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PREPARATION AND SOME REACTIONS OF A PENTACOORDINATE COMPLEX OF RHODIUM(I)

P. R. BROOKES*
William Ramsay and Ralph Forster Laboratories, University College, 20 Gordon Street, London WC1H OAJ (Great Britain)

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SUMMARY

The olefinic phosphine ligand (*o*-vinylphenyl)diphenylphosphine (VP) reacts with several rhodium(I) complexes to give $RhCl(VP)_2$ which is shown to be pentacoordinate, with two rhodium–olefin bonds. With VP the complexes RhCl(diene)-(PPh_3) (diene = 1,5-cyclooctadiene or bicyclo[2.2.1]hepta-2,5-diene) give RhCl-(diene)(VP) having three rhodium–olefin bonds. $RhCl(VP)_2$ gives $Rh(SnCl_3)(VP)_2$ on treatment with stannous chloride, and also undergoes oxidative addition reactions. The stability of the chelate olefin group bonded to rhodium(I) is illustrated.

INTRODUCTION

The preparation of a pentacoordinate olefinic complex of rhodium(I) of formula $RhCl(VP)_2$ has been briefly noted[1] since the present work on that complex was completed**. Earlier it had been shown that certain olefinic tertiary phosphines and arsines, having one olefinic group and one Group V donor atom, form stable chelate complexes with platinum(II)[2–5], palladium(II)[4], the zerovalent Group VI metal carbonyls[5,6], and copper(I) and silver(I)[7]. Recently, tris(*o*-vinylphenyl)phosphine was shown[8] to give a pentacoordinate complex with rhodium(I) having three metal–olefin bonds, and shortly afterwards Clark and Hartwell reported[9] a similar compound prepared from tri-3-butenylphosphine.

Here we describe a novel pentacoordinate complex of rhodium(I) prepared by use of the ligand VP, and having two metal–olefin bonds. We discuss some of its reactions, which indicate the stability of the (chelate) complex.

RESULTS AND DISCUSSION

The action of slightly more than two molar equivalents of VP per rhodium atom on di-μ-chlorobis(1,5-cyclooctadiene)dirhodium(I) in dichloromethane at

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* Present address: Department of Chemistry, The University of the Witwatersrand, Johannesburg, South Africa.

** The first published report of this complex was a report by P.R. Brookes and (the late) R.S. Nyholm, presented at the 21st Convention of the South African Chemical Institute, Grahamstown, Feb. 1–4, 1971.

ambient temperature causes displacement of the strongly bonded chelating diene in an exothermic reaction, and a lemon-yellow crystalline complex analysing for $RhCl(VP)_2$* can be isolated in good yield. Other methods by which this compound can be prepared include the displacement by VP of triphenylphosphine from $RhCl(PPh_3)_3$ or $Rh_2Cl_2(PPh_3)_4$, or of both neutral ligands from $RhCl(C_8H_{12})(PPh_3)$ (C_8H_{12} = 1,5-cyclooctadiene).

Since $RhCl(VP)_2$ is (*i*) monomeric in dilute chloroform solution and has a very low molecular conductivity, (*ii*) in its ^1H NMR spectrum (described in detail below) shows an upfield shift of the olefin resonances, and (*iii*) does not react with "bridge-breaking" ligands such as pyridine, it can be concluded that $RhCl(VP)_2$ is a pentacoordinate species with two metal–olefin bonds. We assume that the structure is a distorted trigonal bipyramid. This assumption is based on the information (contained in footnote 17 of a paper[9] which appeared after the present work was completed) indicating that the complex $RhCl(Ph_2PCH_2CH_2CH{=}CH_2)_2$ exists in this configuration.

As well as a complex resonance (τ 2–3 ppm) due to the phenyl groups, the NMR spectrum of $RhCl(VP)_2$ in deuterochloroform at 60 MHz shows two proton resonances at τ 5.8 and 6.8 ppm, assigned to the $-CH{=}(\alpha)$ and $=CH_2$ (β) protons, respectively. (It must be noted that this assignment was unfortunately mis-quoted in an earlier communication[8]). The complex absorptions centred at τ 5.8 and 6.8 ppm are in the ratio 1/2, as anticipated: that at τ 5.8 ppm consists of a smeared, irregular triplet (complex resonance), width at half-height ca. 25 Hz, assigned to the α-proton; and that at τ 6.8 ppm consists of a smeared, irregular nonet (complex resonance), width at half-height ca. 35 Hz and assigned to the overlapping signals of the β-protons. This spectrum shows the expected upfield shift of the olefinic resonances on coordination, since in the free ligand[6] the α-proton resonates at ca. τ 2.5, the β-*cis* at 4.63 and the β-*trans* at 4.24 ppm. The spectrum described above for $RhCl(VP)_2$ is very similar to that obtained for the five coordinate complexes $RhX(PPh_3)_2(VP)$($X{=}Cl$, Br)[11], and comparable with that reported[12] for $Rh(Acac)(CH_2{=}CHCl)_2$ (Acac = acetylacetonate), where the coordinated vinyl chloride resonance in acetone-d_6 consisted of two broad absorptions in approximate ratio 1/2, at τ 5.50 and 6.95 ppm.

Treatment of $RhCl(VP)_2$ with lithium bromide or sodium iodide in acetone gives a metathetical replacement of the chloride. The far-infrared spectra of the compounds $RhX(VP)_2$($X{=}Cl$, Br, or I) have been recorded in Table 1. The bands in $RhCl(VP)_2$ due to rhodium–chlorine stretching modes are clearly identified by comparison of these spectra. We thus assign the two bands at 253 vs and 239 s cm^{-1} to (predominantly) ν(Rh–Cl) bands. Two bands might arise if $RhCl(VP)_2$, as prepared, consisted of a mixture of isomers with different configurations of the two VP ligands with respect to one another, giving a variable environment for the chlorine atom. We consider this very unlikely, since the compound gives only one spot on chromatography.

$IrCl(1,3\text{-cyclohexadiene})_2$ shows[13] two bands due to ν(Ir–Cl) [at 295 vs and 260 s cm^{-1}] and $IrCl(C_2H_4)_4$ gives two bands also [at 308 (br), (sh) and 280 s cm^{-1}]. We consider that the most likely explanation for the two bands is that the molecules have variable environments in the lattice; all these compounds are coordinatively

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* This complex has also been prepared by M. A. Bennett and S. J. Gruber (private communication)[10].

TABLE 1

FAR IR SPECTRA OF RHODIUM(I)-VP COMPLEXES (NUJOL MULL) (cm^{-1})
ERROR < ±2 cm^{-1}

Compound	*ν(Rh–Cl)*	*ν(Sn–Cl)*	*Other bands in region 450–200 cm^{-1}*
$RhCl(VP)_2$	253 vs, 239 s		439 m, 426 s, 404 m, 382 m, 354 w, 322 m, 292 w, 280 m (sh), 276 m (sh), 272 m, 226 m, 212 m, 208 m
$RhBr(VP)_2$			439 s, 427 vs, 402 m, 374 m, 354 w, 346 vw, 319 m, 286 w, 270 m, 251 m, 242 w (sh), 228 w, 208 m, 204 vw (sh)
$RhI(VP)_2$			438 s, 430 s (sh), 426 vs, 406 w, 370 m, 352 m, 318 m, 282 w, 274 w (sh), 267 m, 255 w, 250 m, 234 vw, 230 w, 212 m, 203 vw
$Rh_2Cl_2(C_8H_{12})(VP)$	276 s[a], 256 vs[a]		440 m, 426 m, 386 m, 338 m (sh), 318 m, 237 m, 208 w, 204 w
$Rh_2Br_2(C_8H_{12})(VP)$			442 m, 426 m, 379 s, 318 w, 247 m
$RhCl(C_8H_{12})(VP)$	285 vs		442 m, 430 s, 419 vs, 320 w, 256 m
$RhBr(C_8H_{12})(VP)$			430 s (sh), 419 s, 300 w, 254 w
$RhCl(C_7H_8)(VP)$	286 vs, 276 s (sh)[b]		446 s, 435 s, 427 s, 394 w (sh), 360 w, 336 w, 250 w, 226 w
$RhCl(CO)(VP)_2$	310 vs		430 s, 409 s, 275 w, 231 w, 219 w
$Rh(SnCl_3)(VP)_2$		317 vs, 298 vs	436 m, 422 m, 377 vw, 351 w

[a] ν(Rh–Cl) bridging. [b] Probably ν(Rh–^{37}Cl).

unsaturated giving rise to much "free space" in the lattice. The splitting between the two bands is too great to be due to isotopic splitting[14,15]. The low value of ν(Rh–Cl) we associate with a long Rh–Cl distance, as was found[16] for the Rh–Cl distance (2.44±0.01 Å) in the butadiene complex, $RhCl(C_4H_6)_2$, and as is implied in the value of 245 cm^{-1} reported[17] for ν(Rh–Cl) in the complex $RhCl(C_{15}H_{20})$ (where the ligand is a cyclic pentamer of allene, coordinated to the metal by four olefinic links). An "average" Rh^I–Cl bond length is 2.34–2.37 Å[18]. Again, $RhCl(C_7H_8)PPh_3$ shows ν(Rh–Cl) at 286 cm^{-1}, a further reflection of the high *trans*- influence of the olefinic group (here norbornadiene)[15].

We have described above the preparation of $RhCl(VP)_2$ by the action of slightly over two molar equivalents of VP per rhodium atom on $[RhCl(C_8H_{12})]_2$. If the proportion is reduced to one molar equivalent, we obtain by reaction at ambient temperature a complex of stoichiometry $Rh_2Cl_2(C_8H_{12})(VP)$ rather than a bridge-splitting reaction to give $RhCl(C_8H_{12})PR_3$ as described by Chatt in the case of non-olefinic phosphine ligands[19]. We consider our complex to have the structure indicated by the formula $(C_8H_{12})RhCl_2Rh(VP)$, *i.e.*, that VP has displaced one diolefin ligand and has itself bonded as a chelate, giving an unusual "asymmetric" complex. The compound is insufficiently soluble for NMR or accurate molecular weight studies, but a value greater than that required for a monomer was obtained. The IR spectrum included two strong bands at 961 and 817 cm^{-1} associated with cyclooctadiene in $[RhCl(C_8H_{12})]_2$[19]; the far-infrared spectrum (Table 1) shows two very strong bands at 276 and 256 cm^{-1} assignable to ν(Rh–Cl) bridging, values which are comparable with those at 278 and 260 cm^{-1} established[20] for $[RhCl(C_8H_{12})]_2$. The unusual nature of the reaction giving $Rh_2Cl_2(C_8H_{12})(VP)$ does not appear to be connected with the chelate nature of VP, since the only other comparable reaction known to the author does not involve the formation of a chelate complex: the action of one molar equivalent of triphenylphosphite (L) per rhodium atom on $[RhCl(C_8H_{12})]_2$ was reported by Haines[21] to give $(C_8H_{12})RhCl_2RhL_2$, and this structure was verified by an X-ray investigation.

The rhodium complexes $[RhClL_2]_2$ ($L=C_2H_4$ or allyl) react readily with VP but the products are not yet fully characterized. The reactions of VP with the rhodium(I)–ethylene complexes $RhCl(C_2H_4)(PPh_3)_2$ and $[RhCl(CO)(C_2H_4)]_2$ are under investigation.

The action of one molar equivalent of VP on the complexes RhCl(diene)(PPh_3) (diene$=C_8H_{12}$ or C_7H_8) leads to replacement of the triphenylphosphine by VP rather than formation of $RhCl(VP)_2$ as by treatment with excess of VP. The products RhCl(diene)(VP) appear to be pentacoordinate, so that there are three olefinic groups bonded to rhodium. Such complexes are uncommon[8,9]. Our complexes are monomeric, virtually non-conductors in nitrobenzene, and show very strong bands in the far-infrared region at ca. 285 cm^{-1}, as anticipated for ν(Rh–Cl) *trans* to an olefinic group[15].

Evidence for the coordination of the vinyl group of the VP ligand comes from the proton NMR spectra (Table 2). Both complexes show resonances due to the various protons of the diene ligands comparable with those recorded for the complexes RhCl(diene)(PPh_3) (diene$=C_8H_{12}$[22] or C_7H_8[23]). No signals which can be unambiguously assigned to the vinyl group of VP can be seen, the only other sharp resonances being in the phenyl region. However, were the complexes RhCl(diene)(VP) to be square-planar, and the VP ligand coordinated only through the phosphorus donor atom, two resonances due to the protons of the *uncoordinated* $=CH_2$ group would be anticipated, as is the case in other examples where VP is bonded to metals only through the Group V atom[7]. Resonances assignable to these protons are not seen, however, and this leads us to suggest that the vinyl group is in fact coordinated, the non-appearance of any signals due to the coordinated vinyl group being explained either by their lying beneath the wide complex resonance due to the dienic methylene protons, or elsewhere in the spectrum but exchange-broadened to such an extent as to be lost in the spectral noise (both spectra were obtained with saturated solutions of the complexes). In the complexes RhCl(diene)(VP) we might expect extremely complex fluxional behaviour[22,23] in solution, including intra-[24] and inter-molecular exchange of all the olefinic groups, although the rhodium–phosphorus bond strength is probably sufficient to prevent significant cleavage of this bond through dissociation[23].

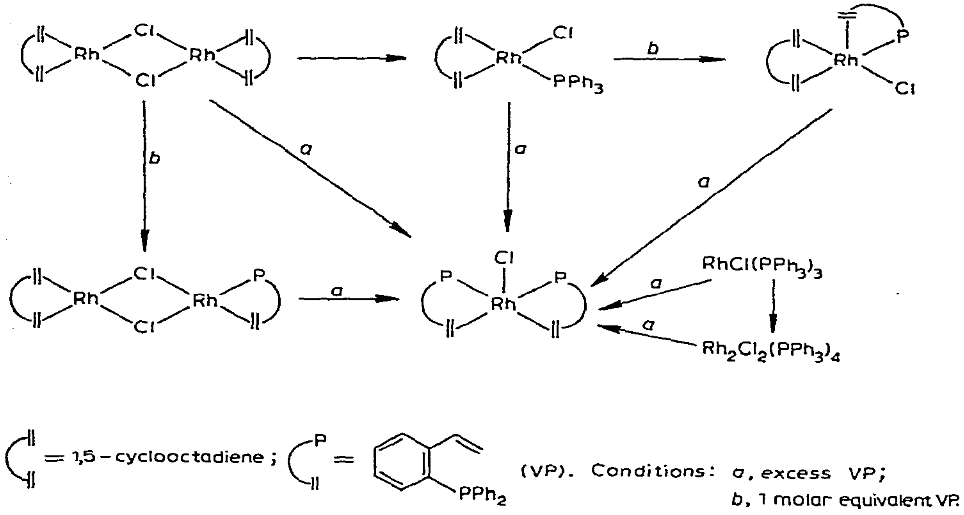
TABLE 2

NMR DATA (τ VALUES) FOR COMPLEXES RhCl(DIENE)(VP). PROTON RESONANCES IN $CDCl_3$, MEASURED AT 60 MHz AND 34°

Diene	H_A[a]	H_B	*Bridgehead*	*Methylene*
C_8H_{12}	4.44	6.80		7.4–8.3
C_7H_8	4.81	7.09	6.32	8.65

[a] *Trans* to P (assumes influence P > Cl)[30].

SCHEME 1



Reactions of VP with various rhodium(I) complexes are summarized in Scheme 1.

Some properties of $RhCl(VP)_2$ illustrate the stability of the olefinic group to displacement from the metal particularly well. Thus the complex can be recovered unchanged after heating under reflux in chloroform solution with a large excess of pyridine for long periods. The olefinic groups are not displaced from the metal under similar conditions by treatment with a large excess of VP, which might *e.g.*, have given $RhCl(VP)_3$, with only the Group V atoms of the VP coordinated, had the strength of the metal–olefin bond been lower. The VP ligand is not displaced by a large excess of the strongly chelating ligand *cis,cis*-1,5-cyclooctadiene in refluxing chloroform solution.

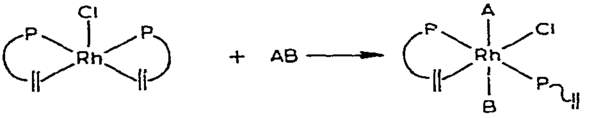
It is predictable that the metal–olefin bond will be stable [relative to mono-olefin complexes on rhodium(I), *e.g.*] since (*i*) it is part of a chelate structure, and here one where the ring size is particularly favourable, having a $5\frac{1}{2}$-membered ring; (*ii*) VP can be regarded as an olefin carrying an electronegative substituent—the phenyl group linking the olefinic group and the phosphorus donor atom—and it is established that coordination of olefins to metals is enhanced by such substituents, which give a stronger π or back bond[12]; (*iii*) in the particular case of $RhCl(VP)_2$, the rhodium atom has an inert gas configuration, in contradistinction to a complex such as $Rh(Acac)(C_2H_4)_2$ which can accommodate another pair of electrons and thus form an activated complex for an S_N2 reaction[25].

The chelate diphosphine, bis(1,2-diphenylphosphino)ethane (Diphos) will displace VP from $RhCl(VP)_2$ under vigorous conditions; thus the action of 2.5 molar equivalents of Diphos in chloroform solution heated under reflux in the presence of perchlorate ion gives the known salt, $[Rh(Diphos)_2]^+ClO_4^-$.

A suspension of sodium carbonate in methanol when heated under reflux, with $RhCl(VP)_2$ gives carbonylation to *trans*-$RhCl(CO)(VP)_2$, with $\nu(CO)$ at 1964 cm^{-1} in a nujol mull [typical value for rhodium(I) complexes] and with a very strong band in the far IR region at 309 cm^{-1} [the normal range for $\nu(Rh–Cl)$ in complexes of rhodium(I) with chlorine *trans* to carbonyl ligand is 309–298 cm^{-1}][15,26]. The molecular conductivity of this compound shows it to be a nonelectrolyte; it is insufficiently soluble for molecular weight studies. This reaction may be an example of the well-established carbonylation of a transition metal halide–tertiary phosphine complex by an alcohol in the presence of base[27], but we have found the reaction to occur in methanol and not to proceed in ethanol. This behaviour is difficult to reconcile with the usual carbonylation schemes. It is possible that an unstable carbonato–rhodium complex or rhodium-carbon dioxide complex[28] is involved as an intermediate in this case. The carbonyl complex is insufficiently soluble for NMR studies, so that we have not been able to establish whether the complex is analogous to Vaska's complex or if the olefinic group also is coordinated as in a pentacoordinate complex. In the preparation of $RhCl(CO)(VP)_2$ there was no evidence for nucleophilic attack of OMe^- at the coordinated double bond, as is the case with *e.g.*, $PtCl_2$ (VP)[29]. To restrict the comparison only to rhodium(I) complexes, nucleophilic attack may occur at the coordinated double bonds of $[RhCl(C_8H_{12})]_2$ with the same reagent, which is less electron rich than $RhCl(VP)_2$, since the action of a methanolic sodium carbonate solution gives the ill-defined $[Rh(C_8H_{12})(MeOH)]_2$[19].

With stannous chloride in methanolic solution, $RhCl(VP)_2$ gives yellow crystals of $RhCl(SnCl_3)(VP)_2$, a pentacoordinate, diolefinic complex having a rhodium–tin bond. This complex is formulated as shown rather than as $[Rh(VP)_2]^+$ $SnCl_3^-$ since (*i*) it is non-conducting in nitrobenzene solution and (*ii*) its far-infrared spectrum shows two very strong bands at 317 and 298 cm^{-1} assignable to ν(Sn–Cl) and comparable with bands due to ν(Sn–Cl) at 332 and 303 cm^{-1} in the spectrum of $Ir(SnCl_3)$-$(1,3\text{-cyclohexadiene})_2$[13]: in contrast the ν_1 and ν_2 bands of $SnCl_3^-$ (in a diethyl ether extract of concentrated hydrochloric acid/stannous chloride solution) were assigned[30] at 297 and 256 cm^{-1}.

Various oxidative addition reactions [Rh^I, d^6, to Rh^{III}, d^8) were attempted with $RhCl(VP)_2$. Simultaneous displacement of one olefin group is to be expected *viz.*,



so as to give rhodium(III) its usual coordination number. Halogens, hydrohalic acids and perchloric acid all react with instant colour change to the orange-red of rhodium(III) but competitive reactions (cleavage of the rhodium–carbon bonds probably formed in the first step in the case of halogens, or in the second step by insertion of the olefin into the Rh–H bond formed from the acids) appear to occur at a comparable rate, and single products cannot be isolated. With more than one molar equivalent of oxidant, there is also the added possibility of a further competitive reaction leading to saturation of the double bond. The IR spectrum of the mixture of products obtained from the action of one molar equivalent of chlorine in carbon tetrachloride solution on $RhCl(VP)_2$ showed a band at 762 cm^{-1} assignable to ν(C–Cl) and after treatment of the mixture with methanol this band disappeared and one at 1096 cm^{-1} assignable to ν(C–O) of a methoxy group appeared, indicating that the initial oxidation by chlorine gives oxidation of the rhodium atom to the trivalent state with a Rh–carbon bond also formed in the process[31]. The carbon–chlorine bond simultaneously formed[3] then undergoes metal-assisted solvolysis by methanol, as demonstrated for similar complexes of other transition metals.

Further oxidation reactions of $RhCl(VP)_2$ with organic halides such as methyl iodide, allyl chloride and acetyl chloride were attempted. In each case a deep orange-red solution characteristic of rhodium(III) was finally obtained, and in some cases reasonable analytical data were obtained, but none of the products could be fully characterised. The product obtained from acetyl chloride did not show IR bands characteristic of either an acetyl or a carbonyl so that the initial product may be a methyl complex formed by loss of carbon monoxide from an acetyl. All the anticipated products of these oxidations are thus Ziegler–Natta "model" compounds, containing two metal–carbon links, π and σ in nature, probably in *cis*-disposition, in the same molecule. Such species, although often postulated as intermediates, especially in homogeneous catalysis, are only very rarely isolable[32], and their instability is to be anticipated.

The action of carbon monoxide on a suspension of $RhCl(VP)_2$ in ethanol over several hours gave a pale yellow solid showing bands in the carbonyl region at 2053 m, 2030 s, and 1990 m cm^{-1}. The band at 2030 cm^{-1} is not characteristic of rhodium in either the mono-or tri-valent oxidation state, and the product may be a rhodium carbonyl cluster compound substituted by VP. Even in dimethylformamide carbonylation is slow. In benzene as solvent no reaction with carbon monoxide is observed.

Fumaronitrile (*trans*-1,2-dicyanoethylene) or acrylonitrile reacts slowly with $RhCl(VP)_2$, and one molar equivalent of tetracyanoethylene (TCNE) rapidly gives a very dark orange-red solution with the complex. The pale orange compound which can be isolated from the reaction with TCNE has a band of medium strength in the IR at 2225 cm^{-1} assignable to ν(CN), comparable to that at 2230 m cm^{-1} found for the complex $RhCl(CO)(PPh_3)_2(TCNE)$ of Baddley[33], obtained by the reactions of the olefin at room temperature with *trans*-$RhCl(CO)(PPh_3)_2$. The somewhat unstable acrylonitrile and the more stable fumaronitrile complexes have also been prepared[34]: since the analysis of our complex with TCNE corresponded to incomplete conversion of $RhCl(VP)_2$ to the six-coordinate complex $[RhCl(VP)(TCNE)]_2$ having a double chloride bridge, we suggest that with $[RhCl(VP)_2]$, acrylonitrile fumaronitrile or TCNE($=$L) give incomplete conversion to the six-coordinate complexes $[RhCl(VP)L]_2$ which are probably unstable because they contain π and σ carbon–metal bonds in the same molecule, and further that the reactions do not go to completion because of the presence of the molar equivalent of VP which is displaced and can compete with L for the two coordination positions.

Finally we note the action of sodium tetraphenylborate on a lemon-yellow suspension of $RhCl(VP)_2$ in dichloromethane: an immediate reaction occurs with formation of a deep orange-red solution (and a fine suspension of sodium chloride) which by analogy with the known[21] $[Rh(C_8H_{12})(PPh_3)_2]^+BPh_4^-$ is assumed to contain the four-coordinate cation $[Rh(VP)_2]^+$. We shall discuss this, and reactions of the cation, in a forthcoming paper[35].

EXPERIMENTAL

Reactions involving free tertiary phosphines, or hot solutions of their complexes were carried out under nitrogen. Physical measurements and the preparation of the ligand were carried out as described previously[3-5,7]. Microanalyses were performed in the laboratories of Alfred Bernhardt, Elsbach über Engelskirchen, West Germany, and the Department of Chemistry, University College London. Analytical data and physical properties for new complexes are reported in Table 3.

TABLE 3

ANALYTICAL, CONDUCTIMETRIC, MOLECULAR WEIGHT AND M.P. DATA FOR THE RHODIUM(I)–VP COMPLEXES

Complex	*M.p. (°C)*	*Molecular conductivity*[a] *(ohm^{-1}·cm^{2}·mol^{-1})*	*Analyses found (calcd.) (%)*				*Mol. wt.*[b] *found (calcd.)*
			C	*H*	*X*	*P*	
RhCl(VP)$_2$	>181 (dec.)	0.1	67.25	5.05	4.85[c]	8.45	744
			(67.2)	(4.75)	(5.0)	(8.65)	(714)
RhBr(VP)$_2$[f]	>192 (dec.)	0	59.4	4.6	9.75[e]	7.5	
			(59.7)	(4.75)	(10.9)	(7.65)	
RhI(VP)$_2$	>185 (dec. slow)	0	59.0	4.45	15.0[d]	7.5	
			(59.55)	(4.25)	(15.75)	(7.7)	
Rh$_2$Cl$_2$(C$_8$H$_{12}$)(VP)	152 (dec.)	0	50.8	(5.0)	10.35[c]	4.4	
			(49.95)	(4.35)	(10.55)	(4.6)	
Rh$_2$Br$_2$(C$_8$H$_{12}$)(VP)	>150 (dec.)	0	43.45	4.5	20.9[e]	3.85	
			(44.1)	(3.85)	(20.95)	(4.05)	
RhCl(C$_8$H$_{12}$)(VP)	128–131 (dec.)	0	62.55	5.65	6.45[c]		485
			(62.9)	(5.45)	(6.65)		(535)
RhBr(C$_8$H$_{12}$)(VP)	144 (dec.)	0	57.3	4.55	13.05[e]	5.6	
			(58.05)	(5.05)	(13.8)	(5.35)	
RhCl(C$_7$H$_8$)(VP)	>125 (dec. slow)	0	61.8	4.9	6.5[c]	5.95	470
			(62.5)	(4.85)	(6.8)	(5.9)	(519)
RhCl(CO)(VP)$_2$	>175 (dec.)	0	65.55	5.3	4.55[c]	8.1	
			(66.2)	(4.6)	(4.8)	(8.35)	
Rh(SnCl$_3$)(VP)$_2$	>191 (dec.)	0.2	52.45	3.95	11.5[c]	6.65	
			(53.0)	(3.8)	(11.8)	(6.9)	

[a] Nitrobenzene; $[M] = 10^{-3}$; 25°; ±0.1 ohm^{-1}·cm^{2}·mol^{-1}. [b] Chloroform; $[M]$ *ca.* 10^{-2}; 37°. [c] X=Cl. [d] X=I. [e] X=Br. [f] As hemi-HCCl$_3$ solvate.

Chlorodi[(o-vinylphenyl)diphenylphosphine]rhodium(I)

(*o*-Vinylphenyl)diphenylphosphine (5.0 g) was added to a solution of di-μ-chlorobis(1,5-cyclooctadiene)dirhodium(I) (1.84 g) in dichloromethane (50 ml). On occasions when the product began to separate out, the reaction mixture was shaken for 15 min. It was then put aside for 1 h, and finally the solvent was removed under reduced pressure while adding methanol. The yellow solid was washed with ethanol and light petroleum (b.p. 30–40°) and dried. It was recrystallised from dichloromethane/light petroleum (b.p. 40–60°) to give lemon-yellow microcrystals; yield 3.51 g (65%).

Bromo- and iodo-bis[(o-vinylphenyl)diphenylphosphine]rhodium(I)

These compounds were prepared from the corresponding chloro-complex (see above) by the action of an excess (10 molar equivalents) of lithium bromide or sodium iodide, respectively, in 1/1 v/v dichloromethane/acetone, heated under reflux for 15 min.

The *bromo-complex* was recrystallised from chloroform/light petroleum (b.p. 40–60°) to give dark yellow crystals; yield 75%.

The *iodo-complex* was recrystallised from dichloromethane/methanol to give dull orange crystals; yield 80%.

Other methods of preparation of $RhCl(VP)_2$

The action of an excess of the ligand VP on various complexes of rhodium(I) leads to the isolation of $RhCl(VP)_2$. In each case below the name of the rhodium(I) complex is followed by the number of molar equivalents of VP it was reacted with, in what solvent, with an indication of the time of reflux, to give $RhCl(VP)_2$ in the stated yield after recrystallisation (C_8H_{12}represents 1,5-cyclooctadiene): $RhCl(C_8H_{12})(PPh_3)$, 2.00 moles, ethanol, 2 h, 25%; $RhCl(PPh_3)_3$, 3.00 moles, benzene, 45 min, 50%; $Rh_2Cl_2(PPh_3)_4$ 3.80 moles, dichloromethane, 5 min, 45%.

Action of the ligand VP on some complexes of rhodium(I)

(*a*). *Di-μ-chlorobis(1,5-cyclooctadiene)dirhodium(I).* To the complex (473 mg) in dichloromethane (15 ml) the ligand (554 mg, 1.00 molar equivalent) was added. The reaction mixture was put aside for 20 min, then evaporated under reduced pressure, adding ethanol. *Asym*-di-μ-chloro(1,5-cyclooctadiene)[(*o*-vinylphenyl)diphenylphosphine]dirhodium(I) was precipitated as pale orange-buff microcrystals; yield, 538 mg (85%).

(*b*). *Di-μ-bromobis(1,5-cyclooctadiene)dirhodium(I).* The reaction was performed as in (*a*) above, and *asym*-di-μ-bromo(1,5-cyclooctadiene)[(*o*-vinylphenyl)diphenylphosphine]dirhodium(I) precipitated out as orange-brown microcrystals; yield 55%.

(*c*). *Chloro(1,5-cyclooctadiene)(triphenylphosphine)rhodium(I).* To the complex (460 mg) in dichloromethane (15 ml) the ligand (260 mg, 1.00 molar equivalent) was added. The reaction mixture was put aside for 30 min, heated to boiling point, and then evaporated under reduced pressure, adding ethanol. Chloro(1,5-cyclooctadiene)[(*o*-vinylphenyl)diphenylphosphine]rhodium(I) separated out as orange microcrystals, which were washed with ether; yield, 270 mg (55%).

(*d*). *Bromo(1,5-cyclooctadiene)(triphenylphosphine)rhodium(I).* The reaction was carried out as in (*c*) above, giving bromo(1,5-cyclooctadiene)[(*o*-vinylphenyl)diphenylphosphine]rhodium(I) as a pale orange-buff solid; yield, 25%.

(*e*). *Chloro(norbornadiene)(triphenylphosphine)rhodium(I).* The reaction was carried out as in (*c*) above, giving chloro(norbornadiene)[(*o*-vinylphenyl)diphenylphosphine]rhodium(I) as a sandy-buff solid; yield, 50%

Some reactions of $RhCl(VP)_2$

(*a*). *With methoxy ion in low concentration.* A suspension of the complex (565 mg) and anhydrous sodium carbonate (390 mg) in methanol (30 ml) was heated under reflux for 3 h. It became very pale orange almost immediately on reaching boiling point. After cooling the mixture, the product was filtered off, washed with water and ethanol, and finally dried, giving pale orange microcrystals of chlorocarbonylbis[(*o*-vinylphenyldiphenylphosphine]rhodium(I); yield, 442 mg (75%).

(*b*). *With* 2.5 *molar equivalents of bis*(1,2-*diphenylphosphino*)*ethane* (Diphos). Diphos (600 mg) was added to the complex (420 mg) in chloroform (20 ml), and the solution was heated under reflux for 1 h, then evaporated under reduced pressure, adding ethanol. A solution of sodium perchlorate monohydrate (90 mg) in ethanol was added, and the product precipitated by the careful addition of ether. Golden yellow crystals of bis[bis(1,2-diphenylphosphino)ethane]rhodium(I) perchlorate separated out, and were washed with ether and water; yield 550 mg (95%). This compound was identical (analysis, molecular conductivity, and melting point) with that reported[36].

(*c*) *With stannous chloride*. The complex (277 mg) and stannous chloride dihydrate (410 mg) were dissolved in dichloromethane (15 ml) and methanol (10 ml) and the solution was heated under reflux for 15 min. Evaporation under reduced pressure with the addition of methanol gave lemon-yellow crystals of (trichlorotin)-bis[*o*-vinylphenyl)diphenylphosphine]rhodium; yield 313 mg (89%).

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