Journal of Organometallic Chemistry, 65 (1974) 93—98

NEW CARBONYL TRICYCLOHEXYLPHOSPHINE COMPLEXES OF RUTHENIUM(II) AND OSMIUM(II)

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(Received May 23rd, 1973)

Summary

The preparation and properties of a new type of monocarbonyl complex $RuCl_2(CO)(PCy_3)_2$ (PCy_3 = tricyclohexylphosphine) is reported. The reaction of carbon monoxide with $RuCl_2(CO)(PCy_3)_2$ or $OsHX(CO)(PCy_3)_2$ with X = Cl or Br results in the formation of the complexes $RuCl_2(CO)_2(PCy_3)_2$ and $OsHX(CO)_2(PCy_3)_2$ respectively. The preparation and properties of the complexes $RuCl(CO)(PCy_3)_2(CS_2H)$ and $OsBr(CO)(PCy_3)_2(CS_2H)$ are described.

Introduction

In previous communications [1, 2] we described the isolation of the complexes $MHCl(CO)(PCy_3)_2$ (M = Ru or Os), monomeric coordinatively unsaturated molecules. These compounds exhibit hydrogen deuterium exchange in the cyclohexyl phosphine ligands.

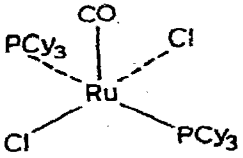
We now describe a new type of monocarbonyl $RuCl_2(CO)(PCy_3)_2$ and the reaction of this complex and the complexes $OsHX(CO)(PCy_3)_2$ (X = Cl or Br) with the small molecules, carbon monoxide and carbon disulphide. The structures of these complexes are discussed.

Results

The reaction of K_2OsCl_6 or hydrated $RuCl_3$ with PCy_3 in 2-methoxyethanol gave a precipitate of $MHCl(CO)(PCy_3)_2$ with M = Ru or Os [2]. On standing at 0°, the mother liquor of the $RuHCl(CO)(PCy_3)_2$ preparation deposited orange crystals of composition $RuCl_2(CO)(PCy_3)_2$. This product also resulted from the addition of PCy_3 to the red solution obtained by passing carbon monoxide into a solution of hydrated $RuCl_3$ in 2-methoxyethanol for 30 min at 80°. The complex was very soluble in ether, in contrast to the hydrido carbonyl complex.

The mass spectrum of $RuCl_2(CO)(PCy_3)_2$ shows the parent ion $RuCl_2(CO)(PCy_3)_2^+$ and the ion $RuCl_2(PCy_3)_2^+$ in high intensity. The relative abundances of the peaks in this cluster agreed with the calculated ratios.

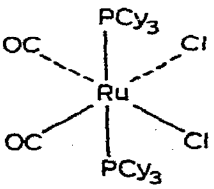
The IR spectrum in the 2000 cm^{-1} region showed one strong band at 1930 cm^{-1} assigned to ν(CO) and a ν(Ru—Cl) band at 335 cm^{-1}, suggesting *trans* configuration of the chlorine atoms. Because of steric hindrance by the bulky PCy_3 ligand, the following configuration is proposed:



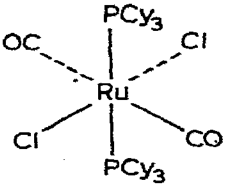
The unoccupied octahedral site of the square-pyramidal configuration may be blocked by a cyclohexyl group. Such a blocking has been found in the complex $RuCl_2(PPh_3)_3$ [3].

On passing carbon monoxide through a benzene solution of $RuCl_2(CO)(PCy_3)_2$ white crystals were obtained which analysed for $RuCl_2(CO)_2(PCy_3)_2$.

The IR spectrum in the 2000 cm^{-1} region showed two strong bands with equal intensity at 2035 and 1965 cm^{-1} which were assigned to ν(CO). The ν(Ru—Cl) band was observed at 305 and 277 cm^{-1}. These data indicate *cis*-configuration of the two chlorine atoms and of the two carbon monoxide molecules. We propose configuration (I) for this complex.



(I)



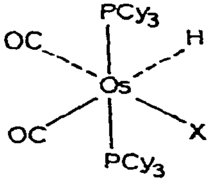
(II)

The reaction of carbon monoxide with solid $RuCl_2(CO)(PCy_3)_2$ leads to the *trans*-$RuCl_2(CO)_2(PCy_3)_2$ with (II) as the most probable choice of configuration.

The IR spectrum showed a ν(CO) band at 1984 cm^{-1} and the ν(Ru—Cl) band at 345 and 334 cm^{-1}. The presence of two metal—halogen stretching vibrations is expected for *cis*-complexes [4], but since in general the ν(M—Cl) frequencies are considerably lower than the single ν(M—X) frequency for the corresponding *trans* isomer [5], and because of the steric hindrance by the bulky tricyclohexylphosphine, we believe that the two halogen atoms in these compounds are *trans* to each other.

A mixture of *cis*- and *trans*-$RuCl_2(CO)_2(PCy_3)_2$ was obtained by treatment of hydrated $RuCl_3$ in boiling 2-methoxyethanol for 12 h at 140° under a carbon monoxide atmosphere, followed by addition of PCy_3. The dicarbonyl complexes are far less volatile than the monocarbonyl complex and mass spectra of these compounds could not be obtained.

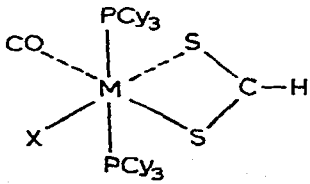
The reaction of carbon monoxide with a benzene solution of $OsHX(CO)(PCy_3)_2$ with X = Cl or Br resulted in the formation of $OsH(CO)_2X(PCy_3)_2$. The hydride resonance in the ^1H NMR spectra of these compounds was a 1/2/1 triplet arising from coupling of the hydride with two equivalent P nuclei which indicates a *trans* disposition for the two phosphine groups. The chemical shift occurred at the lower part of the high field region, indicating a ligand of high *trans* influence *trans* to hydrogen [6, 7]. The IR spectra for these compounds showed two bands attributable to CO stretching in the range 1905 - 2040 cm^{-1} and one band at about 1965 cm^{-1} assigned to ν(Os—H). In the deuteriated chloro complex the band at 1973 cm^{-1} disappeared and the ν(CO) was shifted to 1918 and 1998 cm^{-1}, indicating resonance interaction between the vibrational states of metal—hydrogen and carbonyl stretching modes. This suggests that the hydrogen and one carbonyl molecule are *trans* to one another [8, 9]. From these data we propose the following configuration:

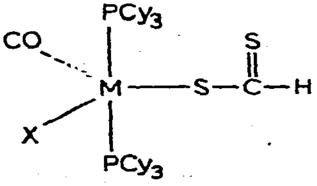


A similar disposition of groups about osmium(II) was also proposed for the complex $OsH(CO)_2Cl[Pr_2(t\text{-}Bu)P]_2$ [10].

Reaction of carbon disulphide with $RuHCl(CO)(PCy_3)_2$ and $OsHBr(CO)(PCy_3)_2$ gave the complexes $RuCl(CO)(PCy_3)_2(HCS_2)$ and $OsBr(CO)(PCy_3)_2(HCS_2)$ respectively. No reaction was observed between carbon disulphide and the complex $RuCl_2(CO)(PCy_3)_2$.

The IR spectra of the carbon disulphide compounds showed bands in the range 780 - 920 cm^{-1}, assignable to ν(C—S) comparable to those found for $Re(CO)_2[P(C_6H_5)_3]_2(HCS_2)$, $Re(CO)_3(DPE)(HCS_2)$ and $Mn(CO)_3(DPE)(HCS_2)$ with DPE = 1,2-diphenylphosphinoethane [11 - 13]. In the region 2550 - 2600 cm^{-1} ν(S—H) was not observed and the ν(C—H) of the HCS_2 group was found as a weak band at 2970 cm^{-1}. From these data we propose one of the following structures for these complexes:





Experimental

Melting/decomposing points were determined with a Leitz - Wetzlar melting point apparatus and are uncorrected. The IR data were obtained with a

Perkin - Elmer 257 spectrophotometer for the range 4000 - 700 cm^{-1} and a Hitachi-EPI-L for the 700 - 200 cm^{-1} region. The 70 eV mass spectra were recorded on a Varian - Atlas SM-1B double focussing instrument under low resolution conditions. The samples were introduced into the mass spectrometer by a direct insertion system.

^1H NMR spectra

These were measured on a Varian XL 100 spectrometer. The samples were prepared by dissolving them in deuterated chloroform; tetramethylsilane was the internal standard.

$OsHCl(CO)_2(PCy_3)_2$, triplet, τ 14.7 ppm, J(P—H) 21 Hz; $OsHBr(CO)_2(PCy_3)_2$, triplet, τ 15.9 ppm, J(P—H) 22 Hz.

Starting materials

$MH(CO)Cl(PCy_3)_2$ with M = Ru or Os and $OsDCl(CO)(PCy_3)_2$ were prepared as previously described [2]. Tricyclohexylphosphine was prepared as described by Issleib et al. [14], and K_2OsBr_6 by the method used for the preparation of K_2OsCl_6 [15], replacing $FeCl_2 \cdot 6H_2O$ by $FeBr_2 \cdot 6H_2O$. All other reagents were analytical grade.

Preparation of the complex $RuCl_2(CO)(PCy_3)_2$

(a). To a solution of PCy_3 (0.84 g, 3mmol) in 50 ml 2-methoxyethanol was added a solution of $RuCl_3 \cdot 3H_2O$ (0.26 g, 1 mmol), and the mixture was heated for 72 h at 130°. After cooling to room temperature the precipitate was filtered off. The mother liquor was set aside for 12 h at ice temperature and the resulting orange crystals were filtered off, washed with ethanol and dried in a high vacuum.

(b). Carbon monoxide was bubbled through a solution of $RuCl_3 \cdot 3H_2O$ (0.26 g, 1 mmol) in ethanol (20 ml) for 30 min at 80°. After cooling the red solution at room temperature a solution of PCy_3 (1.12 g, 4 mmol) in ethanol (50 ml) was added. The yellow brown precipitate was filtered off, washed with ethanol and the pure product was isolated as needles after three recrystallisations from acetone.

Preparation of the complex cis-$RuCl_2(CO)_2(PCy_3)_2$

Carbon monoxide was bubbled through a solution of $RuCl_2(CO)(PCy_3)_2$ (0.38 g, 0.5 mmol) in benzene (20 ml) for 8 h at 80°. After concentrating the solution to 5 ml, the precipitate was filtered off, washed with ethanol and dried in vacuo at 110°.

Preparation of the complex trans-$RuCl_2(CO)_2(PCy_3)_2$

Carbon monoxide was passed over solid $RuCl_2(CO)(PCy_3)_2$ (0.38 g, 0.5 mmol) for 14 days at room temperature. Recrystallisation from $CHCl_3$ gave the pure product.

Preparation of the complex $RuCl(CO)(PCy_3)_2(HCS_2)$

Carbon disulphide (10 ml) was added to a solution of $RuHCl(CO)(PCy_3)_2$ (0.43 g, 0.6 mmol) in benzene (40 ml) under a nitrogen atmosphere. After

TABLE 1

THE MAJOR IR BANDS IN THE RANGE 4000 — 200 CM^{-1}[a,b]

Compound	ν(CO)	ν(M—H)	ν(M—Cl)	Others
$RuCl_2(CO)(PCy_3)_2$	1930^{d}s		335 s	
cis-$RuCl_2(CO)_2(PCy_3)_2$	2035^{c}s 1965^{c}s		305 s 277 s	
trans-$RuCl_2(CO)_2(PCy_3)_2$	1984^{c}vs		345 s 334 (sh)	
$RuCl(CO)(PCy_3)_2(HCS_2)$	1933^{c}s		268 s	917 s ν(CS) 315 m ν(RuS)
$OsHBr(CO)(PCy_3)_2$	1887^{d}s	2020 w?		
$OsBr(CO)(PCy_3)_2(HCS_2)$	1914^{d}s			912 s ν(CS) 782 m ν(CS) 310 m ν(OsS)
$OsHCl(CO)_2(PCy_3)_2$	2041^{d}s 1909^{d}s	1973^{d}s	287 s	
$OsHBr(CO_2)_2(PCy_3)_2$	2038^{d}s 1905^{d}s	1966^{d}s		
$OsDCl(CO)_2(PCy_3)_2$	1998^{d}s 1918^{d}s		288 s	2150 w ν(CD)

[a] Nujol mull, except in cases as otherwise indicated. [b] Abbreviations: m, medium; s, strong; sh, shoulder; vs, very strong; w, weak. [c] In $CHCl_3$ solution. [d] In C_6H_6 solution.

concentrating the solution to 5 ml, the yellow precipitate was collected, washed with chloroform and dried in vacuo. The solid was recrystallised from benzene.

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

K_2OsBr_6 (0.75 g, 1 mmol) was added to a solution of PCy_3 (0.84 g, 3 mmol) in 2-methoxyethanol (50 ml) under a nitrogen atmosphere. The mixture was heated for 60 h at 140°. After cooling to room temperature the brown crystals were filtered off, washed with water and ethanol and dried under high vacuum.

TABLE 2

ANALYTICAL DATA OF THE COMPLEXES

Complex	Analysis found (calcd.) (%)			Yield (%)	Colour	M.p./dec.p (°C)
	C	H	Cl			
$RuCl_2(CO)(PCy_3)_2$	58.34 (58.41)	8.88 (8.74)	9.50 (9.32)	20[a] 35[b]	Orange	210
cis-$RuCl_2(CO)_2(PCy_3)_2$	57.55 (57.86)	8.64 (8.43)	8.76 (8.99)	80	White	251
trans-$RuCl_2(CO)_2(PCy_3)_2$	57.36 (57.86)	8.40 (8.43)		70	Yellow	238
$RuCl(CO)(PCy_3)_2(HCS_2)$	56.69 (56.87)	8.61 (8.41)		50	Yellow	193
$OsHBr(CO)(PCy_3)_2$	51.75 (51.68)	7.93 (7.85)		80	Brown	210
$OsBr(CO)(PCy_3)_2(HCS_2)$	48.08 (48.76)	6.72 (7.21)		60	Orange	206
$OsHCl(CO)_2(PCy_3)_2$	54.28 (54.11)	8.03 (8.01)	4.26 (4.20)	85	White	245
$OsHBr(CO)_2(PCy_3)_2$	51.93 (51.40)	7.48 (7.61)		85	White	242
$OsDCl(CO)_2(PCy_3)_2$	53.39 (54.04)	7.97 (7.99)		80	White	238

[a] By method (a), and [b] by method (b) given in the text.

Preparation of the complex $OsBr(CO)(PCy_3)_2(HCS_2)$ was carried out in a similar way to $RuCl(CO)(PCy_3)_2(HCS_2)$, replacing $RuHCl(CO)(PCy_3)_2$ by $OsHBr(CO)PCy_3)_2$.

Preparation of the complexes $OsXY(CO)_2(PCy_3)_2$ with $X = Cl$ or Br, $Y = H$ or D

Carbon monoxide was passed through a solution of $OsXY(CO)(PCy_3)_2$ (0.4 mmol) in 20 ml benzene for 4 h at room temperature. After evaporating the solution, the product was washed with ether, dried in vacuum and recrystallised from $CHCl_3/C_2H_5OH$ mixture.

Acknowledgements

The authors wish to thank Professor Dr. Ir. J.J. Steggerda for discussions, Dr. F. Gerhartl for recording the mass spectra and Mr. J. Diersmann for performing the elemental analyses.

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