Journal of Organometallic Chemistry, 55 (1973) 133–137

PREPARATION AND PROPERTIES OF MONOORGANOANTIMONY TETRACHLORIDE ADDUCTS

NOBORO NISHII, KATSUYA HASHIMOTO and ROKURO OKAWARA
Department of Applied Chemistry, Osaka University, Yamadakami, Suita, Osaka (Japan)
(Received October 26th, 1972)

SUMMARY

Several adducts of monoorganoantimony tetrachlorides, $RSbCl_4L$ ($R=CH_3$, C_6H_5, p-$CH_3C_6H_4$; L=HMPT, PyO, 4-CH_3PyO, DMSO), were prepared. In the solid state all of these adducts are stable at room temperature. They are monomeric in solution, and the existence of hexacoordinate antimony is indicated. CH_3SbCl_4L (L=PyO, 4-CH_3PyO) exists in two isomeric forms in solution and decomposes above 70° into CH_3Cl and $SbCl_3L$. CH_3SbCl_4(HMPT) decomposes in a similar manner even at room temperature.

INTRODUCTION

It is known[1] that monoalkylantimony tetrachlorides decompose readily at room temperature:

$$RSbCl_4 \rightarrow SbCl_3 + RCl$$

It seemed attractive to attempt to stabilize these chlorides by the addition of a neutral oxygen donor molecule, as has been reported[2,3] with the diorganoantimony trichlorides.

EXPERIMENTAL

All the reactions were carried out under a nitrogen atmosphere. Phenyl- and p-tolyldichlorostibine were prepared as reported[4].

Preparation of $RSbCl_4L$ *(*$R=CH_3$*,* C_6H_5*,* p-$CH_3C_6H_4$*;* L* *= HMPT, PyO, 4-*CH_3*-PyO, DMSO)***

All of these adducts were prepared in an essentially identical manner, so that details of only one typical experiment are given.

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[*] HMPT = hexamethylphosphoric triamide; PyO = pyridine *N*-oxide; 4-CH_3PyO = γ-picoline *N*-oxide; DMSO = dimethyl sulfoxide.

[**] Crystals of what apparently were the triphenylphosphine oxide adducts could also be obtained (*cf.* ref. 2), but the results of the elemental analyses were not satisfactory.

A solution of methyldichlorostibine[1] (3.5 g, 0.017 mol) in dichloromethane (15 ml) was cooled to −70°. A solution of sulfuryl chloride (2.3 g, 0.017 mol) in dichloromethane (10 ml) and then a solution of HMPT (3.1 g, 0.017 mol) in dichloromethane (10 ml) were added dropwise with stirring. After stirring for half an hour, the solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane and petroleum ether to give white crystals of $CH_3SbCl_4(HMPT)$.

These adducts are non-hygroscopic crystalline compounds and can be handled in air. Their properties are listed in Table 1.

TABLE 1

PROPERTIES OF $RSbCl_4L$ AND $SbCl_3L$

Adduct		*M.p.* (°C)	*Analysis found (calcd.) (%)*			*Mol. wt.*[a] *found (calcd.)*
R	*L*		*C*	*H*	*N*	
$RSbCl_4L$						
CH_3	HMPT	60–62	18.22 (18.37)	4.93 (4.62)	9.79 (9.18)	
C_6H_5	HMPT	117	27.32 (27.72)	4.76 (4.46)	8.26 (8.08)	497 (520)
p-$CH_3C_6H_4$	HMPT	189–191	29.29 (29.25)	5.02 (4.72)	7.82 (7.87)	512 (534)
CH_3	PyO	87– 88 (dec.)	18.98 (19.28)	2.12 (2.16)	3.90 (3.75)	337 (374)
C_6H_5	PyO	156–157	29.33 (30.32)	2.40 (2.31)	3.27 (3.21)	475 (436)
p-$CH_3C_6H_4$	PyO	169–170	31.84 (32.04)	2.85 (2.69)	2.89 (3.11)	476 (450)
CH_3	4-CH_3PyO	68– 70 (dec.)	21.48 (21.68)	2.70 (2.60)	3.62 (3.61)	391 (388)
C_6H_5	DMSO[c]	185 (dec.)	21.90 (22.94)	2.84 (2.65)		[d]
p-$CH_3C_6H_4$	DMSO[c]	176 (dec.)	24.35 (24.98)	3.19 (3.03)		[d]
$SbCl_3L$[e]						
	HMPT	81 (dec.)	17.54 (17.69)	4.71 (4.45)	10.58 (10.32)	
	4-CH_3PyO	[f]	21.18 (21.37)	2.33 (2.09)	4.06 (4.15)	

[a] Determined cryoscopically in nitrobenzene. [b] Not determined because of the instability in solution. [c] DMSO adducts could not be recrystallized because of limited solubility. [d] Not determined because of limited solubility. [e] Obtained from an equimolar mixture of $SbCl_3$ and L in dichloromethane. [f] Not solidified.

Physical measurements

IR spectra were obtained in Nujol mulls with a Hitachi EPI-2G, -225 or -L spectrophotometer equipped with gratings, and PMR data were obtained with a

TABLE 2

RELEVANT IR STRETCHING FREQUENCIES OF $RSbCl_4L$ AND $SbCl_3L$ IN NUJOL MULLS (IN cm^{-1})

Adduct	*ν(Sb–Cl)*	*ν(X–O)*[a]
L=HMPT		1212
CH_3SbCl_4L	316	1057
$C_6H_5SbCl_4L$	309	1029
p-$CH_3C_6H_4SbCl_4L$	324	1052
$SbCl_3L$	305, 278	1186
L=PyO		1265
CH_3SbCl_4L	317	1194
$C_6H_5SbCl_4L$	319	1191
p-$CH_3C_6H_4SbCl_4L$	320	1195
L=4-CH_3PyO		1248
CH_3SbCl_4L	320	1195
$SbCl_3L$	298, 275	1197
L=DMSO		1045
$C_6H_5SbCl_4L$	322	880
p-$CH_3C_6H_4SbCl_4L$	322	874

[a] X=P, N or S.

TABLE 3

PROTON CHEMICAL SHIFTS[a] OF $RSbCl_4L$ AND $SbCl_3L$ IN DICHLOROMETHANE AT 22° (5 wt %)

Adduct			*δ(ppm)*
R	*L*		
$RSbCl_4L$			
CH_3	HMPT	Sb–CH_3	2.84
		N–CH_3	2.89, 2.73
C_6H_5	HMPT	N–CH_3	2.71, 2.54
p-$CH_3C_6H_4$	HMPT	C–CH_3	2.36
		N–CH_3	2.71, 2.54
CH_3	PyO	Sb–CH_3	2.94
			2.82
p-$CH_3C_6H_4$	PyO	C–CH_3	2.40
CH_3	4-CH_3PyO	Sb–CH_3	2.93
			2.78
		C–CH_3	2.66
			2.64
$SbCl_3L$			
	HMPT	N–CH_3	2.75, 2.59
	4-CH_3PyO	C–CH_3	2.53[b]

[a] Internal reference: TMS. [b] In nitrobenzene.

Japan Electron Optics JNM-3H-60 spectrometer at 60 MHz or a Japan Electron Optics JNM-PS-100 spectrometer at 100 MHz.

The results are tabulated in Tables 2 and 3.

RESULTS AND DISCUSSION

A lowering of the IR frequency of the P–O, N–O or S–O stretching vibration (Table 2) for all of these adducts indicates that oxygen is the donor atom[5]. Since the determinations of the molecular weights of the adducts in nitrobenzene give monomeric values (Table 1), the presence of hexacoordinate antimony is suggested, as is the case with the diorganoantimony trichloride adducts[2].

As shown in Fig. 1, the PMR spectrum of $CH_3SbCl_4(4\text{-}CH_3PyO)$ in benzene shows two pairs of resonances *a* and *a'* due to the $Sb-CH_3$ protons, and *b* and *b'* due to the $C-CH_3$ protons. Integration of the signals allows the assignment of resonances *a* and *b* to one species while *a'* and *b'* to the other. Since the intensity ratios *a*/*b* and *a'*/*b'* are always equal to unity and the populations of the two different species appear to depend on the nature of the solvent (Table 4), it is most likely that two isomeric forms of the adduct exist, as is the case[6] with dihalodiaryl(acetylacetonato)antimony-(V). As can be seen from the PMR spectra (Tables 3 and 4), $CH_3SbCl_4(PyO)$ also appears to exist in two isomeric forms in solution.

Two isomers (I) and (II) as shown are possible for these hexacoordinate adducts. Since the *cis*-isomer (I) is considered to be more polar than the *trans*-isomer (II), the

TABLE 4

ISOMER RATIOS, *a* (*trans*-)/*a'* (*cis*-), OF CH_3SbCl_4L IN VARIOUS SOLVENTS AT 22°[a]

Solvent	*L*	
	4-CH₃PyO	*PyO*
C_6H_6	1.86	2.00
CH_2Cl_2	1.53	1.48
$C_6H_5NO_2$	1.25	0.75
$C_6H_6+C_6H_5NO_2$	1.40	1.16

[a] An approximately linear relationship exists between *a*/*a'* and the dielectric constants of the solvents.

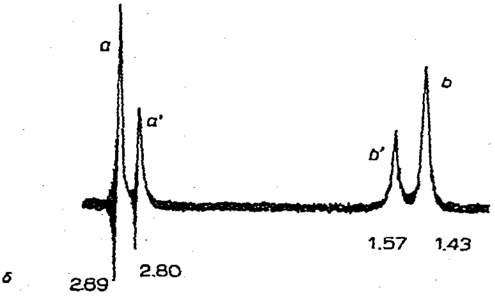
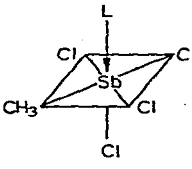
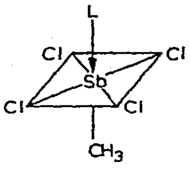


Fig. 1. Methyl region of the PMR spectrum of $CH_3SbCl_4(4\text{-}CH_3PyO)$ in benzene at room temperature.

isomer (I) will be favoured in more polar solvents. Consequently, the signals *a'* and *b'*, the intensities of which increase in more polar solvents (Table 4), may be tentatively assigned to the *cis*-isomer (I).



(I)



(II)

As the temperature of the sample of $CH_3SbCl_4(4\text{-}CH_3PyO)$ in nitrobenzene was raised above 70°, the intensities of the Sb–CH_3 proton resonances *a* and *a'* and those of the C–CH_3 proton resonances *b* and *b'* began to decrease, and two new signals appeared, which are assignable[*] to the protons of CH_3Cl and the C–CH_3 of $SbCl_3(4\text{-}CH_3PyO)$, respectively. This change was shown to be irreversible and a thermal decomposition of the adduct into CH_3Cl and $SbCl_3(4\text{-}CH_3PyO)$ was indicated.

$CH_3SbCl_4(PyO)$ and $CH_3SbCl_4(HMPT)$ in solution also similarly decompose above 70°. The latter adduct gradually decomposes even at room temperature.

ACKNOWLEDGEMENTS

Thanks are due to Prof. D. G. White of The George Washington University for his help in improving our manuscript.

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[*] The chemical shifts of these two new signals at room temperature were 2.95 and 2.53 ppm.