TETRAPHENYLBORATE ION-PROMOTED HYDROGENATION OF PLANAR RHODIUM(I) CATIONS FORMED BY A CHELATING OLEFINIC TERTIARY PHOSPHINE OR ARSINE

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Summary

The tetraphenylborate salts of the planar rhodium(I) cations $[RhL_2]^+$ formed by the chelate ligands o-styryldiphenylphosphine [(o-vinylphenyl)diphenylphosphine], $o\text{-}CH_2=CHC_6H_4PPh_2$ (L = spp) and the arsenic analogue (L = spas) rapidly absorb one mole of hydrogen per mole of complex forming η^6-tetraphenylborate complexes $Rh(\eta^6\text{-}C_6H_5BPh_3)(L)$; in the case of L = spp, (o-ethylphenyl)diphenylphosphine, $o\text{-}C_2H_5C_6H_4PPh_2$, is also formed. A report that hydrogenation of $[Rh(spp)_2]BPh_4$ affords $Rh(\eta^6\text{-}C_6H_5BPh_3)(o\text{-}C_2H_5C_6H_4PPh_2)_2$ could not be confirmed. The synthesis of the η^5-cyclopentadienyl complex $Rh(C_5H_5)(spp)$, which contains chelate spp, is also described.

Introduction

In the preceding paper [1] we showed that o-styryldiphenylphosphine [(o-vinylphenyl)diphenylphosphine], $o\text{-}CH_2=CHC_6H_4PPh_2$(spp) and o-styryldiphenylarsine, $o\text{-}CH_2=CHC_6H_4AsPh_2$ (spas) form red, cationic, presumably planar rhodium(I) complexes $[RhL_2]^+Y^-$ (Y = BF_4, BPh_4 or PF_6; L = spp or spas). The ^1H NMR spectra of these complexes, although complex, show that both vinyl groups are coordinated and, in the case of $[Rh(spp)_2]^+$, detailed $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ NMR studies reveal that there is a solvent-dependent equilibrium between two isomers which probably contain mutually *cis*- and mutually *trans*-phosphorus atoms respectively. In a preliminary communication [2] we mentioned that $[Rh(spp)_2]^+$ reacts with hydrogen, and subsequently a more detailed report of this reaction was made by Brookes [3], who had independently generated in situ, though not isolated, the cation $[Rh(spp)_2]^+$. Because of the obvious potential analogy with homogeneous hydrogenation of olefins catalysed by rhodium(I) complexes which is offered by complexes of olefinic tertiary phosphines [4], it is important to establish the nature of the

TABLE I

NMR DATA FOR RHODIUM(I) COMPLEXES OF SPP AND SPAS [a,b]

Complex	Solvent	Chemical shifts (δ)				Coupling constants (J)			
		Aromatic	H$_1$	H$_2$	H$_3$	J_{12}	J_{13}	J_{23}	Others
Rh(BPh$_4$)(spp) (1a)	CD$_2$Cl$_2$	5.39t(1) [c] 6.3m(4) [c] 6.0–8.2m(30)	4.67sp	3.13(br)dd	1.73(br)dd	8.0	10.5	1.0	Rh–H$_1$ 3, Rh–H$_2$ 3, Rh–H$_3$ < 0.5, P–H$_3$ 4.5
Rh(BPh$_4$)(spas) (1b)	CDCl$_3$	5.54t(1) [c] 6.1m(2) [c] 6.4m(3) [c] 6.8–8.0m(30)	4.64sp	3.13dd	1.71dd	7.5	10.5	1.0	Rh–H$_1$ 3, Rh–H$_2$ 3, Rh–H$_3$ < 0.5
Rh(C$_5$H$_5$)(spp) (II)	C$_6$D$_6$	6.8–8.0m(16) 5.08dd(5) [d]	4.54td	3.17(br)dd	1.40(br)t	8.0	10.0	1.0	Rh–H$_1$ 3, Rh–H$_2$ 3, Rh–H$_3$ < 0.5, P–H$_1$ 5, Rh–C$_5$H$_5$ 0.73 (± 0.05), P–C$_5$H$_5$ 1.05 (± 0.05), Rh–P 200 (± 2) [e]

[a] Recorded at 100 MHz, 32°C. Protons are numbered as in diagram (see text); assignments are made assuming the larger of the two vicinal couplings to be that between the *trans*-protons (J_{13}). Chemical shifts (δ) are in ppm downfield of internal TMS (±0.01), coupling constants are in Hz (±0.5, except where stated). Number in parenthesis after chemical shift and multiplicity is relative intensity. [b] Abbreviations: (br), broad; m, multiplet; t, triplet; dd, doublet of doublets; td, triplet of doublets; sp, septet. [c] Coordinated BPh$_4$ protons. [d] C$_5$H$_5$. [e] Determined by INDOR on C$_5$H$_5$ resonance.

reaction of complexes such as [Rh(spp)$_2$]* with hydrogen correctly. We present here our observations on this reaction, and on the corresponding reaction of hydrogen with [Rh(spas)$_2$]*, which differ substantially from those of Brookes [3].
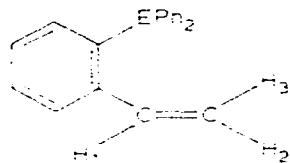
## Results and discussion

When a solution of [Rh(spp)$_2$]BPh$_4$ is stirred in an atmosphere of hydrogen, one mole of hydrogen per mole of complex is rapidly absorbed (within about 6 min), the solution turns from red to yellow, and a yellow crystalline complex of empirical formula Rh(BPh$_4$)(spp) can be isolated, which is monomeric in chloroform and non-conducting in nitromethane. The ^{1}H NMR spectrum (Table 1) shows three equally intense signals, the chemical shifts and coupling constants being typical of a coordinated vinyl group [1,5—7], the β-vinyl proton (H$_3$) which is *trans* to the α-proton (H$_1$) being at higher field than the β-vinyl

(Ia) E = P
(Ib) E = As

(II)
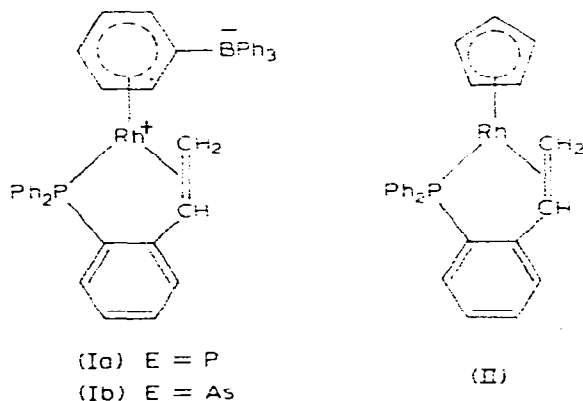
proton (H$_2$) which is *cis* to H$_1$; this is the order generally, though not exclusively, found for spp in its metal complexes, but is the reverse of that found in spp itself [1]. In addition to aromatic resonances in the usual range δ 6.9—8.2 ppm, there is a multiplet at δ 6.3 ppm and a triplet at δ 5.39 ppm (in CD$_2$Cl$_2$), the intensity ratio being 4 : 1. Integration shows that these two signals must arise from aromatic protons, and their chemical shifts and general appearance are similar to those reported for known rhodium complexes in which one of the phenyl rings of a tetraphenylborate ion is η^6-bonded to the metal atom [8—10]; the existence of this type of interaction has been confirmed by single

TABLE 2

ANALYTICAL, MOLECULAR WEIGHT AND SELECTED IR DATA

	Analysis found (calcd.) (%)				IR bands (cm^{-1}) [a]
	C	H	P	Mol. wt.	
Rh(BPh$_4$)(spp) (Ia)	73.9	5.0	4.5	693	1390, 1452
	(74.4)	(5.2)	(4.4)	(710)	(η^6-C$_6$H$_5$BPh$_3$)
Rh(BPh$_4$)(spas) (Ib)	69.8	4.7	--	729	1390, 1455
	(70.0)	(4.9)	--	(754)	(η^6-C$_6$H$_5$BPh$_3$)
Rh(C$_5$H$_5$)(spp) (II)	65.7	5.1	6.6	437	3010, 2922, 1405,
	(65.8)	(4.8)	(6.8)	(456)	1020, 985, 828,
					772 (η^5-C$_5$H$_5$)

[a] Measured in KBr discs. All bands quoted are strong or medium.

crystal X-ray structural analysis of Rh(η^6-C$_6$H$_5$BPh$_3$)[P(OMe)$_3$]$_2$ [9] and η^6-C$_6$H$_6$Ru(η^6-C$_6$H$_5$BPh$_3$) [11]. The protons of the η^6-bonded arene ring in rhodium(I)—tetraphenylborate complexes generally give rise to three resonances in the ratio 1 : 2 : 2 in order of increasing field [8—10]; that due to the unique proton appears as a triplet at lowest field, whereas in Rh(BPh$_4$)-(spp) the triplet is at highest field, and the resonances due to the other four protons overlap. The presence of η^6-bonded tetraphenylborate in Rh(BPh$_4$)(spp) is also indicated by the appearance of strong bands at 1390 and 1452 cm^{-1} in the IR spectrum [8,10] (Table 2). Thus the spectroscopic data strongly support the formulation of Rh(BPh$_4$)(spp) as the zwitter-ionic complex Rh(η^6-C$_6$H$_5$-BPh$_3$)(spp) (Ia, E = P). Hydrogenation of [Rh(spas)$_2$]BPh$_4$ in chloroform solution proceeds similarly to give the analogous yellow crystalline complex Rh(η^6-C$_6$H$_5$BPh$_3$)(spas) (Ib, E = As), the spectroscopic properties of which (Tables 1 and 2) show the presence of chelate spas and η^6-tetraphenylborate.

A bright yellow η^5-cyclopentadienyl complex, Rh(C$_5$H$_5$)(spp) (II), which is analogous to Rh(BPh$_4$)(spp), is obtained in about 30% yield by treatment of RhCl(spp)$_2$ [1,2,12] with cyclopentadienyl-sodium or -thallium. In addition to the usual aromatic and coordinated vinyl resonances (Table 1), the ^{1}H NMR spectrum shows a closely spaced doublet of doublets at δ 5.08 ppm (in C$_6$D$_6$) corresponding to the five cyclopentadienyl protons split by ^{31}P[^{3}J(P—H) 1.05 Hz] and by ^{103}Rh[^{3}J(Rh—H) 0.73 Hz], and the IR spectrum shows bands which are characteristic of η^5-cyclopentadienyl [13] (Table 2). Analogous complexes of the ligands Ph$_2$POCH$_2$CH=CH$_2$ and Ph$_2$PCH$_2$CH$_2$CH=CH$_2$ have been described recently [14].

If the reaction between [Rh(spp)$_2$]BPh$_4$ and hydrogen is carried out in CDCl$_3$ in an NMR tube, the peaks due to the starting complex are seen to be replaced by those of Rh(BPh$_4$)(spp), but in addition there are characteristic ethyl resonances at δ 2.76 ppm (quartet, CH$_2$, J 7.5 Hz) and 1.14 ppm (triplet, CH$_3$, J 7.5 Hz). Chromatography of the resulting yellow solution yields only two fractions, the first of which is a colourless oil having the ethyl resonance pattern described above; it is characterised by its ^{1}H NMR spectrum as

(o-ethylphenyl)diphenylphosphine, o-$CH_3CH_2C_6H_4PPh_2$. The second fraction affords yellow $Rh(BPh_4)(spp)$ on work-up. Thus the formation of $Rh(BPh_4)$-(spp) is accompanied by hydrogenation of one of the coordinated spp ligands, the product being displaced from the coordination sphere. The equation is therefore:

$$[Rh(o\text{-}Ph_2PC_6H_4CH=CH_2)_2]BPh_4 + H_2 \rightarrow Rh(o\text{-}Ph_2PC_6H_4CH=CH_2)(BPh_4)$$
$$+ o\text{-}Ph_2PC_6H_4C_2H_5$$
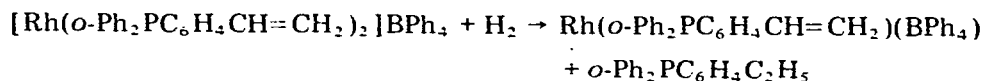
A plausible mechanism for the hydrogenation (Scheme 1) involves initial oxidative addition of hydrogen to the rhodium(I) cation to give a six-coordinate, cationic, dihydridorhodium(III) complex (III). The hydrogen atoms

SCHEME 1

(Ia)
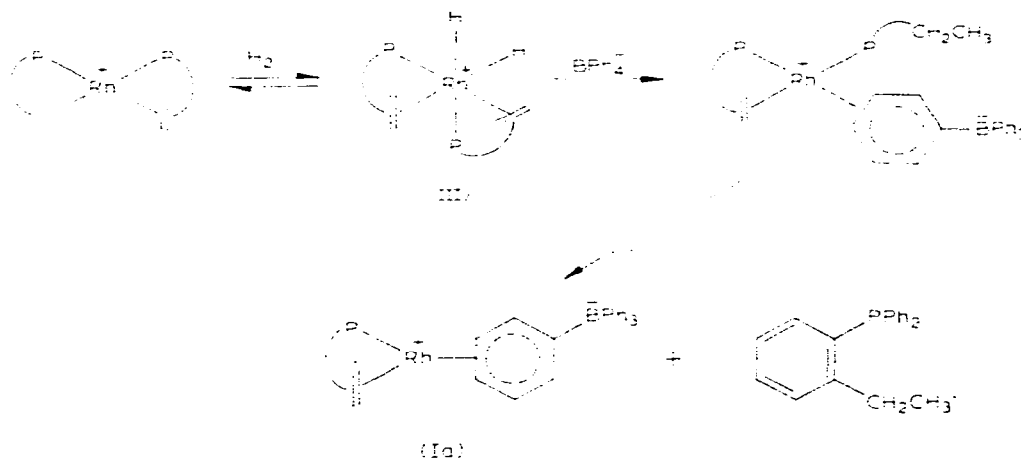
subsequently transfer to one of the coordinated spp ligands, forming P-bonded (o-ethylphenyl)diphenylphosphine and creating a vacant coordination site on the metal. This is occupied by one of the phenyl rings of the BPh_4^-, perhaps acting as a η^2- or η^4-ligand; examples of both bonding modes are well established [15,16]. In the last step, (o-ethylphenyl)diphenylphosphine is completely displaced and the phenyl ring of BPh_4^- becomes η^6-bonded to rhodium. It is also possible that the presence of BPh_4^- induces dissociation of one of the vinyl groups, either in the initial cation $[Rh(spp)_2]^+$, or in the presumed dihydride, and that the hydrogen atoms transfer to an uncoordinated vinyl group. In contrast with a previous claim [3], we [1] have observed no NMR evidence for a π-interaction of one of the phenyl groups of tetraphenylborate with $[Rh(spp)_2]^+$ leading to dissociation of the vinyl groups, but this does not rule out the possibility that such a complex is present in small amounts.

Brookes [3] states that the rapid reaction of $[Rh(spp)_2]BPh_4$ with hydrogen results in hydrogenation of both vinyl groups, the final isolated product being formulated as $[Rh(o\text{-}Ph_2PC_6H_4C_2H_5)_2]BPh_4 \cdot xCH_2Cl_2$ on the basis of microanalytical data $(0.5 < x < 1)$. Although the analytical figures for carbon and hydrogen given by Brookes for this compound do not differ greatly from

those we obtain for Rh(BPh$_4$)(spp), the discrepancy between the phosphorus analyses is outside the experimental error (Table 2). We have also been unable to confirm Brookes' statement [3] that, when rapid hydrogenation of [Rh-(spp)$_2$]BPh$_4$ is complete, there are no signals due to coordinated olefinic protons; we always observe the vinyl resonances of Rh(BPh$_4$)(spp). We suggest that the ethyl resonances of the hydrogenated solution which Brookes ascribes to [Rh(o-Ph$_2$PC$_6$H$_4$C$_2$H$_5$)$_2$]BPh$_4$ are in fact those of free (o-ethylphenyl)-diphenylphosphine, the ^{1}H NMR spectroscopic parameters of which are very similar to those given by Brookes. The important point is that, since in the initial rapid reaction only one mole of hydrogen is absorbed, only one of the vinyl groups must be hydrogenated. We do find, however, that over a much longer period (30 h), [Rh(spp)$_2$]BPh$_4$ absorbs two moles of hydrogen to give a very air-sensitive orange product which has not yet been characterised.

In an unsuccessful attempt to characterise the proposed dihydride intermediate III we briefly investigated the reaction between [Rh(spp)$_2$]BF$_4$ and hydrogen. Surprisingly, there is no initial rapid uptake, but over a 30 h period two moles of hydrogen are absorbed per mole of complex, and an orange, thermally unstable, air-sensitive compound of unknown composition can be isolated. It is presumably similar to the corresponding product from [Rh(spp)$_2$]BPh$_4$ and hydrogen.

Solutions of the cationic iridium(I) complexes generated in situ from IrCl-(spp)$_2$ or IrCl(spas)$_2$ and silver tetrafluoroborate are inert towards hydrogen, which seems surprising in view of the greater tendency of planar iridium(I) complexes relative to their rhodium(I) counterparts to undergo oxidative addition reactions [17]. However, spectroscopic evidence suggests that, in the spp system at least, the cationic species present is a five-coordinate complex containing firmly bound water, i.e. [Ir(H$_2$O)(spp)$_2$]$^+$ [1]; presumably therefore there is no site available at the metal atom for addition of hydrogen.

Finally, it is of interest that hydrogen is the only reagent we have found which converts [Rh(spp)$_2$]BPh$_4$ into Rh(BPh$_4$)(spp), and that oxygen is not effective in this reaction. This is in contrast with the formation of Rh(BPh$_4$){P(OR)$_3$}$_2$ from [Rh{P(OR)$_3$}$_5$]BPh$_4$ [10], which occurs even in the solid state in the presence of air, and in the immediate formation of Rh(BPh$_4$)(mpb) or Rh(BPh$_4$)(mpp) from [RhCl(mbp)]$_2$ or [RhCl(mpp)]$_2$ respectively on treatment with sodium tetraphenylborate (mbp = Ph$_2$PCH$_2$CH$_2$-CH=CH$_2$; mpp = Ph$_2$PCH$_2$CH$_2$CH$_2$CH=CH$_2$) [18].

Experimental

Analytical, IR and NMR spectroscopic procedures have been described elsewhere [6,7]. Ether and tetrahydrofuran were distilled from LiAlH$_4$ and stored over sodium. All other solvents were A.R. grade and were dried over molecular sieves (BDH 4A) before use. Molecular weights were determined by osmometry in chloroform at 25°C. Analytical and selected IR data are in Table 2.

Preparations and reactions

η^6-*Tetraphenylborato(o-styryldiphenylphosphine)rhodium(I), Rh(BPh$_4$)-(spp) (Ia)*. The complex [Rh(spp)$_2$]BPh$_4$ (0.25 g, 0.25 mmol) was dissolved

in dichloromethane (20 ml) and stirred in an atmosphere of hydrogen at room temperature. After the solution had turned yellow (ca. 6 min), solvent was removed by evaporation and the residue was recrystallised from dichloromethane/ n-hexane to give yellow microcrystals of the product (0.54 g, 75%).

The reaction could be carried out using a solution of [Rh(spp)₂]BPh₄ generated in situ from RhCl(spp)₂ and NaBPh₄ [1], and chloroform or chlorobenzene could be used as solvents instead of dichloromethane.

When the reaction was carried out in an NMR tube and CDCl₃ was used as solvent, the yellow solution showed peaks due to Rh(BPh₄)(spp) (Table 1) and to o-C₂H₅C₆H₄PPh₂ (see below).

η⁶-Tetraphenylborato(o-styryldiphenylarsine)rhodium(I), Rh(BPh₄)(spas) (Ib). This was prepared similarly to Ia, starting from [Rh(spas)₂]BPh₄, in 72% yield.

η⁵-Cyclopentadienyl(o-styryldiphenylphosphine)rhodium(I), Rh(C₅H₅)(spp) (II). (a) To a stirred, filtered solution of cyclopentadienylsodium prepared from sodium (0.46 g, 20 mg atoms) and freshly cracked cyclopentadiene (1.6 g, 25 mmol) in tetrahydrofuran (50 ml) was added dropwise freshly prepared, vacuum-dried RhCl(spp)₂ (0.4 g, 0.54 mmol) suspended in tetrahydrofuran (30 ml). The mixture was stirred for 6 h at room temperature, cooled to 0°C, and cautiously treated with aqueous ethanol to remove the excess of C₅H₅Na. The solvent was evaporated in vacuo, the residue was dissolved in a small volume of benzene, and the solution was transferred to a column of silica gel (70—325 mesh). The yellow band which was eluted with benzene gave a yellow oil after removal of the solvent; recrystallisation from isopentane at −78°C gave bright yellow needles of the product (80 mg, 30%).

(b) A solution of RhCl(spp)₂ (0.3 g, 0.4 mmol) in chloroform (20 ml) was stirred with a solution of freshly sublimed cyclopentadienylthallium (0.2 g, 0.74 mmol) in isopropanol (10 ml) for 45 min at room temperature. The dark brown solution was filtered and evaporated to dryness in vacuo. The residue was dissolved in a small volume of benzene and chromatographed as described above. The yield of recrystallised Rh(C₅H₅)(spp) was 25%.

Absorption of hydrogen by [Rh(spp)₂]BPh₄. The reaction vessel consisted of a two-necked flask containing chlorobenzene (20 ml) with a bent side-arm tube containing [Rh(spp)₂]BPh₄ (~50 mg) in one neck; the other neck was connected through a stopcock to a gas burette. The burette and flask were flushed with hydrogen and then evacuated completely by two freeze—thaw cycles. The flask was then immersed in a constant temperature water-bath maintained at room temperature, and the temperature was allowed to rise to room temperature with the stopcock open. After the equilibrium saturation pressure of chlorobenzene had been reached in the gas burette, hydrogen was admitted to the system and the pressure was adjusted to that of the atmosphere. The chlorobenzene was stirred and the bent side-arm twisted, causing the [Rh(spp)₂]- BPh₄ to drop into the solvent. During the reaction, the pressure of gas in the burette was continually adjusted to atmospheric pressure. When the reaction mixture had turned yellow, stirring was stopped and the volume of gas absorbed was measured.

The solution was transferred to a silica gel column and eluted with benzene. Removal of solvent from the eluate left a colourless oil, which was identified as

(*o*-ethylphenyl)diphenylphosphine by its ^{1}H NMR spectrum in CDCl$_3$: δ (ppm) 1.14 (t, 3, CH$_3$), 2.86 (q, 2, CH$_2$, *J* 7.5 Hz), 6.7—7.5 (m, ~17, aromatic).

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