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Oxidation of $RhCl\{P(C_6H_{11})_3\}_2$ and an E.P.R. Study of Some Rhodium(II) Complexes

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$RhX(PCy_3)_2$ (X = Cl, Br, I; Cy = cyclohexyl) can be oxidized with halogens Cl_2, Br_2 and I_2 to paramagnetic complexes $RhXY(PCy_3)_2$ (X = Cl, Y = Br, I; X = Y = Br). From $RhX(PCy_3)_2$ and HY the monohydrides $RhHXY(PCy_3)_2$ (X = Cl, Y = Cl, Br, I; X = Y = Br) have been prepared. $RhCl(PCy_3)_2$ reacts with CH_3I to form either $Rh(Me)ClI(PCy_3)_2$ or $RhMeI_2(PCy_3)_2$, depending on the reaction conditions. The formation of $RhH_2Cl(PCy_3)_2$ and $RhH_2(BH_4)(PCy_3)_2$ is also described.

The E.P.R. spectra of $RhXY(PCy_3)_2$ and of $RhCl_2(P(o\text{-}Tol)_3)_2$ (o-Tol = ortho-tolyl) show large g-anisotropies, with $g_{yy} \sim 4$ and g_{xx}, $g_{zz} \sim 1$ to 1.6. Two possibilities for the Kramers doublet of the ground state, a mixture of approximately 80% d_{z^2}, 20% d_{xz} and 1% d_{yz}, and a mixture of approximately 80% d_{xz}, 20% d_{z^2} and 1% d_{xy}, fit the experimental g-values reasonably well.

Introduction

In a previous paper from this laboratory it was reported that tricyclohexylphosphine (PCy_3) forms paramagnetic complexes $RhX_2(PCy_3)_2$ by reduction of $RhX_3 \cdot 3H_2O$ (X = Cl, Br) [1]. Among the other reported Rh(II) phosphine complexes only $RhCl_2(P(o\text{-Tol})_3)_2$ [2] has a well-defined composition; other compounds, *e.g.* $RhCl_2(P(o\text{-Tol})_2Ph)_2$ [2] and $RhCl_2(P(t\text{-Bu})_2R)_2$ (R = Me, Et, Pr) ref. 3, see also ref. 4) seem from their low magnetic moments to be mixtures containing a fraction of paramagnetic complex together with probably a Rh(III) complex. For the *o*-tolyl complexes E.P.R. g-values strongly deviating from 2 have been reported without interpretation [2]. Interest in the chemistry of paramagnetic Rh(II) with phosphine ligands has arisen from its occurrence during catalytic processes or under circumstances related to catalysis [5–8].

We have extended the investigation of the formation of paramagnetic Rh–PCy_3 complexes to the oxidation of $RhCl(PCy_3)_2$ [9] and related complexes. Halogens, hydrogen halides and methyliodide were used as oxidizing agents. Only in the reaction with halogens were Rh(II) complexes formed. An interpretation of the large g-anisotropy, found in the E.P.R. powder spectra of the Rh(II) complexes is given.

During the preparation of this paper, the reaction of $[RhCl(C_8H_{14})_2]_2$ with PCy_3 and HX in CH_2Cl_2 was reported by Betts *et al.* [10] but they did not obtain well-defined products.

Experimental

^1H and ^{31}P NMR spectra were recorded on a Varian XL 100 spectrometer at 100 and 40.5 MHz. E.P.R. spectra were recorded on a Varian E12 E.P.R. spectrometer at X-band; field measurements were done with an A.E.G. Gaussmeter and the frequency was measured with an H.P. 5245 L frequency counter. IR spectra were recorded with a Perkin Elmer 257 (4000–700 cm^{-1}) and a Hitachi EPI-L (700–200 cm^{-1}) spectrophotometer in KBr and CsI pellets. C, H and N analyses were carried out by Mr. P. J. J. Koonen of this laboratory; other analyses were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany. Analytical data are given in Table I.

All reactions are carried out under nitrogen or argon. $RhCl(PCy_3)_2$ [9], $RhBr(PCy_3)_2$ [11], $RhI(PCy_3)_2$ [11] and $RhCl_2(P(o\text{-Tol})_3)_2$ [2a] were prepared according to the literature.

$RhH_2Cl(PCy_3)_2$ and $RhD_2Cl(PCy_3)_2$

H_2 or D_2 is bubbled through a solution of $RhCl(PCy_3)_2$ in benzene until the solution becomes yellow. Hexane is added, the precipitate collected on a filter, washed with hexane and dried under vacuum. The compounds are stored under nitrogen at 4 °C.

$RhClX(PCy_3)_2$ (X = Cl, Br, I)[†], $RhBr_2(PCy_3)_2$

A slight excess of halogen X_2 (0.15–0.30 mmol), dissolved in benzene, is added to a solution of 0.30 mmol $RhCl(PCy_3)_2$ in 10 ml benzene. After being

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[†] The mixed halogen compounds were impure due to scrambling of the halogens.

TABLE I. Analytical Results.

Compound	%C	%H	%Cl	Others	Mol. Weight[a]
$RhH_2Cl(PCy_3)_2$	62.4	9.8			
	(61.7)	(9.8)			
$RhClX(PCy_3)_2$ (X = Cl, Br)	55.2	8.3			
theoretical for X = Br	(55.5)	(8.5)			
$RhClX(PCy_3)_2$ (X = Cl, I)	53.9	8.4			
theoretical for X = I	(52.4)	(8.0)			
$RhHCl_2(PCy_3)_2$	58.7	9.3	9.5	8.3(P)	725
	(58.9)	(8.9)	(9.7)	(8.4)	(733)
$RhDCl_2(PCy_3)_2$	58.6	9.3			
	(58.9)	(8.9)			
$RhHBr_2(PCy_3)_2$	53.5	8.5			
	(52.6)	(8.0)			
$RhHXY(PCy_3)_2$ (X, Y = Cl, Br)	55.5	8.5			
theoretical for XY = ClBr	(55.5)	(8.5)			
$RhHClX(PCy_3)_2$ (X = Cl, I)	54.4	8.6			
theoretical for X = I	(52.4)	(8.0)			
$RhHCl_2(py)(PCy_3)_2$	61.3	8.9		1.6(N)	
	(60.6)	(8.7)		(1 7)	
$RhMeClI(PCy_3)_2$	53.3	8.7	4.1	14.6(I)	851
	(53.8)	(8.3)	(4.2)	(15.1)	(839)
$RhMeI_2(PCy_3)_2 \cdot C_6H_6$	51.7	7.9		24.1(I)	
	(51.1)	(7.5)		(25.0)	
$RhH_2(BH_4)(PCy_3)_2$	62.6	10.5			
	(63.5)	(10.7)			

[a] Osmometric in benzene.

stirred for a few minutes, the precipitate is filtered off, washed with benzene and ethanol, and dried under vacuum. $RhBr_2(PCy_3)_2$ is similarly prepared from $RhBr(PCy_3)_2$, but $RhI_2(PCy_3)_2$ could not be obtained from $RhI(PCy_3)_2$ and I_2.

$RhHClX(PCy_3)_2$ (X = Cl, Br, I), $RhHBr_2(PCy_3)_2$, $RhDCl_2(PCy_3)_2$*

A freshly prepared solution of HX in acetone is added to a suspension of 0.30 mmol $RhCl(PCy_3)_2$ in 10 ml acetone. The precipitate is collected on a filter, washed with acetone and dried under vacuum. The same products are obtained in the reaction of $RhH_2Cl(PCy_3)_2$ with X_2 or HX in benzene or acetone. $RhHBr_2(PCy_3)_2$ is prepared similarly from $RhBr(PCy_3)_2$. The deuterated complex $RhDCl_2(PCy_3)_2$ is prepared with DCl in acetone-d_6; it can also be isolated as a side-product to $RhCl_2(PCy_3)_2$ (see ref. 1) from the reaction of $RhCl_3 \cdot 3H_2O$ and PCy_3 in a $D_2O-C_2H_5OD$ mixture. The compounds are moderately soluble in benzene, and decompose in chlorinated solvents. $RhHCl_2(PCy_3)_2$ has to be stored in the dark; under the influence of light it converts slowly into $RhCl_2(PCy_3)_2$.

$RhHCl_2(py)(PCy_3)_2$

A few drops of pyridine are added to a suspension of $RhHCl_2(PCy_3)_2$ in benzene. The precipitate is collected on a filter, washed with hexane and dried under vacuum. The compound is insoluble in common solvents.

$RhMeClI(PCy_3)_2$, $Rh(CD_3)ClI(PCy_3)_2$

A slight excess of CH_3I or CD_3I is added to a suspension of $RhCl(PCy_3)_2$ in hexane. After stirring for 1 1/2 hours, the precipitate is filtered off, washed with hexane and dried under vacuum.

$RhMeI_2(PCy_3)_2$, $Rh(CD_3)I_2(PCy_3)_2$

A slight excess of CH_3I or CD_3I is added to a benzene solution of $RhCl(PCy_3)_2$. Hexane is added and the precipitate is collected on a filter, washed with hexane and dried under vacuum. The compounds are isolated as benzene solvates.

$RhH_2(BH_4)(PCy_3)_2$

4.0 mmol $NaBH_4$ is added to a benzene solution of 0.30 mmol $RhCl(PCy_3)_2$. The mixture is stirred for three hours, and ethanol is added. The precipitate is filtered off, washed with ethanol and dried under vacuum.

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*The mixed halogen compounds were impure due to scrambling of the halogens.

TABLE II. NMR Data of Complexes. Solvent C_6D_6, Ambient Temperature. Chemical Shifts in ppm, coupling Constants in Hz. δ Relative to Trimethylphosphate.

Compound	^1H NMR[a]			^{31}P NMR[b]		
	τ	$^1J(Rh-H)$	$^2J(P-H)$	δ	$^1J(Rh-P)$	$^2J(H-P)$
$RhH_2Cl(PCy_3)_2$	32.7	27	14	−47.2	113.7	12
$RhHCl_2(PCy_3)_2$	not found			−32.0	96.2	
$RhH_2(BH_4)(PCy_3)_2$	26.7 10–17(BH_4)	15[c]	15[c]	−52.1	108.3	14

[a] Broad signal 7–9 ppm for PCy_3 protons. [b] Partial ^1H-decoupled. [c] BH_4-decoupled.

Results and Discussion

PCy_3 along with $P(o\text{-}Tol)_3$ and $P(t\text{-}Bu)_3$, is one of the bulkiest phosphines used in coordination chemistry [12]. The steric properties of PCy_3 are reflected in the chemical properties of its rhodium complexes.

$RhCl(PCy_3)_2$ is a very air-sensitive compound. It decomposes slowly under an inert atmosphere into $RhCl_2$ and unidentified products. With nitrogen it forms the adduct $RhCl(PCy_3)_2(N_2)$ [9]. These observations suggest its formulation as a monomeric three-coordinated Rh(I) complex, where three-coordination is imposed by the bulkiness of PCy_3 and by the obvious absence of suitable coordinating agents in the mother liquor. $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$ have similar properties [11].

The addition product of $RhCl(PCy_3)_2$ with hydrogen has a normal stability. The two hydride hydrogens and the two phosphorus atoms are equivalent in the ^1H and ^{31}P NMR respectively (Table II) and the compound shows two Rh–H stretching vibration frequencies in the IR, one of medium and the other of weak intensity. These data agree with a square pyramidal structure in which the phosphines are trans and the chlorine is axially situated (Fig. 1).

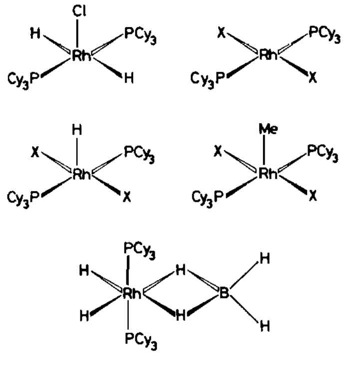

Fig. 1. Proposed structure of complexes. X = Cl, Br or I.

Rhodium(II) Complexes

The oxidative addition of halogens to $RhX(PCy_3)_2$ (X = Cl, Br, I) does not yield Rh(III) complexes, but the paramagnetic $RhXY(PCy_3)_2$ (X = Cl, Y = Cl, Br, I; X = Y = Br). $RhCl_2(PCy_3)_2$ and $RhBr_2(PCy_3)_2$ have previously been prepared by reduction of $RhX_3 \cdot 3H_2O$ (X = Cl, Br) [1]. This route of oxidation of Rh(I) complexes has also made possible the preparation of the compounds $RhClBr(PCy_3)_2$ and $RhClI(PCy_3)_2$, which are interesting for E.P.R. study. When different halogens were used, scrambling always was observed. As a consequence, the species with mixed halogens $RhClBr(PCy_3)_2$ and $RhClI(PCy_3)_2$ have been characterised mainly by E.P.R. and IR data. In the reaction of $RhCl(PCy_3)_2$ with Br_2 and I_2 some tendency to form preferentially $RhCl_2(PCy_3)_2$ has been noted. We were unable to obtain evidence for the existence of $RhI_2(PCy_3)_2$.

The rhodium(II) complexes are assigned a square planar transstructure (Fig. 1) on the basis of the high Rh–X stretching vibration frequencies (Table III). For all complexes, the g-tensor is very anisotropic (Table IV) and the g-values, taken from the E.P.R. powder spectra, are in agreement with such a square planar structure, as is shown below. From the interpretation of these spectra, it was concluded that the E.P.R. spectrum of $RhCl_2(P(o\text{-}Tol)_3)_2$ (blue modification) [2] has been incompletely reported and we have remeasured its spectrum, which is also given in Table IV. The magnetic susceptibilities of $RhCl_2(PCy_3)_2$ and $RhBr_2(PCy_3)_2$ have previously been reported [1] and correspond to magnetic moments between 2.2 and 2.3 BM at room temperature, indicating one unpaired electron, in agreement with the E.P.R. spectra.

It appears that the Rh(II) complexes have no catalytic activity [4]. $RhCl(PCy_3)_2$, itself a hydrogenation catalyst [9], decomposes slowly into $RhCl_2(PCy_3)_2$. These observations have some significance with respect to the behaviour of catalytic systems containing rhodium and bulky phosphines, *e.g.* polymer phosphines.

TABLE III. Infrared Spectroscopic Data, cm^{-1}.

Compound	Color	ν(Rh–H/D)	δ(Rh–H/D)	ν(Rh–Cl)	Others
$RhH_2Cl(PCy_3)_2$	Yellow	2165sh 2120m	622m, br	291m	
$RhD_2Cl(PCy_3)_2$	Yellow	1560sh 1528m	not found	291m	
$RhCl_2(PCy_3)_2$	Blue			354s	
$RhClBr(PCy_3)_2$	Green			335s	271m (νRhBr)
$RhBr_2(PCy_3)_2$	Green				288m (νRhBr)
$RhClI(PCy_3)_2$	Brown			325s	
$RhHCl_2(PCy_3)_2$	Orange	not found	587s, br	342s	
$RhDCl_2(PCy_3)_2$	Orange	not found	350s 335s	350s 335s	
$RhHClBr(PCy_3)_2$	Orange	not found	580s, br	330s	280m (νRhBr)
$RhHBr_2(PCy_3)_2$	Orange	not found	580s, br		268m (νRhBr)
$RhHClI(PCy_3)_2$	Red	not found	597s, br	320s	
$RhHCl_2(py)(PCy_3)_2$	Ochrous	2135m	not found	323s	
$RhMeClI(PCy_3)_2$	Brown			333s	1311w, 1167sh 325m (νRhC)[a]
$Rh(CD)_3ClI(PCy_3)_2$	Brown			333s	2120m, 2215m (νCD) 755m, (δCD), 325m (νRhC)[a]
$RhMeI_2(PCy_3)_2$	Brown				1167m 325m (νRhC)[a]
$Rh(CD_3)I_2(PCy_3)_2$	Brown				2120m, 2215m (νCD) 325m (νRhC)[a]
$RhH_2(BH_4)(PCy_3)_2$	White	2102m 2068m 1926m, br (bridging RhHB)			2450m, br, 2400s, br 2328sh (νBH)

[a] Tentative assignment.

TABLE IV. Experimental g-Values and Calculated Coefficients and Energy Differences. λ(Rh(II)) = 1235 cm^{-1} [30].

Compound	g_{xx}	g_{yy}	g_{zz}	k	$a(d_{z^2})$	$b(d_{xz})$	$c(d_{yz})$	ΔE_{xz-z^2} cm^{-1}	ΔE_{yz-z^2} cm^{-1}
Ground State d_{z^2} (d = 0)									
$RhCl_2(PCy_3)_2$[a]	1.68	4.02	1.33	0.75	0.90	–0.43	–0.094	1050	5050
$RhCl_2(PCy_3)_2$	1.58	3.96	1.27	0.71	0.89	–0.45	–0.093	1000	4650
$RhClBr(PCy_3)_2$	1.56	4.03	1.20	0.71	0.88	–0.47	–0.106	850	3900
$RhClI(PCy_3)_2$	1.65	4.0	1.18	0.71	0.88	–0.47	–0.133	750	2950
$RhBr_2(PCy_3)_2$	1.55	4.09	1.13	0.72	0.86	–0.50	–0.131	700	2800
$RhCl_2(P(o\text{-}Tol)_3)_2$[a]	1.21	4.32	0.92	0.74	0.84	–0.55	–0.094	550	3800
$RhCl_2(P(o\text{-}Tol)_3)_2$[b]	0.98	4.23	0.8	0.70	0.82	–0.57	–0.062	450	5350
Ground State d_{xz} (c = 0)				k	$b(d_{xz})$	$a(d_{z^2})$	$d(d_{xy})$	ΔE_{z^2-xz} cm^{-1}	ΔE_{xy-xz} cm^{-1}
$RhCl_2(PCy_3)_2$[a]				0.80	0.91	–0.41	–0.105	1450	3800
$RhCl_2(PCy_3)_2$				0.74	0.90	–0.43	–0.111	1200	3250
$RhClBr(PCy_3)_2$				0.75	0.89	–0.45	–0.124	1150	2850
$RhClI(PCy_3)_2$				0.75	0.89	–0.45	–0.144	1050	2400
$RhBr_2(PCy_3)_2$				0.75	0.88	–0.47	–0.132	1000	2600
$RhCl_2(P(o\text{-}Tol)_3)_2$[a]				0.77	0.85	–0.52	–0.096	800	3600
$RhCl_2(P(o\text{-}Tol)_3)_2$				0.71	0.84	–0.54	–0.063	650	5350

[a] At –180 °C other values at room temperature. [b] Broad spectrum, approximate g-values.

Hydrido–Rhodium(III) Complexes

The reaction of $RhCl(PCy_3)_2$ with halogenic acids HX (X = Cl, Br, I) results in the formation of compounds $RhHClX(PCy_3)_2$. Here too, halogen scrambling has been observed. The same products have been obtained from the reaction of $RhH_2Cl(PCy_3)_2$ with HX or X_2. From $RhBr(PCy_3)_2$ and HBr, $RhHBr_2(PCy_3)_2$ has also been prepared.

The mono-hydride complexes show no (Rh–H) stretching vibration band around 2000 cm^{-1}, nor in the PMR spectrum a high field hydride resonance, nor in the partially decoupled ^{31}P NMR spectrum a $^2J(P–H)$ coupling. This is in accord with the properties of $RhHCl_2(P(i\text{-}Pr)_3)_2$ [13], where also no Rh–H stretching vibration band nor a hydride NMR resonance could be detected, but it is in contrast with the data reported for $RhHCl_2(P(t\text{-}Bu)_2R)_2$ [3], which has ν(Rh–H) at 1938 cm^{-1}, unassigned infrared bands between 570–620 cm^{-1} and a hydride NMR resonance at τ = 41.4. The presence of a hydride ligand in our compounds was proven by the reaction with CCl_4, resulting in the formation of chloroform, and by a medium–strong infrared absorption at *ca.* 580 cm^{-1}, which we have attributed to a (Rh–H) bending vibration (Table III). In the deuterated complex $RhDCl_2(PCy_3)_2$ this absorption is absent; the corresponding δ(Rh–D), expected at *ca.* 400 cm^{-1}, is obscured by phosphine vibrations. However, the second δ(Rh–D) comes near the ν(Rh–Cl) vibration at 342 cm^{-1} and couples strongly with this vibration, which results in two absorptions at 350 and 335 cm^{-1}. It has been checked with the aid of tabulated G-matrix elements [14] and with the assumption of degenerate ν(Rh–Cl) and δ(Rh–D) vibrations that the observed splitting of 15 cm^{-1} is of the right magnitude. The corresponding δ(Rh–H) is expected at *ca.* 480 cm^{-1}, but is obscured by phosphine absorptions. The δ(Rh–H) value of 580 cm^{-1} is the lowest hitherto reported (*cf.* ref. 15). The unassigned bands between 570–620 cm^{-1} reported for $RhCl_2(P(t\text{-}Bu)_2R)_2$ [3] may also be such low-lying δ(Rh–H) vibration frequencies.

The high position of ν(Rh–X) in these compounds and the doublet in the ^{31}P NMR spectrum of $RhHCl_2(PCy_3)_2$ (Table III) suggest square pyramidal structures with *trans*-phosphines, *trans*-halogens and an axial hydride (Fig. 1). Such a structure has been found in an X-ray analysis of $RhHCl_2(P(t\text{-}Bu)Pr_2)_2$ [3].

Relationship Between $RhCl_2(PCy_3)_2$ *and* $RhHCl_2(PCy_3)_2$

$RhHCl_2(PCy_3)_2$ is converted by light into $RhCl_2(PCy_3)_2$, and the former has to be stored in the dark to avoid contamination by the latter. Conversely, the Rh(II) complexes $RhClX(PCy_3)_2$ are often contaminated by the corresponding Rh(III) hydrido compounds, but some purification can be accomplished by washing the insoluble Rh(II) complexes with benzene.

During the reduction of $RhCl_3 \cdot 3H_2O$ with PCy_3 the initially formed product is $RhCl_2(PCy_3)_2$, contaminated with some $RhHCl_2(PCy_3)_2$; and when the reaction proceeds, relatively more of the latter is formed. We observed that the Rh(II) and Rh(III) complexes are formed less contaminated the one with the other, when the method of oxidation of $RhCl(PCy_3)_2$ is used.

Reactions of $RhHCl_2(PCy_3)_2$

Some reactions of $RhHCl_2(PCy_3)_2$ have been studied. CO adds reversibly to $RhHCl_2(PCy_3)_2$, presumably with formation of $RhHCl_2(CO)(PCy_3)_2$ (in benzene ν(Rh–H) at 2100 and ν(CO) at 2020 cm^{-1}) and of a non-identified compound with an absorption at 2070 cm^{-1}. Upon prolonged treatment with CO, $RhCl(CO)(PCy_3)_2$ is formed by elimination of HCl. $RhCl(CO)(PCy_3)_2$ itself forms with HCl only traces of $RhHCl_2(CO)(PCy_3)_2$ which has ν(Rh–H) at 2060 and ν(CO) at 2000 cm^{-1} [16]. This suggests that with the different procedures isomers of $RhHCl_2(CO)(PCy_3)_2$ are formed, which have CO and HCl respectively as labile groups.

The reaction of acetylene, C_2H_2, with $RhHCl_2(PCy_3)_2$ is very slow, and even after 3 days only traces of the vinyl product $Rh(CH{=}CH_2)Cl_2(PCy_3)_2$ (ν(C=C) at 1555 cm^{-1}) could be isolated. With pyridine, a fast and complete conversion could be achieved into the coordinatively saturated 18-electron complex $RhHCl_2(py)(PCy_3)_2$, for which a Rh–H stretching vibration frequency could be detected at 2135 cm^{-1}. This observation can be considered as an additional proof for the presence of a hydride ligand in the starting complex $RhHCl_2(PCy_3)_2$.

Reaction of $RhCl(PCy_3)_2$ *with MeI and with* $NaBH_4$

The easy formation of Rh(II) complexes in the oxidation of $RhCl(PCy_3)_2$ with halogens was a motive to investigate whether in the reaction with methyliodide Rh(II) complexes could be formed in a substantial amount. The reaction, when carried out in benzene, is very fast and $RhMeI_2(PCy_3)_2$ is formed. No Rh(II) could be detected with E.P.R. in the isolated product. The reaction of MeI with a suspension of $RhCl(PCy_3)_2$ in hexane is slow and yields $RhMeClI(PCy_3)_2$. Here too, no Rh(II) was present in the isolated product. Due to the cyclohexyl groups, the methyl group is not unambiguously detected in the PMR and IR spectra, but its presence is sufficiently proven by the use of CD_3I. The proposed structure of the complexes $RhMeXI(PCy_3)_2$ (X = Cl, I) is square pyramidal with an axial Me, trans-phosphines and trans-halogens (Fig. 1).

The recent paper on $RhH_2(BH_4)(P^tBu_2Me)_2$ [17] prompts us to report the synthesis of $RhH_2(BH_4)(PCy_3)_2$ from $RhCl(PCy_3)_2$ and an excess of

$NaBH_4$. The compound shows in the infrared ν(B–H) near 2400, ν(Rh–H) near 2100 and ν(Rh–H–B) at 1925 cm^{-1}. In the PMR spectrum, the BH_4 protons are dynamically equivalent and appear as a broad resonance centered at τ = 13 ppm at room temperature. The ^1J(Rh–H) of 15 Hz for the terminal hydrides is indicative of an octahedral structure, so we think BH_4 to be a bidentate ligand (Fig. 1). The compound shows the inertness of a coordinatively saturated 18-electron system, and is not able to hydrogenate olefins.

The Stability of Rh(II) Complexes with Bulky Phosphines

The stability of Rh(II) complexes with bulky phosphines needs some further consideration. The alternatives for a Rh(II) complex are so numerous that few paramagnetic Rh(II) complexes yet have been prepared. The role of the bulkiness of the phosphine is to prevent the formation of such alternatives as tris-phosphine complexes $RhCl_3(PR_3)_3$ or $RhHCl_2(PR_3)_3$. It then causes the formation of a Rh(II) complex or of a five-coordinated mono-hydride $RhHCl_2(PR_3)_2$. Discussing the existence of $RhCl_2(PR_3)_2$ then is discussing the non-existence of $RhCl_3(PR_3)_2$ and the relative stability of $RhCl(PR_3)_2$, $RhCl_2(PR_3)_2$ and $RhHCl_2(PR_3)_2$. These four types of complexes belong to classes of compounds with an unfavorable electron configuration and a concomitant small existence range, namely three-coordinated d^8, low spin d^7 and five-coordinated low spin d^6. It seems (i) that electronic effects determine the non-existence of $RhCl_3(PR_3)_2$ and (ii) steric effects decide about the formation of $RhCl_2(PR_3)_2$ or $RhHCl_2(PR_3)_2$.

(i) On the basis of the low polarizability of the halogen and the moderate polarizability of the phosphine ligands, a theoretical order of increasing positive charge on the central metal can be given for the series of known and reported non-existing (*n.e.*) rhodium–halo–phosphine complexes: $[RhCl_2(PR_3)_2]^-$ (*n.e.*) [18] < $[RhCl(PR_3)_2]_2$ [19] < $RhCl(PR_3)_3$ [19] < $RhCl(PR_3)_2$ [9] < $RhCl_2(PR_3)_2$ ~ $[RhCl_4(PR_3)_2]^-$ [18] < $RhCl_3(PR_3)_3$ [20] < $RhCl_3(PR_3)_2$ (*n.e.*). That the extremes of the range do not (yet) exist as isolable complexes is undoubtedly an electronic effect. The low to moderate polarizability of the halogen and the phosphine, and the relatively weak over-all donor properties of the phosphine leave such a high residual positive charge on the $RhCl_3(PR_3)_2$ fragment that this charge should obviously be compensated by the coordination of at least one additional donor ligand. The instability of $RhCl(PCy_3)_2$ has been discussed elsewhere [11]. The stability of $RhCl_2(PCy_3)_2$ in a reduction of $RhCl_3 \cdot 3H_2O$ with PR_3 or in an oxidation of $RhCl(PR_3)_2$ with Cl_2, as well as the stability of the Rh(II) complexes towards disproportionation: $2RhCl_2(PR_3)_2$ = $RhCl(PR_3)_2$ + $RhCl_3(PR_3)_2$ must then be considered to be of thermodynamic origin, caused by the high energy of the Rh(I) and Rh(III) compounds. That $RhHCl_2(PR_3)_2$ does exist as a five-coordinate d^6 complex but $RhCl_3(PR_3)_2$ does not, may be ascribed to the lower electronegativity of the hydrogen compared with the chlorine ligand.

(ii) Preference of $RhHCl_2(PR_3)_2$ over $RhHCl_2(PR_3)_3$ seems to be governed largely by steric effects, *e.g.* small phosphines form the tris-complex [20], and more bulky phosphines, like $P(t\text{-}Bu)R_2$ [3], the bis-complex. PPh_3 and $P(i\text{-}Pr)_3$ have an intermediate position, for these ligands $RhHCl_2(PR_3)_2$ as well as $RhHCl_2(PR_3)_3$ have been reported [13, 21]. With the most bulky phosphines, *e.g.* P^tBu_2R, PCy_3 and $P(o\text{-}Tol)_3$, $RhCl_2(PR_3)_2$ is preferred over $RhHCl_2(PR_3)_2$; the donor–acceptor properties of the phosphine are clearly of minor importance in this preference, as both bulky alkyl- and arylphosphines form Rh(II) complexes.

Interpretation of the E.P.R. g-Values

The first derivative X-band E.P.R. powder spectra of the undiluted rhodium(II) complexes showed one g-value (g_1) near 4 and two g-values ($g_2 > g_3$) near 1.3 (Table IV and Fig. 2). Hyperfine splittings could not be observed on the broad lines. The spectra are temperature dependent. In this section we shall derive from the g-values the possible ground states of the Rh(II) complexes, and the position of the magnetic axes relative to the molecular axes, as far as possible.

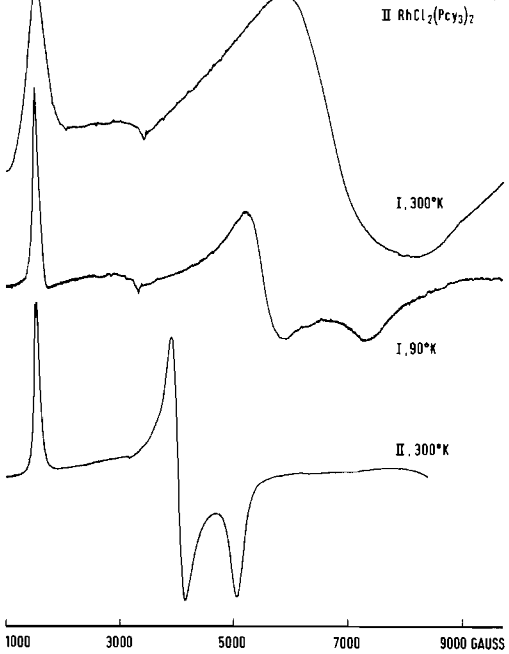

Fig. 2. The X-band E.P.R. powder spectra of $RhCl_2(PR_3)_2$, R = Cyclohexyl, *o*-Tolyl.

The large anisotropy of the g-tensor requires a strong mixing of two or more states. We represent two states $|d_1|$ and $|d_2|$ by the d-orbitals d_1 and d_2 in which the states differ; the modulus signs are used to indicate the states. A mixed state can be written as:

$$\psi = p|d_1| + q|d_2| \qquad (p^2 + q^2 = 1)$$

where p is defined as the larger coefficient. Covalency is taken into account by the introduction of a covalency (orbital reduction) factor k [22]. The equations for the g-values derived from ψ are [23–25]

$$g_{\parallel} = g_e \pm kmpq = g_e \pm kmp(1 - p^2)^{1/2}$$
$$g_{\perp} = g_e(1 - 2q^2) = g_e(2p^2 - 1)$$

The factor m originates from the L operator and is determined by the actual pair of d-orbitals. The value of m is 0, 4, $4\sqrt{3}$ or 8 and the orbitals to which m refers can be read from the 'magic pentagon' in Fig. 3 (*cf.* ref. 26).

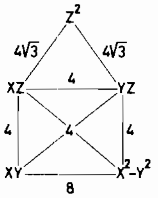

Fig. 3. Value of m as function of the orbital pair (see text).

A graph of $g_{\parallel}$ and $g_{\perp}$ as functions of p^2 for all possible values of m is given in Fig. 4. The graph is valid if the orbitals d_1 and d_2 contain 3 electrons. In this graph, the experimental g-values are also marked. It is obvious that only $4\sqrt{3}$ and 8 are possible values of m; m = 8 refers to the orbitals $d_{x^2-y^2}$ and d_{xy}. It is hard to imagine a four-coordinated d^7 system in which these two orbitals are nearly degenerate, so we reject m = 8 as a possible solution. The remaining possibility, m = $4\sqrt{3}$, corresponds to a mixing of d_{z^2} and d_{xz} (or, what is equivalent by interchange of x and y axes, d_{z^2} and d_{yz}). The result is that there are two possible ground states left for the Rh(II) complexes; *ca.* 80% $|d_{z^2}|$ + 20% $|d_{xz}|$ and *ca.* 80% $|d_{xz}|$ + 20% $|d_{z^2}|$. Such ground states are found for some four-coordinated Co(II) low spin d^7 systems [27, 28] and both of these possible ground states are in agreement with the square planar structure assigned to the Rh(II) complexes in a preceeding section of this paper. Because a square planar *trans*-structure implies D_{2h} as the approximate symmetry of the molecules $RhX_2(PR_3)_2$, it is expected that the magnetic x and y axes are situated along the metal ligand directions. This defines $d_{x^2-y^2}$ as the antibonding, empty orbital. The covalency factor k is found from $g_{\parallel}$ and $g_{\perp}$ in Fig. 4 to be approximately 0.75. This is a realistic value. From the pair of orbitals d_{z^2} and d_{xz}, $g_{\parallel}$ (the g-value near 4) is derived to be g_{yy}. Such an assignment has its precedent in several Co(II) complexes [27, 28].

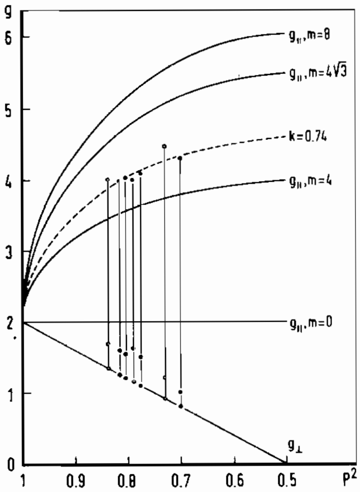

Fig. 4. $g_{\parallel}$ and $g_{\perp}$ as functions of orbital coefficient p, and experimental g-values (○ at –180 °C; ● at room temperature).

The assignment of the g_2 and the g_3 values to one of the remaining principal g-values g_{xx} and g_{zz}, and the position of the x and y axes of the g-tensor with respect to axes in the molecule remain to be determined. $g_{\perp}$ (approximately equal to g_3) has given us an approximate value of the mixing percentage of the two orbitals; $g_{\parallel}$ has been used to determine an approximate value of k; the remaining quantity, $g_{xx} - g_{zz}$, may give some further information. For that purpose we need more elaborate expressions for the g-values; these are given in Table V, where the $d_{x^2-y^2}$ orbital has been neglected, because $d_{x^2-y^2}$ does not contribute to $g_{xx} - g_{zz}$, and because it is expected that its contribution to any of the g-values is small.

Under the assumption that spin–orbit coupling is responsible for the mixing of the states, it is readily verified that c and d (which refer to the filled orbitals d_{yz} and d_{xy}) have to be negative if the leading coefficient a (ground state $|d_{z^2}|$) or b (ground state $|d_{xz}|$) is positive. In both cases g_{xx} is larger than g_{zz}. This permits us to identify with some certainty g_2 with g_{xx} and g_3 with g_{zz}. For square planar d^7 complexes the order $g_{xx} > g_{zz}$ is most usual, although exceptions have been described [28]. Finally, calculations with the experimental g-values and the g-expressions in Table V show that one orbital is mainly responsible for the $g_{xx} - g_{zz}$ difference, namely d_{yz} for the ground state $|d_{z^2}|$ (d_{xy} does not normally mix with d_{z^2} by spin–orbit coupling) and d_{xy} for the ground state $|d_{xz}|$ (the influence of d_{yz} is small by a canceling of terms in the factor ($\sqrt{3}a$ + b) at the values a = –0.45, b = 0.9, see Tables IV and V). This has led us to calculate approximate coefficients, a, b and c for

TABLE V. g-Expressions for d^7, Neglecting $d_{x^2-y^2}$, with Isotropic k (*cf.* ref. 28). $|\pm\rangle = a|d_{z^2}| \pm b\,|d_{xz}| + ic\,|d_{yz}| \pm id\,|d_{xy}|$; $d_{x^2-y^2}$ Empty.

a > b, ground state $|d_{z^2}|$ (p = a, q = b)	b > a, ground state $|d_{xz}|$ (p = b, q = a)
$g_{zz} = g_e(1 - 2b^2 - 2c^2) + 4kbc$	$g_{zz} = g_e(1 - 2a^2 - 2d^2) - 4kbc$
$g_{xx} = g_e(1 - 2b^2 - 2c^2) - 4\sqrt{3}kac + 4kbd$	$g_{xx} = g_e(1 - 2a^2 - 2d^2) + 4\sqrt{3}kac - 4kbd$
$g_{yy} = g_e(1 - 2c^2 - 2d^2) - 4\sqrt{3}kab - 4kcd$	$g_{yy} = g_e(1 - 2c^2 - 2d^2) - 4\sqrt{3}kab - 4kcd$
$g_{xx} - g_{zz} = 4kbd - 4kc(\sqrt{3}a + b)$	$g_{xx} - g_{zz} = 4kc(\sqrt{3}a + b) - 4kbd$

the $|d_{z^2}|$ ground state by putting d = 0, and a, b and d for the $|d_{xz}|$ ground state by putting c = 0 with the aid of the g-expressions in Table V and the normalization condition $a^2 + b^2 + c^2 + d^2 = 1$. In addition ΔE_{xz-z^2} and ΔE_{yz-z^2} or ΔE_{xy-xz} have been calculated under the assumption that spin–orbit coupling is responsible for the mixing of the states. The results are given in Table IV. The two solutions correspond to two possibilities for the Kramers doublet of the ground state, a mixture of approximately 80% $|d_{z^2}|$, 20% $|d_{xz}|$ and 1% $|d_{yz}|$, and a mixture of approximately 80% $|d_{xz}|$, 20% $|d_{z^2}|$ and 1% $|d_{xy}|$. As long as additional information (*e.g.* hyperfine couplings, electronic spectra) is not available, no definitive conclusion can be made about the ground state. For both possibilities the variation in the excitation energies ΔE_{yz-z^2} and ΔE_{xy-xz} is in agreement with expectations for the PCy_3 series, based on the spectrochemical series: ClI ~ Br_2 < ClBr < Cl_2. However, there is no agreement with the expected order $RhCl_2(PCy_3)_2 < RhCl_2(P(o\text{-Tol})_3)_2$.

That, by our choice of magnetic axes, the d_{xz} orbital lies higher in energy than d_{yz} permits us to locate tentatively the axis of the highest g-value (y-axis) along the P–Rh–P axis (Fig. 5), as the better π-acceptor properties of the phosphorus ligands compared to the halogen ligands stabilize then the d_{yz} orbital with respect to d_{xz}. A single crystal study could decide about this, but is still lacking.

The temperature dependence of the spectra (*cf.* Fig. 2) is partly a consequence of small energy changes, and partly a consequence of a change in the value of k. The slight decrease of k on increasing temperature suggests that a small vibronic contribution to the orbital reduction factor is present (Ham effect [29]).

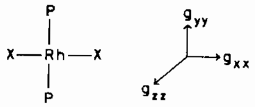

Fig. 5. Magnetic coordinate axis with respect to the molecular axis.

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