

## Oxidation of $\text{RhCl}\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2$ and an E.P.R. Study of Some Rhodium(II) Complexes

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$\text{RhX}(\text{PCy}_3)_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ;  $\text{Cy} = \text{cyclohexyl}$ ) can be oxidized with halogens  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  to paramagnetic complexes  $\text{RhXY}(\text{PCy}_3)_2$  ( $X = \text{Cl}, Y = \text{Br}, \text{I}$ ;  $X = Y = \text{Br}$ ). From  $\text{RhX}(\text{PCy}_3)_2$  and  $\text{HY}$  the monohydrides  $\text{RhHXY}(\text{PCy}_3)_2$  ( $X = \text{Cl}, Y = \text{Cl}, \text{Br}, \text{I}$ ;  $X = Y = \text{Br}$ ) have been prepared.  $\text{RhCl}(\text{PCy}_3)_2$  reacts with  $\text{CH}_3\text{I}$  to form either  $\text{Rh}(\text{Me})\text{Cl}(\text{PCy}_3)_2$  or  $\text{RhMeI}_2(\text{PCy}_3)_2$ , depending on the reaction conditions. The formation of  $\text{RhH}_2\text{Cl}(\text{PCy}_3)_2$  and  $\text{RhH}_2(\text{BH}_4)(\text{PCy}_3)_2$  is also described.

The E.P.R. spectra of  $\text{RhXY}(\text{PCy}_3)_2$  and of  $\text{RhCl}_2(\text{P}(\text{o-Tol})_3)_2$  ( $\text{o-Tol} = \text{ortho-tolyl}$ ) 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 ( $\text{PCy}_3$ ) forms paramagnetic complexes  $\text{RhX}_2(\text{PCy}_3)_2$  by reduction of  $\text{RhX}_3 \cdot 3\text{H}_2\text{O}$  ( $X = \text{Cl}, \text{Br}$ ) [1]. Among the other reported Rh(II) phosphine complexes only  $\text{RhCl}_2\text{-P}(\text{o-Tol})_3)_2$  [2] has a well-defined composition; other compounds, e.g.  $\text{RhCl}_2(\text{P}(\text{o-Tol})_2\text{Ph})_2$  [2] and  $\text{RhCl}_2(\text{P}(\text{t-Bu})_2\text{R})_2$  ( $\text{R} = \text{Me}, \text{Et}, \text{Pr}$ ) 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  $\text{o-tolyl}$  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  $\text{Rh-PCy}_3$  complexes to the oxidation of  $\text{RhCl}(\text{PCy}_3)_2$  [9] and related complexes. Halogens, hydrogen halides and methyl iodide 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  $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$  with  $\text{PCy}_3$  and  $\text{HX}$  in  $\text{CH}_2\text{Cl}_2$  was reported by Betts *et al.* [10] but they did not obtain well-defined products.

### Experimental

$^1\text{H}$  and  $^{31}\text{P}$  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  $\text{cm}^{-1}$ ) and a Hitachi EPI-L (700–200  $\text{cm}^{-1}$ ) 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, Mikro-analytisches Laboratorium, Elbach über Engelskirchen, Germany. Analytical data are given in Table I.

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

#### $\text{RhH}_2\text{Cl}(\text{PCy}_3)_2$ and $\text{RhD}_2\text{Cl}(\text{PCy}_3)_2$

$\text{H}_2$  or  $\text{D}_2$  is bubbled through a solution of  $\text{RhCl}(\text{PCy}_3)_2$  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.

#### $\text{RhClX}(\text{PCy}_3)_2$ ( $X = \text{Cl}, \text{Br}, \text{I}$ )<sup>†</sup>, $\text{RhBr}_2(\text{PCy}_3)_2$

A slight excess of halogen  $\text{X}_2$  (0.15–0.30 mmol), dissolved in benzene, is added to a solution of 0.30 mmol  $\text{RhCl}(\text{PCy}_3)_2$  in 10 ml benzene. After being

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<sup>†</sup> The mixed halogen compounds were impure due to scrambling of the halogens.

TABLE I. Analytical Results.

| Compound                                                                            | %C             | %H             | %Cl          | Others            | Mol. Weight <sup>a</sup> |
|-------------------------------------------------------------------------------------|----------------|----------------|--------------|-------------------|--------------------------|
| RhH <sub>2</sub> Cl(PCy <sub>3</sub> ) <sub>2</sub>                                 | 62.4<br>(61.7) | 9.8<br>(9.8)   |              |                   |                          |
| RhClX(PCy <sub>3</sub> ) <sub>2</sub> (X = Cl, Br)                                  | 55.2           | 8.3            |              |                   |                          |
| theoretical for X = Br                                                              | (55.5)         | (8.5)          |              |                   |                          |
| RhClX(PCy <sub>3</sub> ) <sub>2</sub> (X = Cl, I)                                   | 53.9           | 8.4            |              |                   |                          |
| theoretical for X = I                                                               | (52.4)         | (8.0)          |              |                   |                          |
| RhHCl <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub>                                 | 58.7<br>(58.9) | 9.3<br>(8.9)   | 9.5<br>(9.7) | 8.3(P)<br>(8.4)   | 725<br>(733)             |
| RhDCl <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub>                                 | 58.6<br>(58.9) | 9.3<br>(8.9)   |              |                   |                          |
| RhHBr <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub>                                 | 53.5<br>(52.6) | 8.5<br>(8.0)   |              |                   |                          |
| RhHXY(PCy <sub>3</sub> ) <sub>2</sub> (X, Y = Cl, Br)                               | 55.5           | 8.5            |              |                   |                          |
| theoretical for XY = ClBr                                                           | (55.5)         | (8.5)          |              |                   |                          |
| RhHClX(PCy <sub>3</sub> ) <sub>2</sub> (X = Cl, I)                                  | 54.4           | 8.6            |              |                   |                          |
| theoretical for X = I                                                               | (52.4)         | (8.0)          |              |                   |                          |
| RhHCl <sub>2</sub> (py)(PCy <sub>3</sub> ) <sub>2</sub>                             | 61.3<br>(60.6) | 8.9<br>(8.7)   |              | 1.6(N)<br>(1.7)   |                          |
| RhMeClI(PCy <sub>3</sub> ) <sub>2</sub>                                             | 53.3<br>(53.8) | 8.7<br>(8.3)   | 4.1<br>(4.2) | 14.6(I)<br>(15.1) | 851<br>(839)             |
| RhMeI <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub> · C <sub>6</sub> H <sub>6</sub> | 51.7<br>(51.1) | 7.9<br>(7.5)   |              | 24.1(I)<br>(25.0) |                          |
| RhH <sub>2</sub> (BH <sub>4</sub> )(PCy <sub>3</sub> ) <sub>2</sub>                 | 62.6<br>(63.5) | 10.5<br>(10.7) |              |                   |                          |

<sup>a</sup>Osmometric in benzene.

stirred for a few minutes, the precipitate is filtered off, washed with benzene and ethanol, and dried under vacuum. RhBr<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> is similarly prepared from RhBr(PCy<sub>3</sub>)<sub>2</sub>, but RhI<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> could not be obtained from RhI(PCy<sub>3</sub>)<sub>2</sub> and I<sub>2</sub>.

*RhHClX(PCy<sub>3</sub>)<sub>2</sub> (X = Cl, Br, I)\*, RhHBr<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>, RhDCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>*

A freshly prepared solution of HX in acetone is added to a suspension of 0.30 mmol RhCl(PCy<sub>3</sub>)<sub>2</sub> 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<sub>2</sub>Cl(PCy<sub>3</sub>)<sub>2</sub> with X<sub>2</sub> or HX in benzene or acetone. RhHBr<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> is prepared similarly from RhBr(PCy<sub>3</sub>)<sub>2</sub>. The deuterated complex RhDCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> is prepared with DCl in acetone-d<sub>6</sub>; it can also be isolated as a side-product to RhCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> (see ref. 1) from the reaction of RhCl<sub>3</sub> · 3H<sub>2</sub>O and PCy<sub>3</sub> in a D<sub>2</sub>O–C<sub>2</sub>H<sub>5</sub>OD mixture. The compounds are moderately soluble in benzene, and decompose in chlorinated solvents. RhHCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> has to be stored in the dark; under the influence of light it converts slowly into RhCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>.

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

*RhHCl<sub>2</sub>(py)(PCy<sub>3</sub>)<sub>2</sub>*

A few drops of pyridine are added to a suspension of RhHCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> 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<sub>3</sub>)<sub>2</sub>, Rh(CD<sub>3</sub>)ClI(PCy<sub>3</sub>)<sub>2</sub>*

A slight excess of CH<sub>3</sub>I or CD<sub>3</sub>I is added to a suspension of RhCl(PCy<sub>3</sub>)<sub>2</sub> in hexane. After stirring for 1 1/2 hours, the precipitate is filtered off, washed with hexane and dried under vacuum.

*RhMeI<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>, Rh(CD<sub>3</sub>)I<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>*

A slight excess of CH<sub>3</sub>I or CD<sub>3</sub>I is added to a benzene solution of RhCl(PCy<sub>3</sub>)<sub>2</sub>. 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<sub>2</sub>(BH<sub>4</sub>)(PCy<sub>3</sub>)<sub>2</sub>*

4.0 mmol NaBH<sub>4</sub> is added to a benzene solution of 0.30 mmol RhCl(PCy<sub>3</sub>)<sub>2</sub>. The mixture is stirred for three hours, and ethanol is added. The precipitate is filtered off, washed with ethanol and dried under vacuum.

TABLE II. NMR Data of Complexes. Solvent  $\text{C}_6\text{D}_6$ , Ambient Temperature. Chemical Shifts in ppm, coupling Constants in Hz.  $\delta$  Relative to Trimethylphosphate.

| Compound                                    | $^1\text{H}$ NMR <sup>a</sup>   |                           |                          | $^{31}\text{P}$ NMR <sup>b</sup> |                           |                          |
|---------------------------------------------|---------------------------------|---------------------------|--------------------------|----------------------------------|---------------------------|--------------------------|
|                                             | $\tau$                          | $^1J(\text{Rh}-\text{H})$ | $^2J(\text{P}-\text{H})$ | $\delta$                         | $^1J(\text{Rh}-\text{P})$ | $^2J(\text{H}-\text{P})$ |
| $\text{RhH}_2\text{Cl}(\text{PCy}_3)_2$     | 32.7                            | 27                        | 14                       | -47.2                            | 113.7                     | 12                       |
| $\text{RhHCl}_2(\text{PCy}_3)_2$            | not found                       |                           |                          | -32.0                            | 96.2                      |                          |
| $\text{RhH}_2(\text{BH}_4)(\text{PCy}_3)_2$ | 26.7<br>10-17(BH <sub>4</sub> ) | 15 <sup>c</sup>           | 15 <sup>c</sup>          | -52.1                            | 108.3                     | 14                       |

<sup>a</sup> Broad signal 7-9 ppm for  $\text{PCy}_3$  protons.<sup>b</sup> Partial  $^1\text{H}$ -decoupled.<sup>c</sup>  $\text{BH}_4$ -decoupled.

## Results and Discussion

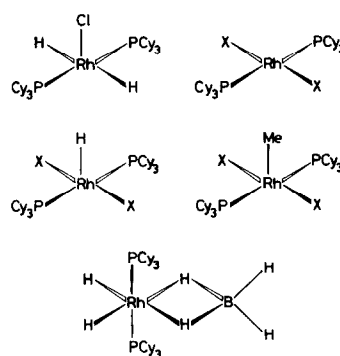
$\text{PCy}_3$  along with  $\text{P}(o\text{-Tol})_3$  and  $\text{P}(t\text{-Bu})_3$ , is one of the bulkiest phosphines used in coordination chemistry [12]. The steric properties of  $\text{PCy}_3$  are reflected in the chemical properties of its rhodium complexes.

$\text{RhCl}(\text{PCy}_3)_2$  is a very air-sensitive compound. It decomposes slowly under an inert atmosphere into  $\text{RhCl}_2$  and unidentified products. With nitrogen it forms the adduct  $\text{RhCl}(\text{PCy}_3)_2(\text{N}_2)$  [9]. These observations suggest its formulation as a monomeric three-coordinated  $\text{Rh}(\text{I})$  complex, where three-coordination is imposed by the bulkiness of  $\text{PCy}_3$  and by the obvious absence of suitable coordinating agents in the mother liquor.  $\text{RhBr}(\text{PCy}_3)_2$  and  $\text{RhI}(\text{PCy}_3)_2$  have similar properties [11].

The addition product of  $\text{RhCl}(\text{PCy}_3)_2$  with hydrogen has a normal stability. The two hydride hydrogens and the two phosphorus atoms are equivalent in the  $^1\text{H}$  and  $^{31}\text{P}$  NMR respectively (Table II) and the compound shows two  $\text{Rh}-\text{H}$  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).

### Rhodium(II) Complexes

The oxidative addition of halogens to  $\text{RhX}(\text{PCy}_3)_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) does not yield  $\text{Rh}(\text{III})$  complexes, but the paramagnetic  $\text{RhXY}(\text{PCy}_3)_2$  ( $\text{X} = \text{Cl}, \text{Y} = \text{Cl}, \text{Br}, \text{I}; \text{X} = \text{Y} = \text{Br}$ ).  $\text{RhCl}_2(\text{PCy}_3)_2$  and  $\text{RhBr}_2(\text{PCy}_3)_2$  have previously been prepared by reduction of  $\text{RhX}_3 \cdot 3\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) [1]. This route of oxidation of  $\text{Rh}(\text{I})$  complexes has also made possible the preparation of the compounds  $\text{RhClBr}(\text{PCy}_3)_2$  and  $\text{RhClI}(\text{PCy}_3)_2$ , 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  $\text{RhClBr}(\text{PCy}_3)_2$  and  $\text{RhClI}(\text{PCy}_3)_2$  have been characterised mainly by E.P.R. and IR data. In the reaction of  $\text{RhCl}(\text{PCy}_3)_2$  with  $\text{Br}_2$  and  $\text{I}_2$  some tendency to form preferentially  $\text{RhCl}_2(\text{PCy}_3)_2$

Fig. 1. Proposed structure of complexes.  $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ .

has been noted. We were unable to obtain evidence for the existence of  $\text{RhI}_2(\text{PCy}_3)_2$ .

The rhodium(II) complexes are assigned a square planar transstructure (Fig. 1) on the basis of the high  $\text{Rh}-\text{X}$  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  $\text{RhCl}_2(\text{P}(o\text{-Tol})_3)_2$  (blue modification) [2] has been incompletely reported and we have remeasured its spectrum, which is also given in Table IV. The magnetic susceptibilities of  $\text{RhCl}_2(\text{PCy}_3)_2$  and  $\text{RhBr}_2(\text{PCy}_3)_2$  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  $\text{Rh}(\text{II})$  complexes have no catalytic activity [4].  $\text{RhCl}(\text{PCy}_3)_2$ , itself a hydrogenation catalyst [9], decomposes slowly into  $\text{RhCl}_2(\text{PCy}_3)_2$ . 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,  $\text{cm}^{-1}$ .

| Compound                                             | Color   | $\nu(\text{Rh-H/D})$                        | $\delta(\text{Rh-H/D})$ | $\nu(\text{Rh-Cl})$ | Others                                                                                                |
|------------------------------------------------------|---------|---------------------------------------------|-------------------------|---------------------|-------------------------------------------------------------------------------------------------------|
| $\text{RhH}_2\text{Cl}(\text{PCy}_3)_2$              | Yellow  | 2165sh<br>2120m                             | 622m, br                | 291m                |                                                                                                       |
| $\text{RhD}_2\text{Cl}(\text{PCy}_3)_2$              | Yellow  | 1560sh<br>1528m                             | not found               | 291m                |                                                                                                       |
| $\text{RhCl}_2(\text{PCy}_3)_2$                      | Blue    |                                             |                         | 354s                |                                                                                                       |
| $\text{RhClBr}(\text{PCy}_3)_2$                      | Green   |                                             |                         | 335s                | 271m ( $\nu\text{RhBr}$ )                                                                             |
| $\text{RhBr}_2(\text{PCy}_3)_2$                      | Green   |                                             |                         |                     | 288m ( $\nu\text{RhBr}$ )                                                                             |
| $\text{RhClI}(\text{PCy}_3)_2$                       | Brown   |                                             |                         | 325s                |                                                                                                       |
| $\text{RhHCl}_2(\text{PCy}_3)_2$                     | Orange  | not found                                   | 587s, br                | 342s                |                                                                                                       |
| $\text{RhDCl}_2(\text{PCy}_3)_2$                     | Orange  | not found                                   | 350s<br>335s            | { 350s<br>335s }    |                                                                                                       |
| $\text{RhHClBr}(\text{PCy}_3)_2$                     | Orange  | not found                                   | 580s, br                | 330s                | 280m ( $\nu\text{RhBr}$ )                                                                             |
| $\text{RhHBr}_2(\text{PCy}_3)_2$                     | Orange  | not found                                   | 580s, br                |                     | 268m ( $\nu\text{RhBr}$ )                                                                             |
| $\text{RhHClI}(\text{PCy}_3)_2$                      | Red     | not found                                   | 597s, br                | 320s                |                                                                                                       |
| $\text{RhHCl}_2(\text{py})(\text{PCy}_3)_2$          | Ochrous | 2135m                                       | not found               | 323s                |                                                                                                       |
| $\text{RhMeClI}(\text{PCy}_3)_2$                     | Brown   |                                             |                         | 333s                | 1311w, 1167sh<br>325m ( $\nu\text{RhC}$ ) <sup>a</sup>                                                |
| $\text{Rh}(\text{CD})_3\text{ClI}(\text{PCy}_3)_2$   | Brown   |                                             |                         | 333s                | 2120m, 2215m ( $\nu\text{CD}$ )<br>755m, ( $\delta\text{CD}$ ), 325m ( $\nu\text{RhC}$ ) <sup>a</sup> |
| $\text{RhMeI}_2(\text{PCy}_3)_2$                     | Brown   |                                             |                         |                     | 1167m<br>325m ( $\nu\text{RhC}$ ) <sup>a</sup>                                                        |
| $\text{Rh}(\text{CD}_3)_2\text{I}_2(\text{PCy}_3)_2$ | Brown   |                                             |                         |                     | 2120m, 2215m ( $\nu\text{CD}$ )<br>325m ( $\nu\text{RhC}$ ) <sup>a</sup>                              |
| $\text{RhH}_2(\text{BH}_4)(\text{PCy}_3)_2$          | White   | 2102m<br>2068m<br>1926m, br (bridging RhHB) |                         |                     | 2450m, br, 2400s, br<br>2328sh ( $\nu\text{BH}$ )                                                     |

<sup>a</sup>Tentative assignment.TABLE IV. Experimental g-Values and Calculated Coefficients and Energy Differences.  $\lambda(\text{Rh(II)}) = 1235 \text{ cm}^{-1}$  [30].

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

<sup>a</sup>At  $-180^\circ\text{C}$  other values at room temperature. <sup>b</sup>Broad spectrum, approximate g-values.

*Hydrido-Rhodium(III) Complexes*

The reaction of  $\text{RhCl}(\text{PCy}_3)_2$  with halogenic acids  $\text{HX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) results in the formation of compounds  $\text{RhHClX}(\text{PCy}_3)_2$ . Here too, halogen scrambling has been observed. The same products have been obtained from the reaction of  $\text{RhH}_2\text{Cl}(\text{PCy}_3)_2$  with  $\text{HX}$  or  $\text{X}_2$ . From  $\text{RhBr}(\text{PCy}_3)_2$  and  $\text{HBr}$ ,  $\text{RhHBr}_2(\text{PCy}_3)_2$  has also been prepared.

The mono-hydride complexes show no  $(\text{Rh}-\text{H})$  stretching vibration band around  $2000\text{ cm}^{-1}$ , nor in the PMR spectrum a high field hydride resonance, nor in the partially decoupled  $^{31}\text{P}$  NMR spectrum a  $^2\text{J}(\text{P}-\text{H})$  coupling. This is in accord with the properties of  $\text{RhHCl}_2(\text{P}(\text{i-Pr})_3)_2$  [13], where also no  $\text{Rh}-\text{H}$  stretching vibration band nor a hydride NMR resonance could be detected, but it is in contrast with the data reported for  $\text{RhHCl}_2(\text{P}(\text{t-Bu})_2\text{R})_2$  [3], which has  $\nu(\text{Rh}-\text{H})$  at  $1938\text{ cm}^{-1}$ , unassigned infrared bands between  $570-620\text{ cm}^{-1}$  and a hydride NMR resonance at  $\tau = 41.4$ . The presence of a hydride ligand in our compounds was proven by the reaction with  $\text{CCl}_4$ , resulting in the formation of chloroform, and by a medium-strong infrared absorption at *ca.*  $580\text{ cm}^{-1}$ , which we have attributed to a  $(\text{Rh}-\text{H})$  bending vibration (Table III). In the deuterated complex  $\text{RhDCl}_2(\text{PCy}_3)_2$  this absorption is absent; the corresponding  $\delta(\text{Rh}-\text{D})$ , expected at *ca.*  $400\text{ cm}^{-1}$ , is obscured by phosphine vibrations. However, the second  $\delta(\text{Rh}-\text{D})$  comes near the  $\nu(\text{Rh}-\text{Cl})$  vibration at  $342\text{ cm}^{-1}$  and couples strongly with this vibration, which results in two absorptions at  $350$  and  $335\text{ cm}^{-1}$ . It has been checked with the aid of tabulated G-matrix elements [14] and with the assumption of degenerate  $\nu(\text{Rh}-\text{Cl})$  and  $\delta(\text{Rh}-\text{D})$  vibrations that the observed splitting of  $15\text{ cm}^{-1}$  is of the right magnitude. The corresponding  $\delta(\text{Rh}-\text{H})$  is expected at *ca.*  $480\text{ cm}^{-1}$ , but is obscured by phosphine absorptions. The  $\delta(\text{Rh}-\text{H})$  value of  $580\text{ cm}^{-1}$  is the lowest hitherto reported (*cf.* ref. 15). The unassigned bands between  $570-620\text{ cm}^{-1}$  reported for  $\text{RhCl}_2(\text{P}(\text{t-Bu})_2\text{R})_2$  [3] may also be such low-lying  $\delta(\text{Rh}-\text{H})$  vibration frequencies.

The high position of  $\nu(\text{Rh}-\text{X})$  in these compounds and the doublet in the  $^{31}\text{P}$  NMR spectrum of  $\text{RhHCl}_2(\text{PCy}_3)_2$  (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  $\text{RhHCl}_2(\text{P}(\text{t-Bu})\text{Pr}_2)_2$  [3].

*Relationship Between  $\text{RhCl}_2(\text{PCy}_3)_2$  and  $\text{RhHCl}_2(\text{PCy}_3)_2$* 

$\text{RhHCl}_2(\text{PCy}_3)_2$  is converted by light into  $\text{RhCl}_2(\text{PCy}_3)_2$ , and the former has to be stored in the dark to avoid contamination by the latter. Conversely, the  $\text{Rh}(\text{II})$  complexes  $\text{RhClX}(\text{PCy}_3)_2$  are often contaminated by the corresponding  $\text{Rh}(\text{III})$  hydrido compounds, but some purification can be accomplished

by washing the insoluble  $\text{Rh}(\text{II})$  complexes with benzene.

During the reduction of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with  $\text{PCy}_3$  the initially formed product is  $\text{RhCl}_2(\text{PCy}_3)_2$ , contaminated with some  $\text{RhHCl}_2(\text{PCy}_3)_2$ ; and when the reaction proceeds, relatively more of the latter is formed. We observed that the  $\text{Rh}(\text{II})$  and  $\text{Rh}(\text{III})$  complexes are formed less contaminated the one with the other, when the method of oxidation of  $\text{RhCl}(\text{PCy}_3)_2$  is used.

*Reactions of  $\text{RhHCl}_2(\text{PCy}_3)_2$* 

Some reactions of  $\text{RhHCl}_2(\text{PCy}_3)_2$  have been studied.  $\text{CO}$  adds reversibly to  $\text{RhHCl}_2(\text{PCy}_3)_2$ , presumably with formation of  $\text{RhHCl}_2(\text{CO})(\text{PCy}_3)_2$  (in benzene  $\nu(\text{Rh}-\text{H})$  at  $2100$  and  $\nu(\text{CO})$  at  $2020\text{ cm}^{-1}$ ) and of a non-identified compound with an absorption at  $2070\text{ cm}^{-1}$ . Upon prolonged treatment with  $\text{CO}$ ,  $\text{RhCl}(\text{CO})(\text{PCy}_3)_2$  is formed by elimination of  $\text{HCl}$ .  $\text{RhCl}(\text{CO})(\text{PCy}_3)_2$  itself forms with  $\text{HCl}$  only traces of  $\text{RhHCl}_2(\text{CO})(\text{PCy}_3)_2$  which has  $\nu(\text{Rh}-\text{H})$  at  $2060$  and  $\nu(\text{CO})$  at  $2000\text{ cm}^{-1}$  [16]. This suggests that with the different procedures isomers of  $\text{RhHCl}_2(\text{CO})(\text{PCy}_3)_2$  are formed, which have  $\text{CO}$  and  $\text{HCl}$  respectively as labile groups.

The reaction of acetylene,  $\text{C}_2\text{H}_2$ , with  $\text{RhHCl}_2(\text{PCy}_3)_2$  is very slow, and even after 3 days only traces of the vinyl product  $\text{Rh}(\text{CH}=\text{CH}_2)\text{Cl}_2(\text{PCy}_3)_2$  ( $\nu(\text{C}=\text{C})$  at  $1555\text{ cm}^{-1}$ ) could be isolated. With pyridine, a fast and complete conversion could be achieved into the coordinatively saturated 18-electron complex  $\text{RhHCl}_2(\text{py})(\text{PCy}_3)_2$ , for which a  $\text{Rh}-\text{H}$  stretching vibration frequency could be detected at  $2135\text{ cm}^{-1}$ . This observation can be considered as an additional proof for the presence of a hydride ligand in the starting complex  $\text{RhHCl}_2(\text{PCy}_3)_2$ .

*Reaction of  $\text{RhCl}(\text{PCy}_3)_2$  with  $\text{MeI}$  and with  $\text{NaBH}_4$* 

The easy formation of  $\text{Rh}(\text{II})$  complexes in the oxidation of  $\text{RhCl}(\text{PCy}_3)_2$  with halogens was a motive to investigate whether in the reaction with methyl-iodide  $\text{Rh}(\text{II})$  complexes could be formed in a substantial amount. The reaction, when carried out in benzene, is very fast and  $\text{RhMeI}_2(\text{PCy}_3)_2$  is formed. No  $\text{Rh}(\text{II})$  could be detected with E.P.R. in the isolated product. The reaction of  $\text{MeI}$  with a suspension of  $\text{RhCl}(\text{PCy}_3)_2$  in hexane is slow and yields  $\text{RhMeClI}(\text{PCy}_3)_2$ . Here too, no  $\text{Rh}(\text{II})$  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  $\text{CD}_3\text{I}$ . The proposed structure of the complexes  $\text{RhMeXI}(\text{PCy}_3)_2$  ( $\text{X} = \text{Cl}, \text{I}$ ) is square pyramidal with an axial  $\text{Me}$ , *trans*-phosphines and *trans*-halogens (Fig. 1).

The recent paper on  $\text{RhH}_2(\text{BH}_4)(\text{P}^t\text{Bu}_2\text{Me})_2$  [17] prompts us to report the synthesis of  $\text{RhH}_2(\text{BH}_4)(\text{PCy}_3)_2$  from  $\text{RhCl}(\text{PCy}_3)_2$  and an excess of

$\text{NaBH}_4$ . The compound shows in the infrared  $\nu(\text{B}-\text{H})$  near 2400,  $\nu(\text{Rh}-\text{H})$  near 2100 and  $\nu(\text{Rh}-\text{H}-\text{B})$  at 1925  $\text{cm}^{-1}$ . In the PMR spectrum, the  $\text{BH}_4$  protons are dynamically equivalent and appear as a broad resonance centered at  $\tau = 13$  ppm at room temperature. The  $^1\text{J}(\text{Rh}-\text{H})$  of 15 Hz for the terminal hydrides is indicative of an octahedral structure, so we think  $\text{BH}_4$  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  $\text{RhCl}_3(\text{PR}_3)_3$  or  $\text{RhHCl}_2(\text{PR}_3)_3$ . It then causes the formation of a Rh(II) complex or of a five-coordinated mono-hydride  $\text{RhHCl}_2(\text{PR}_3)_2$ . Discussing the existence of  $\text{RhCl}_2(\text{PR}_3)_2$  then is discussing the non-existence of  $\text{RhCl}_3(\text{PR}_3)_2$  and the relative stability of  $\text{RhCl}(\text{PR}_3)_2$ ,  $\text{RhCl}_2(\text{PR}_3)_2$  and  $\text{RhHCl}_2(\text{PR}_3)_2$ . 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  $\text{RhCl}_3(\text{PR}_3)_2$  and (ii) steric effects decide about the formation of  $\text{RhCl}_2(\text{PR}_3)_2$  or  $\text{RhHCl}_2(\text{PR}_3)_2$ .

(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:  $[\text{RhCl}_2(\text{PR}_3)_2]^-$  (*n.e.*) [18] <  $[\text{RhCl}(\text{PR}_3)_2]_2$  [19] <  $\text{RhCl}(\text{PR}_3)_3$  [19] <  $\text{RhCl}(\text{PR}_3)_2$  [9] <  $\text{RhCl}_2(\text{PR}_3)_2 \sim [\text{RhCl}_4(\text{PR}_3)_2]^-$  [18] <  $\text{RhCl}_3(\text{PR}_3)_3$  [20] <  $\text{RhCl}_3(\text{PR}_3)_2$  (*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  $\text{RhCl}_3(\text{PR}_3)_2$  fragment that this charge should obviously be compensated by the coordination of at least one additional donor ligand. The instability of  $\text{RhCl}(\text{PCy}_3)_2$  has been discussed elsewhere [11]. The stability of  $\text{RhCl}_2(\text{PCy}_3)_2$  in a reduction of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with  $\text{PR}_3$  or in an oxidation of  $\text{RhCl}(\text{PR}_3)_2$  with  $\text{Cl}_2$ , as well as the stability of the Rh(II) complexes towards disproportionation:  $2\text{RhCl}_2(\text{PR}_3)_2 =$

$\text{RhCl}(\text{PR}_3)_2 + \text{RhCl}_3(\text{PR}_3)_2$  must then be considered to be of thermodynamic origin, caused by the high energy of the Rh(I) and Rh(III) compounds. That  $\text{RhHCl}_2(\text{PR}_3)_2$  does exist as a five-coordinate  $d^6$  complex but  $\text{RhCl}_3(\text{PR}_3)_2$  does not, may be ascribed to the lower electronegativity of the hydrogen compared with the chlorine ligand.

(ii) Preference of  $\text{RhHCl}_2(\text{PR}_3)_2$  over  $\text{RhHCl}_2(\text{PR}_3)_3$  seems to be governed largely by steric effects, e.g. small phosphines form the tris-complex [20], and more bulky phosphines, like  $\text{P}(\text{t-Bu})\text{R}_2$  [3], the bis-complex.  $\text{PPh}_3$  and  $\text{P}(\text{i-Pr})_3$  have an intermediate position, for these ligands  $\text{RhHCl}_2(\text{PR}_3)_2$  as well as  $\text{RhHCl}_2(\text{PR}_3)_3$  have been reported [13, 21]. With the most bulky phosphines, e.g.  $\text{P}^t\text{Bu}_2\text{R}$ ,  $\text{PCy}_3$  and  $\text{P}(\text{o-Tol})_3$ ,  $\text{RhCl}_2(\text{PR}_3)_2$  is preferred over  $\text{RhHCl}_2(\text{PR}_3)_2$ ; 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

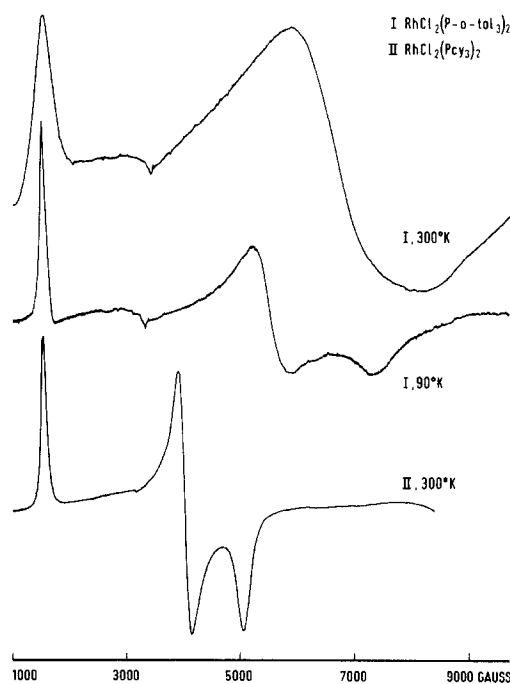


Fig. 2. The X-band E.P.R. powder spectra of  $\text{RhCl}_2(\text{PR}_3)_2$ , R = Cyclohexyl, *o*-Tolyl.

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.

The large anisotropy of the  $g$ -tensor requires a strong mixing of two or more states. We represent two states  $|d_1\rangle$  and  $|d_2\rangle$  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:

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

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  $\psi$  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).

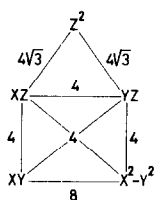


Fig. 3. Value of  $m$  as function of the orbital pair (see text).

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-

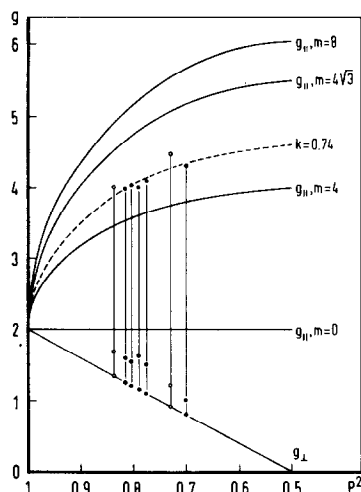


Fig. 4.  $g_{\parallel}$  and  $g_{\perp}$  as functions of orbital coefficient  $p$ , and experimental  $g$ -values ( $\circ$  at  $-180^\circ\text{C}$ ;  $\bullet$  at room temperature).

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  $\text{Rh(II)}$  complexes; *ca.* 80%  $|d_{z^2}\rangle + 20\% |d_{xz}\rangle$  and *ca.* 80%  $|d_{xz}\rangle + 20\% |d_{z^2}\rangle$ . Such ground states are found for some four-coordinated  $\text{Co(II)}$  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  $\text{Rh(II)}$  complexes in a preceding section of this paper. Because a square planar *trans*-structure implies  $D_{2h}$  as the approximate symmetry of the molecules  $\text{RhX}_2(\text{PR}_3)_2$ , 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  $\text{Co(II)}$  complexes [27, 28].

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  $|d_{z^2}\rangle$ ) or  $b$  (ground state  $|d_{xz}\rangle$ ) 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  $|d_{z^2}\rangle$  ( $d_{xy}$  does not normally mix with  $d_{z^2}$  by spin-orbit coupling) and  $d_{xy}$  for the ground state  $|d_{xz}\rangle$  (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).  $|\pm\rangle = a|d_{z^2}\rangle \pm b|d_{xz}\rangle + ic|d_{yz}\rangle \pm id|d_{xy}\rangle$ ;  $d_{x^2-y^2}$  Empty.

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

the  $|d_{z^2}\rangle$  ground state by putting  $d = 0$ , and  $a, b$  and  $d$  for the  $|d_{xz}\rangle$  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  $\Delta E_{xz-z^2}$  and  $\Delta E_{yz-z^2}$  or  $\Delta E_{xy-xz}$  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%  $|d_{z^2}\rangle$ , 20%  $|d_{xz}\rangle$  and 1%  $|d_{yz}\rangle$ , and a mixture of approximately 80%  $|d_{xz}\rangle$ , 20%  $|d_{z^2}\rangle$  and 1%  $|d_{xy}\rangle$ . 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  $\Delta E_{yz-z^2}$  and  $\Delta E_{xy-xz}$  is in agreement with expectations for the  $PCy_3$  series, based on the spectrochemical series:  $ClI \sim Br_2 < ClBr < Cl_2$ . However, there is no agreement with the expected order  $RhCl_2(PCy_3)_2 < RhCl_2(P(o-Tol)_3)_2$ .

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  $\pi$ -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]).

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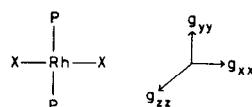


Fig. 5. Magnetic coordinate axis with respect to the molecular axis.

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