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Monosubstituted Derivatives of Rutheniumtetracarbonyl Dihalides

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Ruthenium carbonyl compounds of the type $RuX_2(CO)_3L$ [X = Br, I; L = C_5H_5NO, $OP(C_6H_5)_3$] are reported, which represent the first monosubstituted derivatives obtained from $Ru(CO)_4X_2$.

Introduction

Compounds of the type RuX_2L_4, $RuX_2(CO)L_3$, $RuX_2(CO)_2L_2$ (X = Cl, Br, I; L = tertiary phosphine, arsine, etc.) are well known[1] and must be considered as derivatives of the rutheniumtetracarbonyldihalides, $Ru(CO)_4X_2$, by substitution respectively of four, three or two CO groups by the same number of ligand molecules.

In this note we report the preparation of some compounds of the type $RuBr_2(CO)_3L$ (L = pyridine oxide, triphenylphosphine oxide) and $RuI_2(CO)_3L$ (L = pyridine oxide), which are the first monosubstituted derivatives of $Ru(CO)_4X_2$ so far described.

Results

Our compounds are obtained by reacting, in chloroform solution, the rutheniumtetracarbonyldihalide with the ligand at room temperature. The reaction with pyridine oxide goes to completion very rapidly (~5′); the analogous reaction of rutheniumtetracarbonyldihalide with triphenylphosphine oxide is considerably slower.

These complexes are crystalline, pale yellow solids, insoluble in water and aliphatic hydrocarbons, very soluble in common organic solvents such as chloroform, benzene, etc.. Their formulae are supported by elemental analyses, molecular weight determinations and by their strong tendency to react with additional ligand, forming disubstituted derivatives.

Carbonyl stretching frequencies are reported in Table I.

Table I. Infrared Data[a]

Compound	$\nu_{CO}(cm^{-1})$	
$RuBr_2(CO)_3(Opy)$	2126 vs	2056 vs
$RuBr_2(CO)_3(OPPh_1)$	2125 vs	2056 vs
$RuI_2(CO)_3(Opy)$	2105 vs	2040 vs

[a] Recorded on a Perkin-Elmer Mod. 621 spectrophotometer in $CHCl_3$ solution.

As is known, carbon monoxide, which is a very strongly double-bonding ligand, prefers not to be in a *trans*-position to another CO group; triphenylphosphine oxide and pyridine oxide, which are on the contrary much weaker π-acceptors, are more likely in a *trans*-position to a CO group. Therefore, as in analogous cases,[2] a structure in which the three CO groups are in *cis*-position is probable. In such a case, three bands are expected for a C_s symmetry ($2A'+A''$); we assume that the lower frequency band, which is broader, (Figure), is resulting from the overlap of two peaks. This assumption is supported by the IR spectra of analogous complexes which we have recently investigated[3] and which show two distinct but very near peaks at lower frequency.

The progress of the reaction was followed by recording periodically the IR spectra in solution until the higher frequency band of $Ru(CO)_4X_2$ had disappeared. At this point (substitution of one CO group),

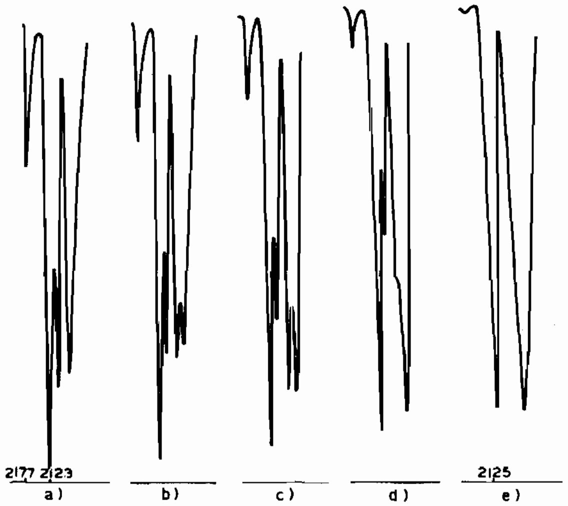

Figure 1. Series of IR spectra obtained in $CHCl_3$ solution during the reaction of $Ru(CO)_4Br_2$ with $OPPh_3$.

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(1) (a) A. Aràneo and S. Martinengo, *Rend. Ist. Lomb. Sc. Lett.*, *99A*, 829 (1965); (b) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, *28*, 945 (1966).

(2) W. Hieber and T. Kruck, *Chem. Ber.*, *95*, 2027 (1962).

(3) A. Trovati, A. Aràneo, and F. Zingales, submitted to *Inorg. Chem.*

(4) F. Calderazzo and F. L'Eplattenier, *Inorg. Chem.*, *6*, 1220 (1967).

Table II. Analytical Data

	Mp°C	Mol. Weight [a]		%C	%H	%N	%Hal.
$RuBr_2(CO)_3(Opy)$	131	Calcd.	440	21.84	1.15	3.18	36.32
		Found	437	21.72	1.14	3.20	36.95
$RuBr_2(CO)_3(OPPh_3)$	113	Calcd.	623	40.47	2.43	—	25.65
		Found	605	39.50	2.42	—	26.00
$RuI_2(CO)_3(Opy)$	114	Calcd.	534	18.00	0.94	2.62	47.53
		Found	549	18.60	1.03	2.81	47.90

[a] Determined in $CHCl_3$ solution using a Mechrolab 301 A osmometer.

the resulting product was precipitated by adding n-hexane and filtered off; thus the reaction is stopped and more extensive CO substitution is avoided.

In Figure 1 the series of spectra for the reaction of $Ru(CO)_4Br_2$ with triphenylphosphine oxide at different reaction times is reported.

Attempts to carry out the monosubstitution reaction of $Ru(CO)_4Br_2$ with triphenylphosphine were unsuccessful: even under the mildest conditions we have always obtained the disubstituted derivative, $RuBr_2(CO)_2(PPh_3)_2$, previously obtained in a different way by other Authors[1b] and characterized by two ν_{CO} absorption bands at 2061 and 1980 cm^{-1}.

Experimental Section

The compounds $Ru(CO)_4Br_2$ and $Ru(CO)_4I_2$ were prepared according to the procedure of the literature.[4]

Preparation of dibromo(tricarbonyl)pyridine-oxide-ruthenium(II), $RuBr_2(CO)_3(C_5H_5NO)$.

A solution of $Ru(CO)_4Br_2$ (200 mg; ~0.5 mmoles) in chloroform (50 ml) was treated with 12 ml of 0.05 *M* pyridine oxide in chloroform solution and stirred at room temperature for 5 minutes. After concentration under reduced pressure and upon addition of n-hexane, a pale yellow precipitate was deposited, which was collected on a filter, washed with 5 ml of n-hexane, and dried *in vacuo*. Purification was effected by recrystallization from chloroform-hexane. Yield 80 mg (~30%).

Preparation of dibromo(tricarbonyl)triphenylphosphine-oxide-ruthenium(II), $RuBr_2(CO)_3[OP(C_6H_5)_3]$.

The reaction between $Ru(CO)_4Br_2$ and $OPPh_3$ was carried out for 1 hour in the same way as described before. Yield 100 mg (~30%).

Preparation of diiodo(tricarbonyl)pyridine-oxide-ruthenium(II), $RuI_2(CO)_3(C_5H_5NO)$.

By a procedure similar to that described above, 80 mg (~35%) of $RuI_2(CO)_3(Opy)$ were obtained by reacting 230 mg of $Ru(CO)_4I_2$ in chloroform (50 ml) and 12 ml of 0.05 *M* C_5H_5NO in chloroform solution.