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Interaction of Rhodiumdicarbonylhalides with Triarylstibines[1]

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The reaction in benzene solution of triarylstibines with $[Rh(CO)_2X]_2$ *(X = Cl, Br) has been reinvestigated in order to elucidate the nature of the products, previously described as* $[RhCl(CO)\{(C_6H_5)_3Sb\}_2]$, $[RhCl(CO)_2\{(C_6H_5)_3Sb\}_3]$ *or* $[RhCl(CO)\{(C_6H_5)_3Sb\}_3]$ *in different papers. From analytical evidence and electronic spectra we formulate the products as* $[RhX(CO)\{(RC_6H_4)_3Sb\}_3] \cdot C_6H_6$ *(X = Cl, Br; R = H, CH₃), with a benzene molecule strongly clathrated in the lattice.*

Introduction

The reaction of triarylstibines with $[Rh(CO)_2Cl]_2$ have been previously investigated by several workers. First Vallarino[2] described the compound of formula $[RhCl(CO)\{(C_6H_5)_3Sb\}_2]$ obtained by interaction of $[Rh(CO)_2Cl]_2$ with $(C_6H_5)_3Sb$. A compound, obtained in a similar way, was formulated by Hieber and coworkers[3] as $[RhCl(CO)_2\{(C_6H_5)_3Sb\}_3]$ and recently briefly as $[RhCl(CO)\{(C_6H_5)_3Sb\}_3]$ [4]. In a preliminary note[1] we pointed out the complexity of the system and we wish now to report our final results.

Experimental Section

All the compounds (Table I) were prepared from a benzene or ether solution of the rhodiumdicarbonylhalide and a benzene or ether solution of the triarylstibine, and they were isolated by concentration in vacuo and addition of an excess of hexane.

Carbon, hydrogen analyses were carried out in the analytical laboratory of Milan University. Halogens were determined, with a potentiometric method, in the analytical laboratory of Istituto Donegani, Montecatini-Edison S.p.A. (Novara). Oxygen was determined in the analytical laboratory of Padua University. The infrared spectra were recorded on a Perkin-Elmer 237 Spectrometer and the solution and reflectance electronic spectra on a Beckmann DK-2A Spectrometer. The molecular weights have been determined on a Mechrolab Osmometer, mod. 301 A. Thermogravimetric analyses have been carried out in the Istituto Donegani, Montecatini-Edison S.p.A. (Milan).

Results

When a benzene solution of the triarylstibine was added to a benzene solution of rhodiumdicarbonylhalide, one mole of carbon monoxide was evolved for every mole of rhodium. The red diamagnetic and non conducting compounds showed in solid state or in solution, only one infrared carbonyl stretching (Table I). These data support the presence of only one carbonyl ligand in the compounds.

Repeated analyses (Table II) agreed very well with the formula $[RhX(CO)L_4]$ (X = Cl, Br; L = $(C_6H_5)_3Sb$, $(p\text{—}CH_3C_6H_4)_3Sb$) or $[RhX(CO)L_3]C_6H_6$.

The first formulation, which we tentatively proposed in our preliminary communication[1] should require a coordination number which is not common for Rh^I. The analogous compounds with phosphines,[2] arsines,[2] amines[5] and nitriles[6] are square planar, while only some hydrido compounds[7,8] and some isonitriles derivatives[9] with a solvent molecule, seem to be pentacoordinate. Other cases of pentacoordination of Rh^I have been recently reviewed.[10]

Indeed in the formula $[RhX(CO)L_4]$ the rhodium atom should be hexacoordinate with two electrons more than the rare gas configuration. Only one other rhodium compound of this type is reported, namely $[Rh(CO)\{(C_6H_5)_3Sb\}_3(C_5H_7O_2)]$.[11]

It follows that the second formulation with a pentacoordinate Rh^I and a clathrated benzene molecule is more probable although the compounds did not lose any benzene while being heated at 100°C and 5 mm Hg for six days or by repeated washing with ether.

The presence of a benzene molecule was deduced from an infrared absorption at 680 cm^{-1} which was tentatively assigned to the clathrated benzene.[12]

This absorption did not appear when the reaction was carried out in diethyl ether. In this case the isolated red compound analysed quite nicely as $[RhCl(CO)L_3]$ (Table II). The benzene molecule seems to be strongly bound in the lattice; indeed a termogravimetric analysis in nitrogen atmosphere showed that the benzene was released only between 145° and 155°C.

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Table I. Properties of the compounds obtained

Compound	Colour	m.p.°C	$\nu_{C=O}$ nujol, cm^{-1}	$\nu_{C=O}$ CH_2Cl_2, cm^{-1}
$[RhCl(CO)\{(C_6H_5)_3Sb\}_3] . C_6H_6$	magenta-red	154-5	1980	1985
$[RhBr(CO)\{(C_6H_5)_3Sb\}_3] . C_6H_6$	violet-red	163-4	1982	1987
$[RhCl(CO)\{(pCH_3C_6H_4)_3Sb\}_3] . C_6H_6$	orange-red	152-3	1995	1990
$[RhBr(CO)\{(pCH_3C_6H_4)_3Sb\}_3] . C_6H_6$	red	160-3	1995	1992

Table II.

Analytical data for $[RhCl(CO)L_x]$; L = $(C_6H_5)_3Sb$

	X	C%	H%	O%	Cl%
Calculated	3+C_6H_6	56.20	3.84	1.23	2.75
	3	54.05	3.67	1.31	2.89
	4	55.60	3.80	1.01	2.28
Found (reaction in benzene)	—	56.10	3.89	1.09	2.53
		55.70	3.93	1.19	2.44
		56.26	3.78	—	—
Reaction in ether		54.42	3.68	—	—

Analytical data for $[RhBr(CO)L_x]$; L = $(C_6H_5)_3Sb$

	X	C%	H%	O%	Br%
Calculated	3+C_6H_6	54.30	3.79	1.19	5.92
	3	52.10	3.55	1.26	6.30
	4	54.00	3.70	0.99	4.93
Found in benzene	—	54.12	3.72	1.09	4.91
		54.30	3.75	—	5.42

Analytical data for $[RhX(CO)L_3] . C_6H_6$; L = $(pCH_3C_6H_4)_3Sb$

	C%		H%	
X	Calcd.	Found	Calcd.	Found
Cl	59.15	58.62	4.88	4.70
Br	57.60	56.40	4.73	4.58

Table III. Molecular weight determinations

Compound mg	$CHCl_3$ g	M.W. Found
$[RhCl(CO)\{(C_6H_5)_3Sb\}_3] . C_6H_6$		(1302.1) [a]
7.3	1.279	710
23.5	1.893	790
18.0	0.646	732
$[RhBr(CO)\{(C_6H_5)_3Sb\}_3] . C_6H_6$		(1347.1) [a]
13.3	2.3223 [b]	818
13.4	1.9501 [b]	966
12.7	0.645	805

[a] Calculated value; [b] Benzene.

The compounds were found to be extensively dissociated in solution, from which however they could be recovered unchanged in presence of a slight excess of triarylstibine. From molecular weight determinations (Table III) the dissociation $[RhX(CO)L_3] \rightleftharpoons [RhX(CO)L_2]+L$ was shown to be nearly complete both in benzene and chloroform solutions. A different type of coordination of the rhodium atom in the solid state and in $CHCl_3$ solution was confirmed by the electronic spectra (Figure 1). Indeed an absorption band at 510 mμ (X = Cl) and at 487 mμ (X = Br) appeared in the reflectance spectra while such a band was not detected in the solution spectra in a range of molar concentration between 10^{-2} and 10^{-3}. The

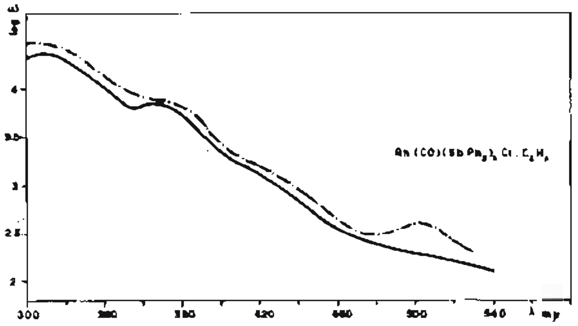

Figure 1a ——— solution spectrum (in $CHCl_3$).
— · — · — reflectance spectrum (the scale of log ε is arbitrary).

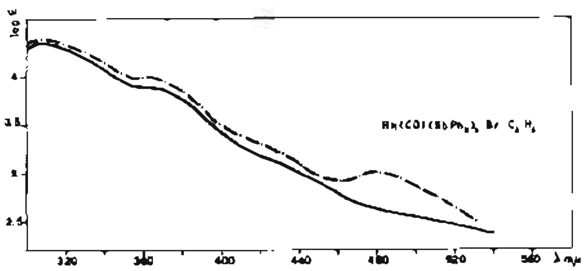

Figure 1b ——— solution spetcrum (in $CHCl_3$).
— . — . — reflectance spectrum (the scale of log ε is arbitrary).

proposed dissociation equilibrium was easily confirmed by the visible spectrum in $CHCl_3$ solution in the presence of a variable excess of stibine (Figure 2). New bands at 480-500 mμ and 418 mμ, which could be attributed to the formation of a compound with a type of coordination similar to that shown in the solid state, appeared when the ratio of added stibine to the rhodium complex was more than 10.

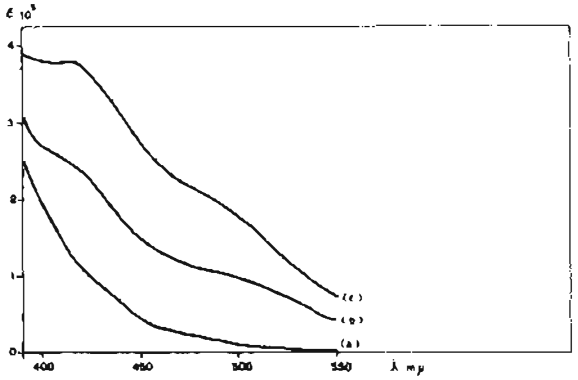

Figure 2. Visible spectrum of $[RhCl(CO)(SbPh_3)_3]$ in $CHCl_3$. (a) free complex ($c = 1.8 \times 10^{-4}$ *M*); (b) added stibine/complex = 10; (c) added stibine/complex = 25.

The electronic spectra confirm therefore the pentacoordination of the rhodium atom in the solid state; indeed a similar pattern of the visible spectrum was found for related Rh^I surely pentacoordinated compounds with similar donor atoms.[13]

The previous formulation[3] of these complexes must be attributed to the incorrect analytical data. The rhodium and halogens analysis in presence of antimony cannot be carried out in a convenient way. Indeed we found that the determination of rhodium by ignition is incorrect because of the presence of Sb_2O_4; besides, in these compounds, the gravimetric analysis of halogens, through their silver salts, gave always a variable and higher content of halogens.

On the contrary, we have found that the determination of carbon, hydrogen, oxygen and of halogens (by a potentiometric method) were the only well reproducible analyses for these compounds.

The square planar complexes $[RhCl(CO)(R_3Sb)_2]$, analogous to the related phosphine and arsine complexes, are present in dilute solutions and can be isolated in the solid state only by conducting the synthesis under controlled conditions (*e.g.* in petroleum ether at low temperature,[14] with defect of stibine).

Conclusion

It appears, therefore, that stibines do not necessarily behave as the corresponding phosphines and arsines and may yield complexes with a different stereochemistry or a different coordination number. Many factors may be operative, and indeed the observed difference between phosphine or arsine and stibine complexes seems to be less evident when the related $[(1,5\text{-cyclooctadiene})RhCl]_2$ is reacted, $[(1,5\text{-cyclooctadiene})Rh(L)Cl]$ ($L = (C_6H_5)_3P, (C_6H_5)_3As, (C_6H_5)_3Sb$) being the isolated product.[15]

However also in this case a very unstable orange compound of formula $[(1,5\text{-cyclooctadiene})Rh(L)_2Cl]$ ($L = (C_6H_5)_3Sb$) was sometimes isolated. The ratio 1,5-cyclooctadiene to stibine was confirmed by integration of the n.m.r. spectrum. This compound loses one stibine just by washing with diethyl ether.

It seems than rhodium(I) with stibine ligands has a great tendency to stabilize five coordinated species.

This is in agreement with some recent kinetic investigation[16] and with our recent observation[17] that the oxidative $d^8 \rightarrow d^6$ addition reactions are easier with stibine complexes than with related phosphine or arsine compounds.

Finally a similar stabilisation of the pentacoordinate arrangement of ligands has been noted for tertiary stibine complexes of platinum.[18]

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