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TRICYCLOHEXYLPHOSPHINE COMPLEXES OF RHODIUM(I), RHODIUM(II), IRIDIUM(I) AND IRIDIUM(II)

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Abstract—The preparation of iridium and rhodium complexes with tricyclohexylphosphine (PCy_3) is reported. Paramagnetic rhodium(II) complexes of the type $\text{RhX}_2(\text{PCy}_3)_2$ with $\text{X}=\text{Cl}$ or Br were prepared. The reaction between iridium salts with PCy_3 in propanol-2 resulted in diamagnetic complexes with iridium halogenide ratio 1:2. The possible structures of these compounds are discussed. Complexes of the type $\text{MCl}(\text{CO})(\text{PCy}_3)_2$ with $\text{M}=\text{Rh}$ or Ir and $\text{IrHCl}_2(\text{CO})(\text{PCy}_3)_2$ are described and characterized.

INTRODUCTION

IN PREVIOUS communications we described the preparation of stable complexes of tricyclohexylphosphine with copper(I), ruthenium(II) and osmium(II) [1–3]. The copper complexes with this ligand have a different structure in comparison to other copper phosphine complexes. The hydrido carbonyl complexes of osmium and ruthenium with the formula $\text{MHCl}(\text{CO})(\text{PCy}_3)_2$ show a hydrogen deuterium exchange of the cyclohexyl groups of the phosphine. Different behaviour of these complexes with PCy_3 as ligand in comparison with other phosphine complexes may be due to the steric hindrance of the bulky cyclohexyl groups [1, 4] and to the strongly basic nature of this ligand [5]. The reaction of rhodium and iridium halide compounds with substituted phosphine in alcohols or benzene give products with various compositions. Complexes with the formula, e.g. $\text{MX}_3(\text{P}(\text{C}_2\text{H}_5)_3)_3$ with $\text{M}=\text{Rh}$ or Ir and $\text{X}=\text{Cl}$ or Br [6, 7], $\text{RhCl}_2(\text{P}(o\text{-CH}_3\text{C}_6\text{H}_4)_3)_2$ [8], $\text{RhCl}_2(\text{P}(t\text{-C}_4\text{H}_9)_2\text{C}_2\text{H}_5)_2$ [9], and $\text{IrHCl}_2(\text{PPh}_3)_3$ and $\text{IrHCl}_2(\text{PPh}_3)_2$ [10] have been obtained.

The present study describes rhodium and iridium complexes with the general formula $\text{MX}_2(\text{PCy}_3)_2$, $\text{MCl}(\text{CO})(\text{PCy}_3)_2$ and $\text{MHCl}_2(\text{CO})(\text{PCy}_3)_2$ with $\text{X}=\text{Cl}$, Br and $\text{M}=\text{Rh}$ or Ir .

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2. F. G. Moers, *Chem. Comm.* **2**, 79 (1971).
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EXPERIMENTAL

Preparation of tricyclohexylphosphine

The ligand was prepared as described by Issleib *et al.* [11].

Rhodium and iridium salts

All the platinum metal halides were commercially available from Fa. Drijfhout.

Preparation of the complexes $RhX_2(PCy_3)_2$ with $X=Cl$ or Br

A solution of 1 mmole $RhX_3 \cdot 3H_2O$ in propanol-2 was added with stirring to a solution of 5 m-mole PCy_3 in 50 ml propanol-2 in an atmosphere of nitrogen at 25°C for 48 hr. The precipitate was filtered, washed with water and propanol-2 and dried in vacuum over P_2O_5 .

The complexes $IrX_2(PCy_3)_2$ were prepared on a similar way by reaction of an aqueous solution of Na_3IrX_6 , PCy_3 and propanol-2 for 24 hr at 70°C.

Preparation of the pyridine complex $IrCl_2(PCy_3)_2(py)$

The pyridine adduct was prepared by addition of an excess pyridine with stirring to a solution of $IrCl_2(PCy_3)_2$ in chloroform under a nitrogen atmosphere. The mixture was stirred for 12 hr at room temperature. The yellow precipitate was filtered, washed with propanol-2 and dried in a high vacuum.

Preparation of the complex $IrCl(CO)(PCy_3)_2$

Carbon monoxide was passed through a boiling solution of K_3IrCl_6 in diethleneglycol for 2 hr with continuous stirring. After cooling to 70°C an ethanolic solution of 4 m-mole PCy_3 was added. The black precipitate was extracted with a toluene-chloroform mixture, and yellow needles were formed on cooling the solution.

Preparation of the complex $RhCl(CO)(PCy_3)_2$

After passing carbon monoxide through a boiling solution of 2 m-mole $RhCl_3 \cdot 3H_2O$ in ethanol for 30 min an ethanolic solution of 4 m-mole PCy_3 was added. The mixture was heated whilst stirring for about 15 min at 78°C. Recrystallization of the yellow precipitate was performed with chloroform-methanol mixture.

Preparation of the complexes $IrYCl_2(CO)(PCy_3)_2$ with $Y=H$ or D

Hydrogen- or deuteriumchloride was bubbled through a suspension of $IrCl(CO)(PCy_3)_2$ in ether for 2 hr. The white precipitate was filtered, washed with ethanol and dried in vacuum.

The complex $IrHCl_2(CO)(PCy_3)_2 \cdot CHCl_3$ was prepared by adding a concentrated solution of HCl in water to a saturated solution of $IrCl(CO)(PCy_3)_2$ in chloroform.

The DCl gas for preparation of the deuteriated complex was obtained as described by Lux [12].

Physical measurements

Magnetic susceptibilities were measured on a Gouy balance. A Perkin Elmer 257 spectrophotometer was used for obtaining spectral data in the range 4000–700 cm^{-1} , using the potassium bromide pellet technique. For the range 700–200 cm^{-1} a Hitachi EPI-L was used with solid samples in cesium-iodide. The 70 eV mass spectra were recorded on a Varian-Atlas SM-1B double focussing instrument under low resolution conditions. The sample, after being introduced into the mass spectrometer by a direct insertion system was heated to 180°C. Rapid heating and scanning was necessary in order to minimize thermal decomposition for $IrDCl_2(CO)(PCy_3)_2$. Nuclear magnetic resonance spectra were determined with a Varian HA-100 NMR spectrometer. The samples were prepared by dissolving them in deuterated chloroform.

RESULTS AND DISCUSSION

The new compounds dealt with in the present investigation are listed in Table 1 along with their colours and analytical data. The complexes with the formula $MX_2(PCy_3)_2$ with $M=Rh$ or Ir and $X=Cl$ or Br were formed by reaction of the

11. K. Issleib and A. Brack, *Z. anorg. allg. Chem.* **227**, 258 (1954).

12. H. Lux, *Anorganische-chemische Experimentierkunst*, 374 (1959).

Table 1. Analysis data of the complexes

Complex	Colour	C (%)	H (%)	X (%)	N (%)
RhCl ₂ (PCy ₃) ₂	red-brown	59.95 (58.85)	9.33 (9.06)	9.26 (9.65)	—
RhBr ₂ (PCy ₃) ₂	green	53.37 (52.50)	8.42 (8.08)	19.40 (19.40)	—
IrCl ₂ (PCy ₃) ₂	rose	52.23 (52.48)	7.94 (8.07)	8.34 (8.61)	—
IrBr ₂ (PCy ₃) ₂	brown	48.23 47.37	7.63 7.29		—
IrCl ₂ (PCy ₃) ₂ Py	yellow	54.02 (54.53)	8.28 (7.92)	7.91 (7.85)	1.49 (1.49)
IrCl(CO)(PCy ₃) ₂	yellow	54.34 (54.44)	8.13 (8.17)		—
RhCl(CO)(PCy ₃) ₂	yellow	60.84 (61.26)	8.88 (9.17)	5.52 (4.89)	—
IrHCl ₂ (CO)(PCy ₃) ₂	white	51.59 (52.10)	8.13 (7.80)	7.80 (8.30)	—
IrDCl ₂ (CO)(PCy ₃) ₂	white	52.74 (52.04)	7.74 (7.79)		—
IrHCl ₂ (CO)(PCy ₃) ₂ · CHCl ₃	white	46.38 (46.99)	7.02 (7.06)	17.94 (18.25)	—

Theoretical values are given in parentheses.

M(III) salts with PCy₃ in propanol-2. Only a few examples of this type of compound are known[8, 9]. This composition suggests that in these compounds the metal ion contains the divalent oxidation state with a d^7 -configuration. As should be expected for rhodium (II) compounds the RhCl₂(PCy₃)₂ and RhBr₂(PCy₃)₂ are paramagnetic with $\mu = 2.2$ – 2.3 B.M. between room temperature and 83°K, indicating one unpaired electron. The magnetic data are given in Table 2. The magnetic susceptibility measurements pointed out that in the temperature range from 83–293°K the Curie-Weiss law is followed. For the chloride compound a Weiss temperature of -39°K and for the bromide -24°K was found (Fig. 1).

The most important infrared absorption bands are given in Table 3. These compounds show no bands attributable to ν Rh-H or ν C=O. In the range 700–200 cm^{-1} the ν RH-Cl vibrations have been found at 355 cm^{-1} with a shoulder at 344 cm^{-1} and the ν Rh-Br at 287 and 268 cm^{-1} . These vibrations lie in the same region as for the corresponding planar palladium compounds. The ν Pd-Cl and ν Pd-Br are found at 350 cm^{-1} and 284,270 cm^{-1} respectively[13]. The presence of two metal halogen vibrations should be expected for *cis*-complexes[14] but since in general the ν M-X frequencies are considerably lower than the single ν M-X frequency for the corresponding *trans* isomer[15] and because of the steric hinderance of the bulky tricyclohexylphosphine, we believe that in these compounds the two halogen atoms are approach *trans* to each other.

13. Unpublished results.

14. F. G. Moers and J. P. Langhout, *Recl. Trav. Chim. Pays. Bas.* **89**, 1237 (1970).

15. D. M. Adams, *Metal-Ligand and Related Vibrations*. Edward Arnold, London (1967).

Table 2. Magnetic data after correction for diamagnetism according to Figgis and Lewis*

Compound	Temperature (°K)	Molar suscept. $\times 10^6$, (cgsu)	Magnetic moment (BM)
RhCl ₂ (PCy ₃) ₂	293.5	1877	2.24
	273	1929	2.20
	248	2121	2.22
	223	2313	2.24
	198	2539	2.20
	173	2854	2.21
	148	3308	2.23
	123	3779	2.22
	95	4878	2.29
RhBr ₂ (PCy ₃) ₂	294	1931	2.23
	263	2088	2.20
	233	2353	2.21
	203	2825	2.27
	173	3195	2.25
	143	3774	2.25
	113	4630	2.26
	83.5	5882	2.26

*I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part I, Vol 4, pp. 1778-1781. Interscience, New York (1963).

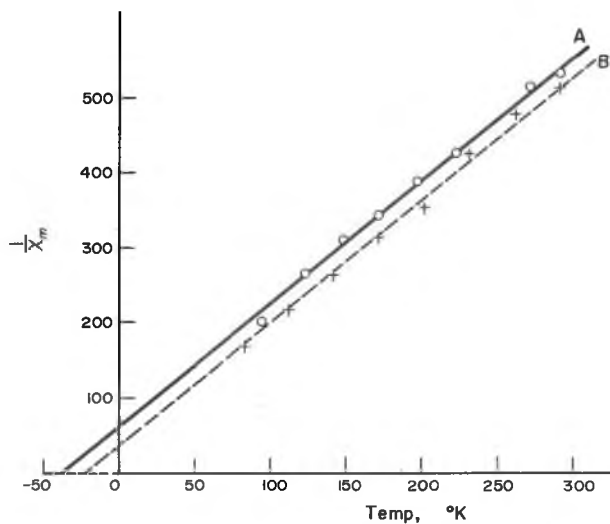


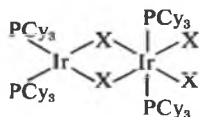
Fig. 1. Temperature dependence of $1/\chi_m$ for RhCl₂(PCy₃)₂ (A) and RhBr₂(PCy₃)₂ (B).

In contrast to the corresponding rhodium compounds the iridium complexes show diamagnetic behaviour, suggesting a low spin d^6 -configuration. This may be explained either by the presence of a hydride ion, resulting in the composition IrHX₂(PCy₃)₂, or formation of a metal carbon bond by splitting of a hydrogen atom of a cyclohexyl group. In the i.r. spectrum a ν Ir-H at about 2000 cm⁻¹ was

Table 3. The major infrared absorption bands (cm^{-1}) in the range 4000–200 cm^{-1}

Compounds	ν M-H or		
	ν CO	ν M-D	ν M-X
$\text{RhCl}_2(\text{PCy}_3)_2$	—	—	354(s), 343 ^{sh} (m)
$\text{RhBr}_2(\text{PCy}_3)_2$	—	—	288(m), 270 ^b (m)
$\text{IrCl}_2(\text{PCy}_3)_2$	—	—	317(s), 312 ^{sh} (m)
$\text{IrBr}_2(\text{PCy}_3)_2$	—	—	238 ^b (m)
$\text{IrCl}_2(\text{PCy}_3)_2(\text{py})$	—	—	303(s)
$\text{RhCl}(\text{CO})(\text{PCy}_3)_2$	1941(s)	—	305(s)
$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	1961(s)	—	315(s)
$\text{IrCl}(\text{CO})(\text{PCy}_3)_2$	1931(s)	—	309(s), 304 ^{sh} (m)
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	1944(s)	—	321(s)
$\text{IrHCl}_2(\text{CO})(\text{PCy}_3)_2$	2015(s)	2276(m)	310(s), 255(s)
$\text{IrDCl}_2(\text{CO})(\text{PCy}_3)_2$	2015(s)	1723(m)	309(s), 254(s)
$\text{IrHCl}_2(\text{CO})(\text{PCy}_3)_2 \cdot \text{CHCl}_3$	2012(s)	2270(m)	302(s), 259(s)

not observed and the hydrido resonance signal could not be found in the nmr spectrum. The ν Ir–Cl and ν Ir–Br vibrations lie about 15–20 cm^{-1} lower than the corresponding platinum compounds. The ν Pt–Cl and ν Pt–Br are found at 335, 325 cm^{-1} and 246 cm^{-1} respectively [13]. Recently a metal carbon bond formation has been found in the rhodium complex $\text{RhCl}_2(\text{py})_2(\text{P}(o\text{-C}_6\text{H}_4\text{Me})_2o\text{-C}_6\text{H}_4\text{CH}_2)$. 0.61 CHCl_3 [16] and a metal carbon bond formation was also postulated for explaining the hydrogen deuterium exchange in the complex $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$ [3]. These data suggest a metal–carbon bond formation. However in the diamagnetic pyridine complex $\text{IrX}_2(\text{PCy}_3)_2(\text{py})$, prepared by addition of pyridine to $\text{IrX}_2(\text{PCy}_3)_2$, a weak absorption band has been found at 2160 cm^{-1} . This may be assigned to a ν Ir–H vibration. A dimeric formula of the complex $\text{IrX}_2(\text{PCy}_3)_2$ with hydrogen bridge atoms may not be excluded. Identification of ν Ir–H vibrations with the hydrogen atom as bridge at about 1200 cm^{-1} [17] was not possible because of overlap of phosphine absorption bands in this region. It may also be possible that the complex is a Ir(I), Ir(III) compound with the structure:



Distinguishing between the possible structure of the iridium-compounds with X-ray structure determination meets with difficulties because suitable crystals have not yet been obtained.

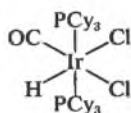
The complex $\text{IrCl}(\text{CO})(\text{PCy}_3)_2$ was prepared according to Stromeier [5] with some modification, which are described in the experimental part. The rhodium complex $\text{RhCl}(\text{CO})(\text{PCy}_3)_2$ was obtained on a similar way by passing carbon monoxide through a boiling mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and PCy_3 in ethanol for 40

16. R. Mason and A. D. C. Towl, *J. chem. Soc. (A)*, 1601 (1970).

17. P. M. Maitlis, C. White, D. S. Gill, J. W. Kang and H. B. Lee, *Chem. Comm.* 2, 734 (1971).

min. The i.r. spectra show a very intense absorption band at about 1900 cm^{-1} due to a carbonyl stretching mode of vibration (Table 3). We have found for these complexes a decrease of the $\nu\text{ C=O}$ stretching frequencies in comparison with the complexes with PPh_3 as ligand [18, 19]. This may be explained assuming the ligand PCy_3 to be a better σ -donor and poorer π -back acceptor. This results in an increase of the basicity of the metal [20]. The transition metals generally become more basic going down a group [20]. In agreement with this we found a higher frequency for the $\nu\text{ C=O}$ stretching vibration in the rhodium complex than for the iridium complex.

The complex $\text{IrHCl}_2(\text{CO})(\text{PCy}_3)_2$ was easily prepared by addition of HCl to a saturated solution of $\text{IrCl}(\text{CO})(\text{PCy}_3)_2$ in ether. Performing the reaction in chloroform as solvent, the solvated complex $\text{IrHCl}_2(\text{CO})(\text{PCy}_3)_2 \cdot \text{CHCl}_3$ was isolated. The deuteriated complex $\text{IrDCl}_2(\text{CO})(\text{PCy}_3)_2$ was prepared with DCl . In the mass spectra we found the parent ion with the lowest fragment ion having m/e 851 which is in agreement with the formula $^{191}\text{IrD}^{35}\text{Cl}_2(\text{CO})(\text{PCy}_3)_2$. The i.r. spectrum for the complex $\text{IrHCl}(\text{CO})(\text{PCy}_3)_2$ in the range $2300\text{--}2000\text{ cm}^{-1}$ shows one band attributable to $\nu\text{ CO}$ stretching at 2015 cm^{-1} and one band at 2276 cm^{-1} assigned to $\nu\text{ M-H}$. In the deuteriated complex the expected frequency shift for a covalent iridium hydrogen bond was found ($\nu\text{ M-D}$ at 1723 cm^{-1}). The $\nu\text{ CO}$ remains unshifted in the deuteride, indicating no resonance interaction between the vibrational states of metal-hydrogen and carbonyl stretching motions. This suggests that the hydrogen and carbonyl are *cis* to another [21]. The $\nu\text{ Ir-H}$ is so high that the hydrogen is probably *trans* to chlorine. One $\nu\text{ Ir-Cl}$ has been found near 310 cm^{-1} , indicating that one halide is *trans* to CO in the adduct. These observations point to the structure with the following figuration as most probable:



A similar structure around iridium(III) was also proposed for the complex with triphenylphosphine as ligand [22]. The complex $\text{RhCl}(\text{CO})(\text{PCy}_3)_2$ reacts with HX , but pure compounds with the formula $\text{RhHXCl}(\text{CO})(\text{PCy}_3)_2$ could not be isolated. The reaction is very slow and after passing of HX -gas for 8 hr under various conditions the end product always contains $\text{RhCl}(\text{CO})(\text{PCy}_3)_2$ as indicated by the i.r. spectrum.

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19. J. Chatt and B. L. Shaw, *J. chem. Soc. (A)*, 1437 (1966).

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21. L. Vaska, *J. Am. chem. Soc.* **88**, 4100 (1966).

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