PREPARATION AND SOME REACTIONS OF THE BIS[(o-VINYLPHENYL)-DIPHENYLPHOSPHINE]RHODIUM(I) CATION

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SUMMARY

A suspension of the pentacoordinate complex $RhCl(VP)_2$ [$VP=(o$-vinylphenyl)diphenylphosphine] in dichloromethane reacts with sodium tetraphenylborate to give a solution thought to contain $[Rh(VP)_2]BPh_4$. The coordinated double bonds in this salt can be hydrogenated very readily. Ligands Q = CO or pyridine react with the coordinatively unsaturated cation to give the salts $[Rh(VP)_2Q]BPh_4$, and the small molecules $Q=C_2H_4$, CS_2 or SO_2 are activated to give very labile products of similar formula. Oxidative additions to $[Rh(VP)_2]^+$ have been attempted.

INTRODUCTION

Previously we have described pentacoordinate complexes of an olefinic phosphine with rhodium(I), of formula $RhX(VP)_2$ (X = Cl, Br, or I), together with some of their reactions[1]. These complexes were remarkable in their stability, associated with the chelate effect. Although we have not isolated salts of $[Rh(VP)_2]^+$ in a pure state, we believe we have prepared this cation in solutions containing tetraphenylborate ion, analogous to the $[Rh(C_8H_{12})(PPh_3)_2]^+$ (C_8H_{12} = cyclooctadiene) salts described by Haines[2] and by Osborn[3]. After our work had been completed, Hartwell reported[4] the hydrogenation of the related cation $[Rh(CO)L_2]^+$ (L = $Ph_2PCH_2CH_2CH=CH_2$).

Here we discuss some reactions of $[Rh(VP)_2]^+$, including its very rapid hydrogenation and its ability to activate small molecules to give complexes which also have two olefin groups in coordination with rhodium. Many oxidative addition reactions were also attempted, since the addition of (*e.g.*) an alkyl halide to $[Rh(VP)_2]^+$ can be expected to give a Ziegler–Natta "model" compound. In all the above reactions there is the additional possibility of interaction with the BPh_4^- ion in solution, since this group has recently been shown to be capable of interaction with rhodium(I) through one of its arene rings[5-8]; in some cases we did find interaction of this kind.

RESULTS AND DISCUSSION

The action of one or more molar equivalents of sodium tetraphenylborate on a

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solution of the lemon-yellow complex $RhCl(VP)_2$ in dichloromethane under nitrogen gives immediately a dark orange-red solution. If the solution is left under nitrogen it becomes opalescent and eventually a white solid precipitates out, which can be shown to be sodium chloride. Presumably the lattice energy of this ionic compound provides the driving force for the reaction. We believe this red solution contains the cation (almost certainly square-planar) $[Rh(VP)_2]^+$, so that the reaction is:

$$RhCl(VP)_2 + NaBPh_4 \rightarrow [Rh(VP)_2]^+ \, BPh_4^- + NaCl$$
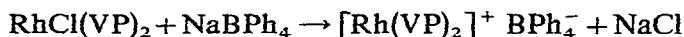
Attempts to precipitate a *pure* product from this reaction mixture were unsuccessful*. The red colour of the cation did not appear when alternative common solvents (other than chloro-substituted hydrocarbons) were used. We were unable to isolate products when salts of alternative anions such as perchlorate, hexafluorophosphate, or tetrafluoroborate were added to dichloromethane solutions of $RhCl(VP)_2$. A polar solvent will be necessary for the reaction, and it is possible to explain that no reaction occurs in (*e.g.*) acetone by suggesting that the lattice energy of sodium chloride must be gained if the reaction is to go, which will not be the case in acetone since the salt is too soluble.

We can describe the reaction of the red solution in terms of the presence of $[Rh(VP)_2]^+$, where two olefin groups and two phosphorus donor atoms are coordinated to rhodium(I). Haines[2] and others[3] have described similar species $[Rh(diolefin)(PPh_3)_2]^+$ (diolefin = cyclooctadiene or norbornadiene). Complexes of this type with ClO_4^- or PF_6^- as counterion are stable, but with BPh_4^- as the anion, the solution behaviour may be complicated[7]. $[Rh(C_8H_{12})(PPh_3)_2]^+ \, BPh_4^-$ (C_8H_{12} = cyclooctadiene) in acetone solution gives the two neutral species $[Rh(C_8H_{12})]^+ \, BPh_4^-$ and $[Rh(PPh_3)_2]^+ \, BPh_4^-$ both of which contain BPh_4^- as a ligand, coordinated to the metal ion via a π-interaction of an arene ring. Other examples of this type of coordination of tetraphenylborate are known[6,8], and the crystal structure of $\{Rh[P(OMe)_3]_2^+ - BPh_4^-\}$ has been reported[5].

We suggest that $[Rh(VP)_2]^+$ is only stable in solution when tetraphenylborate is present simultaneously because there is to some extent a π-interaction with an arene ring of BPh_4^-, leading to a zwitterionic compound, a possible representation of which is:
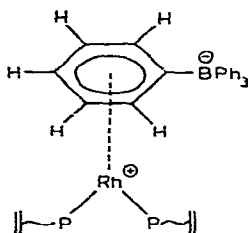
This species may be in equilibrium in solution with $[Rh(VP)_2]^+ \, BPh_4^-$. In support of this, ^1H NMR spectra of $RhCl(VP)_2$ in $CDCl_3$ saturated with sodium tetraphenylborate show various weak complex resonances in the region τ 3.5–4.8 which may be

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* A brief preliminary report[9] of the isolation of $[Rh(VP)_2]^+$ appeared as this work was being prepared for publication. The first report of this work was by the present authors[10].

TABLE 1

^{1}H NMR DATA^a FOR COMPLEXES OF THE TYPE [Rh(ligand)(VP)$_2$]$^+$BPh$_4^-$

Ligand	Olefinic proton resonances	
	$\tau(-CH=)^{b,c}$	$\tau(=CH_2)^{b,c}$
CO	5.55	6.70
Pyridine	5.62	6.70
CS$_2$	5.5	6.6
SO$_2$	5.62	6.73

^{a} CDCl$_3$ solution, measured at 60 MHz and 34°. ^{b} In view of the similarity of these values, the possibility of decomposition in solution cannot be ruled out, especially for the CS$_2$ and SO$_2$ complexes. ^{c} All resonances were complex multiplets.

due to the coordinated arene ring[5,6] as well as two complex resonances at higher field, centred at ca. τ 5.55 and 6.75 in the ratio 1/2, attributable to protons of coordinated olefinic groups. In many reactions of the red 'cation, the rhodium(I)–arene link is broken. Such a reaction has not been previously reported; in our case this is assisted by the possibility of re-chelation of the olefin groups of the two VP ligands, with simultaneous displacement of the coordinated BPh$_4$.
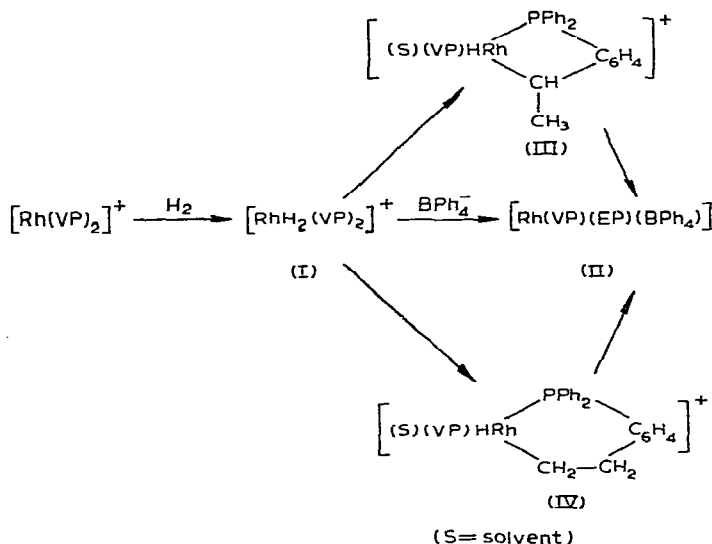
Reaction of the red cation with hydrogen gas

A dichloromethane solution of [Rh(VP)$_2$]$^+$ reacts immediately with hydrogen gas at ambient temperature and $\leqslant$ 1 atm pressure; the colour of the solution becomes pale orange-red. The ^{1}H NMR spectrum at 100 MHz of a similar solution of a reaction done in CDCl$_3$ as solvent shows that the coordinated olefin groups have been hydrogenated, *i.e.*, that the phosphine ligand is now the monodentate (*o*-ethylphenyl)-diphenylphosphine (EP), since there are no signals assignable to olefinic protons but there is a quartet resonance at τ 7.14 [4H, with further splitting due to $J(^{31}$P–H) or $J(^{103}$Rh–H) of ca. 0.6 Hz] assignable to CH$_2$ of an ethyl group, and a triplet at τ 8.86 [6H, J(CH$_2$–H) 7.25 Hz] assignable to CH$_3$ of an ethyl group. These values are closely similar to (*e.g.*) ethylbenzene, which gives signals at τ in (CCl$_4$) 7.38 (2H, q, CH$_2$) and 8.80 (3H, t, CH$_3$). Again there are also a number of complex weak signals in the region τ 3.3–4.7 attributable to protons of a coordinated arene ring (of tetraphenylborate).

The compound which can be precipitated from solution analyses for [Rh-(EP)$_2$]$^+$ BPh$_4^-$, with a conductivity in 10^{-3} *M* nitrobenzene solution at 25° initially very near zero (as expected for a non-electrolyte), but which increases linearly with time over about 50 min to reach a limiting value of ca. 6 ohm^{-1}·cm^2·mol^{-1}, about one-third of the value expected for a 1/1 electrolyte in this solvent.

This evidence indicates that the structure of the hydrogenation product and its change in conductivity can be represented by:

(S = solvent)
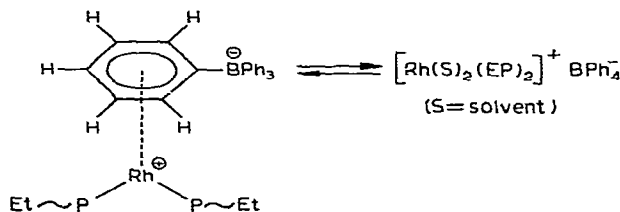
A suggested mechanism for this hydrogenation is shown in the reaction scheme, which leads to hydrogenation of one double bond only, a further sequence being necessary to give the observed product. The first step is expected to be formation of (I), a dihydridorhodium(III) cation with the normal coordination number of six. If the hydrogen adds so as to occupy *cis* positions in (I), a fast simultaneous transfer of both

$$\left[\begin{array}{c} (S)(VP)HRh \stackrel{PPh_2}{\diagdown}_{\diagup C_6H_4} \\ \diagdown CH \diagup \\ | \\ CH_3 \end{array}\right]^+$$

(III)

$$[Rh(VP)_2]^+ \xrightarrow{H_2} [RhH_2(VP)_2]^+ \xrightarrow{BPh_4^-} [Rh(VP)(EP)(BPh_4)]$$

(I)   (II)

$$\left[\begin{array}{c} (S)(VP)HRh \stackrel{PPh_2}{\diagdown}_{\diagup C_6H_4} \\ \diagdown CH_2-CH_2 \diagup \end{array}\right]^+$$

(IV)

(S = solvent)

hydrogen atoms, as suggested by Wilkinson[11], leads to (II) directly if followed by co-ordination of the arene group of BPh_4. The intermediate species (III) and (IV) may alternatively be involved. Similar compounds were suggested to explain the fairly fast hydrogenation of $[Rh(CO)(Ph_2PCH_2CH_2CH=CH_2)_2]^+$ Cl^- in methanol[4], a reaction which was investigated after the present work had been completed. Cation (III) has a five-membered ring and many provide a more important pathway than (IV), containing a six-membered ring. Insertion of the olefinic portion of VP into metal–hydrogen bonds has been shown to give either ring size[12,13], and several factors appear to be involved.

Solutions of $[Rh(C_7H_8)(PPh_3)_2]^+A^-$ (C_7H_8 = norbornadiene; A = ClO_4 or PF_6) with molecular hydrogen give salts of the cation $[RhH_2(PPh_3)_2S_2]^+$ (S = solvent), with elimination of norbornane[3]. During hydrogenation of the red cation $[Rh(VP)_2]^+$, as the coordinated olefin is hydrogenated and eventually falls away from the first coordination sphere it is replaced as ligand by the arene group of a BPH_4^- group in the mechanism which we have suggested. (There are no alternative ligands available for coordination). Similarly, hydrogenation of $[Rh(C_7H_8)(PPh_3)_2]^+BPh_4^-$ yields $[Rh(PPh_3)_2]^+BPh_4^-$ and norbornane[3].

Attempted activation of other small molecules by the red cation

A coordinately unsaturated d^8 complex can be expected to activate a variety of covalent molecules[14], and in the particular case of $[Rh(VP)_2]^+$ we can hope to gain information related particularly to the many important rhodium-promoted reactions of olefins[15] and patterns of other organometallic reactions related to homogeneous

catalysis[16], since olefins are important ligands in this area.

We found no evidence for the activation of dinitrogen at pressures of $\leqslant 1$ atm by the red cation in dichloromethane. Bubbling dioxygen gas through the solution gave rise to a novel absorption in the IR spectrum at 849 cm^{-1} (w), i.e., in a region characteristic of the dioxygen ligand. We were unable to isolate an oxygen complex from such a solution: our coordinatively unsaturated d^8 complex is a sterically crowded one, and it has recently been shown[17] that the ability of such complexes to activate oxygen is not related simply to the electron density on the central atom, but is also sensitively dependent on steric effects.

The saturation of a solution of $[Rh(VP)_2]^+$ in dichloromethane with carbon dioxide gas leads to the appearance of new bands in the IR region at 1358 w and 1480 m cm^{-1}, although we were not able to isolate a solid product. The carbon dioxide complex $[Rh_2(CO)_2(CO_2)(PPh_3)_3] \cdot C_6H_6$ shows[18] absorption bands due to coordinated carbon dioxide at 1368 s and 1498 s cm^{-1}.

Ethylene is rapidly taken up by a solution of the red cation, giving a very pale yellow solution[9,10]. Passage of nitrogen gas regenerates the original solution, showing that the ethylene is reversibly bonded. The ethylene–rhodium(I) bond is often thermodynamically strong but kinetically labile[15]. It is possible to isolate an ethylene complex $[Rh(C_2H_4)(VP)_2]^+BPh_4^-$, but this tends to lose ethylene readily. A ^1H NMR spectrum of this compound was therefore obtained directly from the pale yellow solution mentioned above, i.e., one prepared in situ and saturated with ethylene. At 100 MHz in CDCl$_3$ the spectrum showed broad signals at τ 5.05 (2H) and τ 6.65 (4H) assignable to the α- and β-vinylic protons respectively. These resonances indicate that the double bonds of the two VP ligands are both coordinated, there being a considerable upfield shift relative to the resonances[19] of free VP. They occur at τ 5.8 and 6.8 in $[RhCl(VP)_2]$ in the same solvent[1]. In addition there is a signal at τ 8.51 (4H), having some fine structure and in addition a splitting $J(^{103}Rh–H)$ ca. 1.2 Hz, assignable to coordinated ethylene. This coupling due to ^{103}Rh is the same as that (ca. 1.5 Hz) reported[20] for the tri-olefinic complex $RhCl[P(CH_2CH_2CH=CH_2)_3]$. Both this latter complex and the only other reported tri-olefinic complex of rhodium, $RhCl[P(o\text{-}C_6H_4CH=CH_2)]$[21] give vinylic resonances (one of the β-protons in each case) no higher than τ 6.60. In both these tri-olefinic complexes, all the olefin groups are part of a chelate structure and thus are held in proximity to the metal. In our tri-olefinic complex, the one olefinic group only loosely held (the ethylene group) shows a very high upfield shift to τ 8.51. Exchange of this coordinated ethylene with free (dissolved) ethylene is not occurring, since there is also a strong singlet resonance at ca. τ 5.41 due to free ethylene. The only other absorption in the spectrum of $[Rh(C_2H_4)(VP)_2]^+BPh_4^-$ is that due to the phenyl groups.

The conductivity of this complex in nitrobenzene solution (see Table 2) was only about one-third that expected for a 1/1 electrolyte in this solvent. Since the complex is unstable in the absence of ethylene, this may be due to loss of ethylene. Such loss and partial formation of $[Rh(VP)_2]^+ BPh_4^-$, as described above, would explain the low conductivity.

Attempts to prepare the analogous tetrafluoroethylene complex $[Rh(C_2F_4)(VP)_2]^+BPh_4^-$ by the action of C_2F_4 on the red cation at a partial pressure of ca. 0.75 atm over several days at ambient temperatures were unsuccessful; neither did any fluorine appear in the product when $[Rh(C_2H_4)(VP)_2]^+BPH_4^-$ solution was exposed

TABLE 2

ANALYTICAL AND CONDUCTIMETRIC DATA FOR THE NOVEL RHODIUM COMPLEXES

Complex[a,b]	Molecular conductivity[c] $(ohm^{-1} \cdot cm^2 \cdot mol^{-1})$	Colour[d]	Analysis found (calcd.) (%)					
			C	H	Cl	N	P	S
Rh(EP)$_2$(BPh$_4$) (A)	0–6[e]	O	74.95 (75.3)	5.8 (5.7)	1.5 (1.7)		6.3 (6.05)	
[Rh(C$_2$H$_4$)(VP)$_2$]BPh$_4$ (B)	7.0[f]	O-Y	71.9 (72.4)	5.45 (5.4)	5.65 (6.4)		5.65 (5.55)	
[Rh(SO$_2$)(VP)$_2$]BPh$_4$[g] (C)	9.4[f]	Y	68.25 (68.8)	5.35 (5.4)	0.0 (0.00)		6.0 (5.55)	3.2 (2.9)
[Rh(CS$_2$)(VP)$_2$]BPh$_4$ (D)	12.8[f]	O-R	71.85 (71.4)	5.25 (5.0)	2.5 (1.95)		5.7 (5.65)	2.7 (2.9)
[Rh(CO)(VP)$_2$]BPh$_4$ (E)	16.3	Y	72.85 (73.2)	5.05 (5.15)	4.1 (3.95)		5.9 (5.75)	
[Rh(Py)(VP)$_2$]BPh$_4$[h] (F)	17.2	Y	74.95 (75.8)	5.3 (5.4)	1.25 (1.65)	1.2 (1.3)	5.75 (5.65)	

[a] For abbreviations, see Discussion. [b] Most of these substances retained x moles of lattice CH$_2$Cl$_2$ ($0 < x < 1$); for (A), $x = 0.25$; (B) $x = 1.0$; (D) $x = 0.3$; (E) $x = 0.6$; (F) $x = 0.25$. [c] Nitrobenzene; $M = 10^{-3}$; 25°. [d] O = Orange; R = red; Y = yellow. [e] Time-variable; see Discussion. [f] Some decomposition (activated molecule is easily lost; see Discussion). [g] Trihydrate. [h] Py = Pyridine.

to C$_2$F$_4$ over several days. It has been shown[15] that C$_2$F$_4$ displaces ethylene from certain rhodium(I) complexes, but only very slowly although the coordination of C$_2$F$_4$ is strong compared to that of ethylene.

Carbon monoxide was rapidly absorbed by a solution of [Rh(VP)$_2$]$^+$BPh$_4^-$ in dichloromethane. A pale yellow pentacoordinate cationic carbonyl complex was isolated, [Rh(CO)(VP)$_2$]$^+$BPh$_4^-$ having v(CO) 2030 cm^{-1} (nujol mull). This cation has previously been reported as a PF$_6^-$ salt, prepared by a different route[9], and having v(CO) 2039 cm^{-1} in CHCl$_3$.

Similarly [Rh(VP)$_2$]$^+$ gives pentacoordinate diolefinic cationic complexes with neutral donor ligands (Q), [Rh(Q)(VP)$_2$]$^+$BPh$_4^-$ (Q=pyridine, tertiary phosphines). In each case the upfield shift of the olefin resonances with respect to the free ligand VP in the ^{1}H NMR spectrum shows that both olefin groups are coordinated to the metal (see Table 1).

Both the small molecules SO$_2$ and CS$_2$ are activated by [Rh(VP)$_2$]$^+$. A solution of the latter became paler in colour when treated with either sulphur compound, and precipitation with methanol after reaction at ambient temperature gave products analysing for [Rh(VP)$_2$L]$^+$BPh$_4^-$ (L=SO$_2$ or CS$_2$), in which L is only weakly held (cf. many other complexes of these small molecules with rhodium). The CS$_2$ complex has a band in the IR region at 1179 cm^{-1} (s) assignable[22] to v(C–S) of CS$_2$ bonded with a geometry similar to that of its first excited state (i.e. acting as a Lewis acid)[22,23]. The SO$_2$ complex has new bands assignable to coordinated SO$_2$ as follows: 1060 cm^{-1} (s, sym. stretch); 1140 and 1161 cm^{-1} (both s, asym. stretch), so that the ligand is bonded through the sulphur atom.

The reaction of various nitriles with [Rh(VP)$_2$]$^+$ in dichloromethane solution was instantaneous at ambient temperatures with all the nitriles investigated. With even

a large excess of RCN (R = Me, Et, or Ph) very pale yellow products were isolated by precipitation with methanol, but analysis showed incomplete conversion to [Rh-$(VP)_2(RCN)$]$^+$BPh$_4^-$. This instability parallels that of [Rh(VP)$_2$(CO)]$^+$Cl$^-$, which loses CO easily[9]. Coordinated RCN acting as a σ-donor is easily displaced also from the four coordinate cation [Rh(C$_8$H$_{12}$)(CH$_3$CN)$_2$]$^+$[24].

Reaction with the olefinic nitriles, acrylonitrile and fumaronitrile appeared to be instantaneous but was incomplete even over long periods at room temperature, analysis showing that the products contained insufficient nitrogen for formulation as [Rh(VP)$_2$(L)]$^+$BPh$_4^-$. The IR spectra showed ν(CN) almost unchanged from the free ligand, which rules out donation from the cyanide nitrogen atom and possibly suggests that these olefinic nitriles give products with [Rh(VP)$_2$]$^+$ which have three olefin-rhodium bonds.

Attempted dissociative addition reactions on the red cation

Oxidative addition reactions of d^8 complexes[14], giving octahedral d^6 complexes, are well-established and in the case of olefinic complexes, are often postulated as intermediate steps in catalytic reactions[15,16]. We attempted oxidations of [Rh-$(VP)_2$]$^+$ by molecules such as halogens and alkyl, allyl or acyl halides. Very few studies of addition reactions to rhodium(I) cationic complexes have previously been reported[25], other than with hydrogen.

The action of one molar equivalent or an excess of chlorine over a short period gave a mixture of products under the conditions used, as did the action of one molar equivalent of iodine over a long period. The action of halogens in various proportions on similar complexes in low oxidation state having coordinated double bonds can variously[26] give formation (by an oxidative process) and cleavage of metal–carbon σ-bonds, as well as saturation of the double bonds, and it appears that these reactions may not be well differentiated here.

Alkyl iodides gave an instantaneous reaction with the red cation, but we were not able to characterise the products. Trityl bromide gave a mixture including some hexaphenylethane. Chlorotriphenyltin reacted slowly to give a yellow solution from which only tetraphenyltin could be isolated analytically pure: this may result from the reaction between SnClPh$_3$ and the BPh$_4^-$ ion without the intervention of rhodium, but is not produced from these reactants in the absence of rhodium at such a fast rate.

With allyl halides again no pure rhodium complex could be isolated, but the reaction mixture was shown to contain 1,5-hexadiene, produced through combination of two allyl fragments at the rhodium centre.

Acyl and aroyl chlorides quickly reacted to give mixtures of products, not containing an RCORh- or ArCORh-grouping since there is no absorption near 1640 cm^{-1}. Traces of [Rh(VP)$_2$(CO)]$^+$BPh$_4^-$ were identified in the products by IR, showing that a minor route from the initial addition product involves loss of (*e.g.*) MeCl. The major route would thus appear to involve loss of CO and hence formation of the addition products of RCl or ArCl, which are no isolable.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are corrected. Other physical measurements, and the preparation of the ligand and of

[RhCl(VP)$_2$], were carried out as described previously[1].

Microanalyses were performed in the laboratories of Alfred Bernhardt, Elbach über Engelskirchen, West Germany, and the Department of Chemistry, University College London. Analytical data and physical properties for new complexes are given in Table 2. All reactions were done in an atmosphere of dinitrogen.

Action of sodium tetraphenylborate on chlorodi[(o-vinylphenyl)dipenylphosphine]-rhodium(I)

To a solution of the rhodium(I) complex (0.39 g) in degassed dichloromethane (20 ml) was added a large excess (0.31 g) of sodium tetraphenylborate, and the suspension was stirred for a few minutes. Some of the tetraphenylborate salt dissolved up, and the colour of the solution changed from lemon-yellow to an intense red. [This solution, containing these amounts of reactants, is subsequently referred to as "the red solution" (of the rhodium(I) cation)].

Action of hydrogen on the rhodium(I) cation

Hydrogen gas was slowly bubbled for 10 min through the red solution prepared as above at room temperature. The solution rapidly paled in colour. Evaporation of the solution with addition of methanol gave the hydrogenation product, (tetraphenylborato)bis[(o-ethylphenyl)diphenylphosphine]rhodium(I), (0.24 g), which was washed with water and cold methanol.

Activation of small molecules by the rhodium(I) cation

(a). *Ethylene*. Ethylene was slowly bubbled through the red solution prepared as above, which immediately became very pale yellow, and no further change occurred over the 20 min for which the gas was passed. Because ethylene is so easily lost from the product, it was isolated by addition of methanol and evaporation of dichloromethane by blowing a fast stream of ethylene over the solution. A solid was precipitated (0.43 g) and washed with de-oxygenated water and cold methanol. Ethylenebis[(o-vinylphenyl)diphenylphosphine]rhodium(I) tetraphenylborate was dried only for 30 min at 20 mmHg pressure over calcium chloride, since at 0.015 mmHg ethylene was lost rapidly, and the solid became orange. It was stored at −20° under an atmosphere of ethylene before analysis, which was done within an hour of drying.

(b). *Sulphur dioxide*. A rapid stream of sulphur dioxide was bubbled for 2 min through the red solution prepared as above. Methanol was slowly added to the resultant yellow-orange solution whilst the dichloromethane was displaced by the passage of a rapid stream of SO$_2$ through the solution. After cooling, the product (0.29 g) was filtered off and washed with water and then methanol.(Sulphur dioxide)bis[(o-vinylphenyl)-diphenylphosphine]rhodium(I) tetraphenylborate was dried at 15 mmHg pressure over calcium chloride for 30 min, so as to avoid loss of SO$_2$ from the product.

(c). *Carbon disulphide*. To the red solution prepared as above, carbon disulphide (1 ml) was added, and the mixture put aside at room temperature for 3 days. Evaporation under reduced pressure with addition of methanol and in addition a few drops of carbon disulphide from time to time, precipitated the product (0.16 g). (Carbon disulphide)bis[(o-vinylphenyl)diphenylphosphine]rhodium(I) tetraphenylborate was washed by ether saturated with water and finally dried as for the sulphur dioxide complex.

Carbonylbis[(o-vinylphenyl)diphenylphosphine]rhodium(I) tetraphenylborate

Carbon monoxide was passed through a solution of the red cation prepared as described above: the solution rapidly became pale yellow. After 30 min the solution was filtered from sodium chloride, and evaporated under reduced pressure with the addition of methanol. The solid (0.54 g) which separated out was filtered off and washed first with water and then with methanol.

Pyridinebis[(o-vinylphenyl)diphenylphosphine]rhodium(I) tetraphenylborate

Pyridine (0.06 ml) was added to a solution of the red cation prepared as above. The solution, which had become pale yellow, was evaporated under reduced pressure with the addition of methanol and also water (0.25 ml). After cooling, the product (0.46 g) was filtered off and washed with water and methanol.

ACKNOWLEDGEMENTS

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