J. Chem. Soc. (A), 1969

Adducts of Tertiary Stibines with Mercury(II) Halides

By G. Deganello, G. Dolcetti, and M. Giustiniani, Laboratorio di Chimica e Tecnologia dei Radioelementi, C.N.R., Università di Padova, Padova, Italy

U. Belluco, Facultè Chemica Industriale, Università di Bologna, Bologna, Italy

The preparation of Lewis-acid–base adducts of the type R_3SbHgX_2 (R = phenyl, o- and p-tolyl; X = Cl, Br, and I) are reported. Reaction of the o-tolylstibine with HgCl₂ in benzene yields Hg₂Cl₂ and R₃SbCl₂. In tetrahydrofuran the reaction products are R₂SbCl and RHgCl. These results are interpreted in terms of a scrambling occurring via a five-co-ordinate antimony labile intermediate formed via oxidative addition of the stibine by HgCl₂. Reaction of R₃Bi with HgCl₂ leads to the scrambling products R₂BiCl and RHgCl.

EXAMPLES of Lewis-acid-base adducts between mercury-(II) halides and transition-metal complexes such as $(\pi-C_6H_3Me_3)M(CO)_3$ (M = Cr or Mo),¹ Co(CO)₂($\pi-C_5H_5$), M($\pi-C_5H_5$)(diolefin) (M = Co or Rh; diolefin = cyclooctadiene or norbornadiene),² and $Fe(CO)_{3}L_{2}$ (L = phosphine, phosphite, arsine, or stibine),³ have been recently reported. Both spectroscopic and conductometric evidence suggests that they should be formulated as com-

¹ K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, J.

Chem. Soc. (A), 1968, 2851.

plexes containing metal donor atoms such as $L_2(CO)_3Fe \rightarrow$ HgX₂. The X-ray structure of $(\pi$ -C₅H₅)(CO)₂CoHgCl₂ has been recently studied and the bond distance Hg-Co is 2.58 Å, quite near to the sum of the covalent radii (2.56 Å). The two Hg-Cl distances are nearly equal and considerably greater than in HgCl₂ thus indicating a

² D. J. Cook, J. L. Dawes, and R. D. W. Kemmitt, *J. Chem. Soc.* (A), 1967, 1547. ³ D. M. Adams, D. J. Cook, and R. D. W. Kemmitt, *J. Chem.*

Soc. (A), 1968, 1067.

large electronic redistribution on the mercury atom in the complex. $\!\!\!\!^4$

During a study of the reactions of tertiary stibines with mercury(II) salts we have isolated the Lewis-acidbase adducts which are characterized by elemental analysis, i.r. spectra, conductivity measurements, and chemical reactions.

The reactions in benzene at room temperature of stibines (R_3Sb) with mercury(II) halides lead to the formation of l: l adducts:

$$R_{3}Sb + HgX_{2} \longrightarrow R_{3}Sb, HgX_{2}$$
(1)
(R = phenyl, o- and p-tolyl; X = Cl, Br, or I).

The adducts are nonconductors in dichloromethane or nitromethane. They are soluble in tetrahydrofuran, slightly soluble in benzene, dichloromethane, and nitromethane, and insoluble in alcohols and acetone. Analytical data and other properties for the *o*-tolyl adducts are reported in the Table. Their i.r. spectra

Analytical data and physical properties o	of the
$R_{o}Sb.HgX_{o}$ adducts ($R = o$ -tolvl)	

	3 , 0 4		`			5,			
	М.р.			Found (%)			Calc. (%)		
Adduct	(°C)	Colour	С	н	х	С	н	Х	
$R_3Sb,HgCl_2$	189	Colour- less	38 ·1	3.1	10.5	38 ·0 5	3.15	10.6	
R ₃ Sb,HgBr ₂	199	Colour- less	32.9	$2 \cdot 8$	21.6	33.4	2.75	21.75	
R₃Sb,HgI₂	205	Pale yello	29·5 ₩	$2 \cdot 5$	29.7	29.65	2.45	29·9	

differ from those of the parent stibines in the frequency range corresponding to the C-H out-of-plane vibrations (760—700 cm.⁻¹) and in the far i.r. (400—200 cm.⁻¹). It was impossible to identify the Hg-Cl stretching frequency because of the presence, in this region, of the stibine bands.

The donor character of antimony in the R_3Sb compounds is well known ⁵ and adducts with $AgClO_4$ have been reported recently.⁶ Because of these and bearing in mind the existence of the mercury(II) halide adducts of iron and cobalt carbonyl derivatives, we are inclined to formulate these compounds in the solid state as donoracceptor complexes containing antimony-mercury bonds:



Tri-o-tolylstibine reacts when heated under reflux in tetrahydrofuran with $HgCl_2$ according to the stoicheiometry:

$$R_3Sb + HgCl_2 \rightarrow R_2SbCl + RHgCl$$

The products have been characterized by elemental analysis and i.r. spectra. The same products have been obtained by heating the $R_3Sb_1HgCl_2$ adducts under reflux in tetrahydrofuran. This indicates that only mercury(II) halides form adducts with R_3Sb or

2139

 R_2SbCl whereas there is no reaction between R_2SbCl and the organometallic compound RHgCl. On carrying out the reactions under experimental conditions which would favour the exchange of the groups bonded to antimony and mercury (high temperature and methanol or tetrahydrofuran solution) the adduct with the Hg–Sb bond cannot be isolated. A parallel observation is that, in the reaction of tertiary stibines with mercury(II) acetate (a salt which is more dissociated than the halides), both in benzene and methanol, metallic mercury is formed according to the stoicheiometry:

$$R_2Sb + HgAc_2 \longrightarrow R_3SbAc_2 + Hg$$

1

It could be possible to relate the low stability of $R_3Sb,HgAc_2$ adducts, leading to the reduction of mercury(II), to the polarity of the HgAc bond. In other words, the formation of the Sb-Hg bond results in an increase of negative charge on the mercury atom and this can be responsible for the reduction if the groups bonded to mercury can easily accept negative charge and co-ordinate the antimony (which increases its oxidation state and co-ordination number):

$$\begin{array}{c} R \\ R \\ R \end{array} Sb \rightarrow Hg \begin{array}{c} X \\ X \\ X \end{array}$$

Such a process is facilitated by the $Hg^{+}-X^{-}$ bond polarity.

By heating the adduct $R_3Sb,HgCl_2$ under reflux in benzene Hg_2Cl_2 , R_3Sb , and R_3SbCl_2 are formed, whereas in methanol and tetrahydrofuran R_2SbCl and RHgCl are the final products. This solvent dependence is due to the scrambling of the groups bonded to the two metals. This may occur by way of the intermediate:



which can be formed via oxidative addition of $HgCl_2$ to the stibine (see Scheme).

$$\begin{array}{cccc} R_{3}Sb \rightarrow Hg & Cl & \longrightarrow \\ R_{3}Sb \rightarrow Hg & Cl & \longrightarrow \\ R & & & \\ R & & \\ Cl & & \\ Cl & & \\ &$$

Attempts to isolate adducts with triarylbismuthines were unsuccessful. Even in ether at 0° a compound R_3Bi (R = phenyl, o- and p-tolyl) reacts with HgCl₂ with the scrambling of the organic groups:

$$R_3Bi + HgCl_2 \longrightarrow R_2BiCl + RHgCl_2$$

The inability to isolate intermediates in these reactions makes it difficult to interpret the differences in the ⁶ R. H. Nuttal, E. R. Roberts, and D. W. A. Sharp. J. Chem. Soc., 1962, 2854.

⁴ I. N. Nowell and D. R. Russell, Chem. Comm., 1967, 817.

⁵ G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' vol. 1, Methuen, London, 1967, p. 510.

behaviour of the Bi^{III} and Sb^{III} derivatives when they react with HgCl₂.

One can tentatively suggest that the R_3Bi adducts are much more labile so that scrambling reaction occurs immediately. This hypothesis is supported by the isolation of adducts of the type $Ph_3Bi,AgClO_4^6$ and Ph_3Bi,SO_3 ;⁷ a certain degree of donor character has been attributed to Ph_3Bi in carbonyl complexes of nickel and molybdenum.⁸

EXPERIMENTAL

Materials.—Triphenyl-, tri-o-tolyl- and tri-p-tolyl-stibines, and the analogous bismuth compounds were prepared from corresponding trihalides and Grignard reagents. The products were recrystallized from alcohol.

Adducts of Type $R_3Sb,HgX_2.-(a)$ (o-MeC₆H₄)₃Sb,HgCl₂. A solution of HgCl₂ (5 mmoles) in benzene (15 ml.) was added to a solution of tri-o-tolylstibine (5 mmoles) in benzene (5 ml.). A microcrystalline solid precipitated after 1 hr. and after 24 hr. was filtered off, washed with ether, and dried. More product was obtained by concentration of the solution (85%).

(b) (o-MeC₆H₄)₃Sb,HgBr₂. This was prepared as in (a) (75%).

(c) $(o-\text{MeC}_6H_4)_3\text{Sb},\text{HgI}_2$. This was prepared as in (a); with ether as solvent in place of benzene, in which HgI_2 is insoluble (78%).

Nearly quantitative yields of the adducts (a), (b), and (c) were obtained by mixing ethereal solutions of the stibines and mercury halides.

Reaction of $(o-MeC_6H_4)_3Sb$ with $HgAc_2$.—A solution of tri-o-tolylstibine (5 mmoles) in benzene (5 ml.) was treated with an equimolar amount of mercury acetate. Metallic

⁷ M. Becke-Goehring and H. Thielemann, Z. anorg. Chem., 1961, **33**, 308.

mercury was formed after a few min. and was filtered off, and the solution evaporated to dryness. The white residue was recrystallized from benzene-pentane giving a product which had analysis corresponding to tri-o-tolyl-stibine diacetate (Found: C, 58.0; H, 5.1. Calc. for $C_{25}H_{27}O_4Sb$: C, 58.4; H, 5.25%).

Reaction of $(o-\text{MeC}_6\text{H}_4)_3$ Sb with HgCl₂ in Hot Benzene.—A solution of HgCl₂ (5 mmoles) in benzene (15 ml.) was added to a solution of tri-o-tolylstibine (5 mmoles) in hot benzene and heated under reflux with stirring. The white solid which had formed after 2 hr. was filtered off from the hot reaction mixture and identified as Hg₂Cl₂ by elemental analysis. The solvent was removed under reduced pressure and the residue washed with a little ether which was then found to contain R₃Sb. The residue was identified as R₃SbCl₂ by i.r. spectroscopy. Their i.r. spectra differ from that of the original stibine in the C–H stretching region (760—700 cm.⁻¹) and in the far-i.r. region (400—200 cm.⁻¹). The attribution of the stretching frequencies of Hg–X was prevented because of the presence of the stibine bands.

Reaction of $(o-\text{MeC}_{6}H_{4})_{3}$ Sb with HgCl₂ in Hot Tetrahydrofuran.—A hot solution of tri-o-tolylstibine (5 mmoles) in tetrahydrofuran was treated with a stoicheiometric amount of HgCl₂ in the same solvent. The reaction mixture was heated under reflux for 10 hr. and the white solid which had formed was filtered off and identified by analysis as $(o-\text{MeC}_{6}H_{4})_{2}$ SbCl₂. The solution was concentrated under reduced pressure and a white solid [Hg($o-\text{MeC}_{6}H_{4}$]Cl, m.p. 138°, was obtained by addition of alcohol. Its i.r. spectrum shows a band at 320 cm.⁻¹ attributable to v(Hg-Cl).

We thank the Italian National Research Council (C.N.R.) for financial support of this work.

[9/106 Received, January 20th, 1969]

⁸ D. Benlian and M. Bigorgne, Bull. Soc. chim. France, 1963, 1583.