AN UNUSUAL RHODIUM IODOCARBONYL SYSTEM

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Abstract – Interaction of tertiary phosphines, arsines and stibines with iodocarbonylrhodium solutions yields the complexes, $[Rh(CO)L_2I]$ and $[Rh(CO)L_2I_3]$, whereas with pyridine and aniline, anions of the type $[Rh(CO)LI_4]^-$ are the only products obtained. The isolation of geometrical isomers of $[Rh(CO)_2I_4]^-$ from the same iodocarbonyl solution is discussed.

INTRODUCTION

THE SYNTHESES of several halocarbonyl anions of rhodium(I) and rhodium(III) have recently been reported[1]. Methods of preparation involved treating $[Rh(CO)_2Cl]_2$ with the corresponding hydrohalic acid to give $[Rh(CO)_2X_2]^-$ (X = Cl, Br, I), and $[Rh_2(CO)_2X_4]^{2-}$ (where X = Br and I only). Reacting rhodium triodide and sodium iodide with carbon monoxide at high pressure and temperature gave the rhodium(III) species $[Rh(CO)I_4]^-$; since only one carbonyl band is exhibited by this compound, it is rather doubtful whether the postulated dimeric formulation is correct[1]. Subsequently, it has been demonstrated that $[Rh(CO)_2Cl_2]^-$ is present in the yellow solution obtained by reducing rhodium trichloride in the presence of carbon monoxide and ethanol[2, 3]. This yellow solution undergoes halogen exchange with lithium bromide to give the corresponding bromo complex. The preparation of iodocarbonyl solutions by (a) halogen exchange between this yellow chlorocarbonyl solution and sodium iodide and (b) refluxing a mixture of rhodium trichloride and sodium iodide and sodium iodide and sodium iodide under carbon monoxide, is now reported.

Halogen-containing carbonyl phosphine, arsine and stibine complexes of rhodium(I) and rhodium(III) have been extensively studied, although less emphasis has been placed on the iodides than on the corresponding chlorides and bromides[4]. The rhodium(I) compounds $[Rh(CO)(PPh_3)_2I][5, 6]$ and $[Rh(CO)(PEt_2Ph)_2I][2]$, are known, but no rhodium(III) species of the type $[Rh(CO)L_2I_3]$ have been prepared. There are, however, some rhodium(III) complexes containing mixed halogens, e.g., $[Rh(CO)L_2CII_2][7]$, and others with alkyl groups $[Rh(CO)(PPh_3)_2MeI_2]$. It has now proved possible to obtain

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a series of rhodium(I) and rhodium(III) iodocarbonyl complexes by reacting the tertiary phosphine, arsine or stibine dissolved in various solvents, with the new iodocarbonyl solutions.

EXPERIMENTAL

Materials. Rhodium trichloride, $RhCl_3 . 3H_2O$, was from Johnson Matthey Ltd. Triphenylphosphine and tri-*n*-butylphosphine were obtained from Albright and Wilson and triphenylarsine and triphenylstibine from Aldrich Chemical Company. Absolute ethanol and acetone (A.R.grade) were used as the solvents in all the reactions.

Preparation of the complexes. All preparations were carried out in carbon monoxide or a nitrogen atmosphere and in every case, a standard amount (0.1 g) of RhCl₃. 3H₂O was used. The yellow chloro-carbonyl solution was prepared by the method of Chatt [2]. Analytical data are recorded in Table 1.

Preparation of iodocarbonyl solutions

Solution A. Sodium iodide (0.5 g) was added to the yellow chlorocarbonyl solution and the mixture warmed on a water bath for 15 min. The resulting dark red solution was filtered to remove precipitated sodium chloride.

Solution B. Carbon monoxide was passed through a refluxing ethanol solution of rhodium trichloride and sodium iodide (0.5 g). After 5 hr the dark red solution was cooled and then separated from the sodium chloride.

Tetraphenylarsoniumdicarbonyltetraiodorhodium(III). An ethanolic solution of tetraphenylarsonium chloride was added to solution (A). After 4 hr, the complex separated as red-black crystals which were collected, washed with diethyl-ether and dried *in vacuo*.

Tetraethylammoniumdicarbonyltetraiodorhodium(III). This complex was prepared in a similar fashion from solution (A). On addition of tetraethylammonium chloride, in ethanol, the black crystalline compound was obtained on standing overnight.

Tetraethylammoniumpyridinecarbonyltetraiodorhodium(111). Pyridine (0.1 ml) was added to either solution (A) or solution (B), followed by a dilute ethanol solution of tetraethylammonium chloride. This caused the immediate precipitation of a black compound, which was recrystallized from acetone to yield the pure species.

Tetraethylammoniumanilinecarbonyltetraiodorhodium(III). As for the pyridine derivative. Black crystals were deposited on standing over night.

Bis(triphenylphosphine)carbonyliodorhodium(1). When triphenylphosphine (0.25 g in 20 ml warm ethanol) was added to solution (A) or solution (B), a slow colour change (ten minutes) from dark red to yellow occurred with the precipitation of the yellow compound.

The filtrate on standing over night reverted to its original deep red colour and a small quantity of red crystals were deposited. The i.r. spectrum of this complex is identical with that of a pure sample of $[Rh(CO)(PPh_3)_2I_3]$.

Bis(triphenylphosphine)carbonyltriiodorhodium(III). Solution (B) and triphenylphosphine (0.25 g in 15 ml acetone) were shaken together for 3 hr. A small amount of the red compound precipitated over this time and it was collected, washed with diethylether and dried in air.

Bis(tri-n-butylphosphine)carbonyltriiodorhodium(III). Tri-n-butylphosphine, when added to solution (A) or solution (B), caused an immediate colour change to yellow-red, but no precipitation occurred. On standing for 10 min, the colour changed to red-orange and when the solution is concentrated to a small volume (10 ml) the red crystalline compound is obtained.

Bis(triphenylarsine)carbonyltriiodorhodium(III). As for the triphenylphosphine complex, giving a red crystalline compound.

Bis(triphenylstibine)carbonyltriiodorhodium(III). As for the triphenylphosphine complex. Red crystals were deposited.

Analyses. Microanalyses were by the Australian Microanalytical Service, Melbourne.

Physical measurements. Molecular weight determinations in chloroform and acetone were obtained using a Mechrolab model 302 osmometer. Conductivities were measured in 10^{-3} M nitromethane solutions on a Philips type PR 9500 conductivity bridge. Infra-red spectra were recorded on a Perkin-Elmer model 225 spectrophotometer.

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			Fo (3)	bun (%)					ల ల	alc. 8)		
Compound	С	H	Z	Ч	As	Rh	С	Н	Z	Р	As	Rh
Rh(CO) ₂ I ₄][As(C ₆ H ₅) ₄]	29-3	2.6		1	7.0	1	29.7	1.7			7.1	
Xh(CO)₂I 4][N(C ₂ H ₅)4]	15-3	2.9	1·8	l	ļ	13.6	15.1	2.5	1.8	j	.	9.01
Xh(CO)(C₅H₅N)I₄][N(C₂H₅)₄]	20.0	3.1	3.2	ļ		12.1	19.8	3.0		ļ	ł	2.1
Rh(CO)(C ₆ H ₇ N)I ₄][N(C ₂ H ₅) ₄]	20-9	3.2	3.0	ļ	}	ł	20-9	3.7	2.5	(ł	
Xh(CO)(PPh₃)₂I]*	56.3	4-4	1	6.7		1	56.8		,	7.9	{	
th(CO)(PPh ₃) ₂ 1 ₃]	42.8	3.7	1	I	ł	ł	42.9	2.9	1	<u> </u>	}	1
th(CO)(PBu ⁿ ₃)₂I₃]†	31-9	6.3	ł	6.2	l	}	32-8	5.9	ł	6-8	ł	ļ
th(CO)(AsPh ₃) ₂ l ₃]	40-0	3.3	}]	13.7	ļ	39.5	2.7	}	1	[3-3	
th(CO)(SbPh ₃) ₂ l ₃]	36-4	3.0	ļ	[- man gange	i	36.5	2.5		ļ		

Table 1. Analytical data

*Mol. wt. in chloroform: Found, 700; Required 782. †Mol. wt. in acetone: Found, 865; Required 916.

		Molar conductance 10 ⁻³ M nitromethane solutions	
Compound	Colour	(ohm ⁻¹ cm ² mole ⁻¹)	$\nu_{co}^* \mathrm{cm}^{-1}$
$[Rh(CO)_2I_4][As(C_6H_5)_4]$	red-black	80	2084, 2042(w), 1970(w)
$[Rh(CO)_{2}I_{4}][N(C_{2}H_{5})_{4}]$	black	70	2075(m), 2052
$[Rh(CO)(C_5H_5N)I_4][N(C_2H_5)_4]$	black	79	2063
$[Rh(CO)(C_{6}H_{7}N)I_{4}][N(C_{2}H_{5})_{4}]$	black	80	2057, 2053, 2045
[Rh(CO)(PPh ₃)I]	yellow	< 1†	1970
$[Rh(CO)(PPh_3)_2I_3]$	red	insoluble	2086
$[Rh(CO)(PBu_{3}^{n})_{2}I_{3}]$	red	< 1†	2054
$[Rh(CO)(AsPh_3)_2I_3]$	red	insoluble	2085, 2010(vw), 1953(vw)
$[Rh(CO)(SbPh_3)_2I_3]$	red	insoluble	2076

Table 2. Some physical data of the rhodium complexes

*KBr discs. All bands strong unless otherwise noted.

[†]In 10⁻³M chloroform solutions.

RESULTS AND DISCUSSION

Iodocarbonyl anions

When carbon monoxide is passed into a boiling ethanol solution of rhodium trichloride for one hour a yellow solution is formed[2]. Subsequent addition of a large excess of sodium iodide yields a dark-red solution from which the anionic complex $[Rh(CO)_2I_4]^-$ can be precipitated in isomeric forms by simply varying the cation used. The tetraethylammonium salt shows two strong bands (2075, 2052 cm⁻¹) of approximately equal intensity in the terminal carbonyl region of the infra-red spectrum, indicating a *cis* carbonyl arrangement, while the single strong (2084 cm⁻¹) and two very weak (2042, 1970 cm⁻¹) absorptions in the tetraphenylarsonium salt, suggest *trans* character. These weak bands may be due to traces of $[Rh(CO)_2I_2]^-$, which exhibits bands at 2043, 1967 cm⁻¹. However, in no instance could this rhodium(I) complex be isolated from the reaction mixture. Although there is a possibility of aerial oxidation in this reaction, it is more likely that some other species, presumably rhodium(IIII), is present with the rhodium(I) entity, $[Rh(CO)_2Cl_2]^-$, in the yellow chlorocarbonyl solution.

If carbon monoxide is bubbled through an ethanolic solution of rhodium trichloride and sodium iodide (in large excess) for several hours, a deep-red solution (B) is formed. Addition of large cations to (B), such as $As(C_6H_5)_4^+$ and $N(C_2H_5)_4^+$ (as their chlorides), result only in the precipitation of mixtures. The dark-brown compounds obtained in this way show strong broad absorptions centred near 2060 cm⁻¹ in the i.r. spectrum, and successive analytical determinations suggested that these species were mixtures of rhodium(I) and rhodium(III) complexes. Reaction times of four to five hours are necessary to make sure that carbonylation of the rhodium (I) state.

Nitrogen-containing complexes

The reaction of excess pyridine or aniline with solution (A) led to the isolation of the ionic species, $[N(C_2H_5)_4][Rh(CO)LI_4]$ (L = pyridine or aniline) in moderate

yields. Replacement of one carbonyl group can occur quite readily since the species *trans*-[Rh(CO)₂I₄]⁻, present in this solution, has, by the *trans* effect, one carbonyl group more labile than the other. It has not been possible to obtain any neutral complexes from this solution, nor have any rhodium(I) compounds been isolated. Solution (B) gives the same complexes, [Rh(CO)LI₄]⁻, when treated with pyridine and aniline, thereby suggesting that the same rhodium(III) species must be present. Both compounds are uni-univalent electrolytes in nitromethane solution. The pyridine complex exhibits a single i.r. stretching frequency in the terminal carbonyl region, whereas three bands, all of approximately the same intensity, are recorded for the aniline derivative. This observation may be explained by solid state splitting or by the presence of more than one isomer, but because the complex was not soluble in solvents suitable for spectroscopic studies, it was not possible to determine which explanation was correct.

Tertiary phosphine, arsine and stibine derivatives

The unusual nature of the iodocarbonyl solutions A and B is adequately demonstrated by the reactions with these ligands. By simply varying the solvent used to dissolve the ligand, rhodium complexes in the +3 or +1 oxidation state may be obtained. Thus, when a solution of triphenylphosphine or arsine or stibine (2 fold excess) in acetone is added to either iodocarbonyl solution, there is slow precipitation over a period of 3 hr, of [Rh(CO)L₂I₃] (L = PPh₃, AsPh₃, SbPh₃). Only small amounts of the triphenylphosphine complex are obtained, but moderate yields are observed for the arsine and stibine derivatives. Due to the insolubility of these complexes, it was not possible to determine their molecular weights, but they are most likely six co-ordinate monomers. The appearance of two very weak carbonyl bands (2010, 1953 cm⁻¹) in the i.r. spectrum of the arsine complex is probably caused by impurities. Only one strong band is exhibited by the phosphine and stibine derivatives.

If a two fold excess of triphenylphosphine, dissolved in warm ethanol, is added to solution A or B, there is a slow colour change from deep-red to yellow and the yellow compound $[Rh(CO)(PPh_3)_2I]$ precipitates. The yellow filtrate from this reaction turns red when left over night and a small amount of $[Rh(CO)-(PPh_3)_2I_3]$ separates from the solution. Since the interchange between the rhodium (1) and rhodium(111) states is quite slow, isolation of both products is easily effected.

Triphenylstibine, when added in warm ethanol solution, to either iodocarbonyl solution gave an immediate precipitate whose i.r. spectrum (carbonyl region) showed two peaks at 2076 and 1978 cm⁻¹. One absorption (2076 cm⁻¹) is readily assigned to the rhodium(III) stibine derivative [Rh(CO)(SbPh₃)₂I₃], and the other is presumably due to a rhodium(I) complex (the rhodium(I) phosphine shows a band at 1970 cm⁻¹). Shaking the mixture in acetone yields an insoluble red compound (the rhodium(III) species) and a red solution which on evaporation afforded an orange-red material. A broad absorption of 1640 cm⁻¹ indicates that this compound contains co-ordinated acetone[8]. Analytical results, although not reproducible, suggested that the compound is of type [Rh(CO)(SbPh₃)₂I(Me₂CO)_x] where the value of x is not certain.

8. T. A. Stephenson and G. Wilkinson, J. inorg. nucl. Chem. 28, 945 (1966).

When triphenylarsine is used in place of triphenylstibine, there is again precipitation of a mixture, but even after repeated recrystallizations, from acetone, it was not possible to obtain the rhodium(I) complex in its pure form. Prolonged standing in acetone solution led to decomposition of the compound with the disappearance of all bands in the carbonyl region.

Attempts to prepare a rhodium(I) tri-n-butylphosphine complex have not been successful. On addition of the ligand to either iodocarbonyl solution, there is a immediate colour change to yellow-red but no precipitation occurs at this point. Removal of the solvent under vacuum yields only copious amounts of sodium iodide. However if the solution is left over night, the colour returns to red and evaporation at this point to a small volume (about 10 ml) *affords* red crystals of $[Rh(CO)(PBu_3^n)_2I_3]$. This complex has a single strong carbonyl band at 2054 cm; it is highly soluble in most organic solvents (e.g. acetone, chloroform, diethylether) and molecular weight measurements in acetone indicate its monomeric nature.

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