

PDF hosted at the Radboud Repository of the Radboud University Nijmegen

The following full text is a publisher's version.

For additional information about this publication click this link.

<http://hdl.handle.net/2066/143057>

Please be advised that this information was generated on 2021-09-23 and may be subject to change.

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

F. G. MOERS, J. A. M. DE JONG and P. M. H. BEAUMONT
Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld, Nijmegen,
The Netherlands

(Received 8 August 1972)

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 .

1. F. G. Moers and P. H. op het Veld, *J. inorg. nucl. Chem.* **22**, 3225 (1970).
2. F. G. Moers, *Chem. Comm.* **2**, 79 (1971).
3. F. G. Moers and P. J. Langhout, *Recl. Trav. Chim. Pays. Bas.* **91**, 591 (1972).
4. P. L. Bellon, V. Albano, V. D. Bianco, F. Pompa and V. Scatturin, *Ric. Sic., Rend. ser. A3*, 1213 (1963); *Chem. Abstr.* 14106a (1964).
5. W. Stromeier and T. Onoda, *Z. Naturf.* **23B**, 1377 (1969).
6. J. Chatt, A. E. Field and B. L. Shaw, *J. chem. Soc.* 3371 (1963).
7. J. Chatt, N. P. Johnson and B. L. Shaw, *J. chem. Soc.* 2508 (1964).
8. M. A. Bennett and P. A. Longstaff, *J. Am. chem. Soc.* **91**, 6266 (1969).
9. C. Masters and B. L. Shaw, *J. chem. Soc. (A)*, 3679 (1971).
10. A. Araneo and S. Martinengo, *Gazz. chim. ital.* 61 (1965).

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).

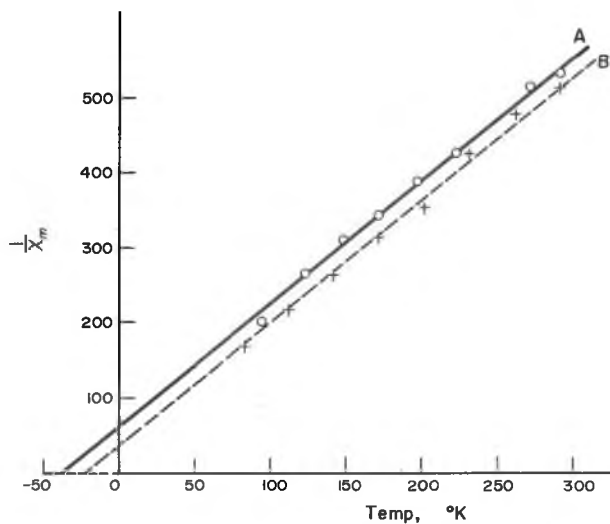


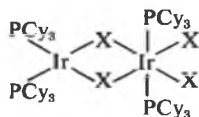
Fig. 1. Temperature dependence of $1/\chi_m$ for RhCl₂(PCy₃)₂ (A) and RhBr₂(PCy₃)₂ (B).

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.

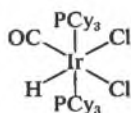
The complex $\text{IrCl}(\text{CO})(\text{PCy}_3)_2$ was prepared according to Stromeier [5] with some modification, which are described in the experimental part. The rhodium complex $\text{RhCl}(\text{CO})(\text{PCy}_3)_2$ was obtained on a similar way by passing carbon monoxide through a boiling mixture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

Acknowledgement—The authors wish to thank Professor Dr. Ir. J. J. Steggerda for discussions, Mr. J. P. M. Langhout for experimental assistance and Mr. J. Diersman for performing the elemental analyses.

18. L. Vaska and J. W. Diluzio, *J. Am. chem. Soc.* **83**, 2784 (1961).

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

20. D. F. Shriver, *Acc. chem. Res.* **73**, (1966).

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

22. L. Vaska, *J. Am. chem. Soc.* **88**, 5326 (1966).