coord. Ar, *meta*), 88.1 (coord. Ar, *ortho*), 109.4, 121.9, 125.8, 129.8, 130.2, 131.3, 131.5, 132.9, 134.0, 136.2, 164.3 ppm.

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