Journal of Organometallic Chemistry, 184 (1980) 57—62

SYNTHESIS AND SPECTRAL STUDIES OF (1,3-DIKETONATO)TRIPHENYLANTIMONY(V) COMPLEXES

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(Received June 26th, 1979)

Summary

Ph_3SbBr_2 reacts with Na[RCOCHCOR′] to form compounds of the type $Ph_3SbBr(RCOCHCOR')$ (where $R = R' = CH_3$, $C(CH_3)_3$ and $R \neq R' = CH_3$, C_6H_5; CH_3, 4′-MeC_6H_4; CH_3, 4′-$MeOC_6H_4$; CH_3, 4′-ClC_6H_4; CH_3, 4′-BrC_6H_4 and CF_3, 2-C_4H_3S). Reactions of $Ph_3Sb(OMe)_2$ with $RCOCH_2COR'$ yield $Ph_3Sb(OMe)$ (RCOCHCOR′). From molecular weight, IR and NMR data, it is concluded that 1,3-diketone ligand moiety behaves as a bidentate ligand in these complexes. The stereochemistries of the complexes containing both symmetrical and unsymmetrical ligands are discussed.

Introduction

This paper is concerned with the synthesis and structure of a number of 1,3-diketonates of triphenylantimony(V), which have received little attention [1]. It has been observed that the reaction of triphenylantimony dibromide with the sodium salt of a 1,3-diketone even in excess always yields the monosubstituted product in which the coordination number of antimony is apparently six.

Results and discussion

On refluxing triphenylantimony dibromide with the sodium salt of a 1,3-diketone in benzene (1 : 1 or even higher molar ratios), complexes of the type, $Ph_3SbBr(RCOCHCOR')$, were obtained:

$$Ph_3SbBr_2 + Na(RCOCHCOR') \xrightarrow{\text{benzene}} Ph_3SbBr(RCOCHCOR') + NaBr$$

(where R and R′ = CH_3, CH_3 (Acac); $C(CH_3)_3$, $C(CH_3)_3$ (Dpm); CH_3, C_6H_5

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(Bzac); CH_3, 4'-MeC_6H_4 (4'-MeBzac); CH_3, 4'-$MeOC_6H_4$ (4'-MeOBzac); CH_3, 4'-ClC_6H_4 (4'-ClBzac); CH_3, 4'-BrC_6H_4 (4'-BrBzac) and CF_3, 2-C_4H_3S (Ttfac))

Similarly, the reactions of triphenylantimonydimethoxide with 1,3-diketone in 1 : 1 or in 1 : 2 ratios yielded $Ph_3Sb(OMe)(RCOCHCOR')$:

$$Ph_3Sb(OMe)_2 + RCOCH_2COR' \xrightarrow{\text{benzene}} Ph_3Sb(OMe)(RCOCHCOR') + MeOH$$

(where R and R' = CH_3, CH_3 and CH_3, C_6H_5)

The lack of replacement of the halide or methoxide by a second 1,3-diketone moiety in these cases may be ascribed either to steric factors or to the reluctance of antimony to increase its coordination number beyond six. The bromine atom of the $Ph_3SbBrBzac$ compounds can, however, be replaced by other monodentate ligands:

$$Ph_3SbBrBzac + NaX \xrightarrow{\text{benzene}} Ph_3SbXBzac + NaBr$$

(where X = OEt or OAc)

It may be relevant to mention here that in the reactions of niobium and tantalum pentaalkoxides with 1,3-diketones, the highest substituted products obtained are dialkoxide tris(1,3-diketonates), in which these transition metals probably attain the coordination number eight [2—5].

All the 1,3-diketonato complexes are white to cream coloured crystalline solids, monomeric in refluxing benzene and sensitive to moisture. They can be recrystallized from benzene-hexane or benzene—light petroleum mixtures.

The absence of free carbonyl absorptions in the IR spectra and the presence of absorptions due to the coordinated carbonyl group (ν(C$\because$O)) in the region 1560—1605 cm^{-1} indicate that the ligand moieties are chelated [1,5]. Compared to the free ligand the C$\because$C stretching band appears at slightly lower wave numbers. Weak absorptions in the region 380—425 cm^{-1} may be assigned to the ν(Sb—O) stretching frequency [1,6—8].

The PMR spectra of some of these compounds were recorded in $CDCl_3$ at room temperature (Table 1). The presence of one methine signal in these derivatives indicates only one configuration at the room temperature [1]. Appearance

TABLE 1

PMR SPECTRAL DATA FOR COMPLEXES $Ph_3SbX(RCOCHCOR')$ IN $CDCl_3$ AT ROOM TEMPERATURE

Complexes	Chemical shifts (δ, ppm)			
	=CH	—CH_3	—$C(CH_3)_3$	—OMe
$Ph_3SbBrAcac$	5.65	2.27		
$Ph_3Sb(OMe)Acac$	5.50, 5.72	2.07, 2.18 2.30		3.39, 3.74 3.95
$Ph_3SbBrDpm$	5.98		1.51	
$Ph_3SbBrBzac$	6.40	2.48		
$Ph_3Sb(OMe)Bzac$	6.19, 6.40	2.30, 2.45		3.37, 3.73, 4.04
Ph_3SbBr4'-MeBzac	6.34	2.41, 2.64		

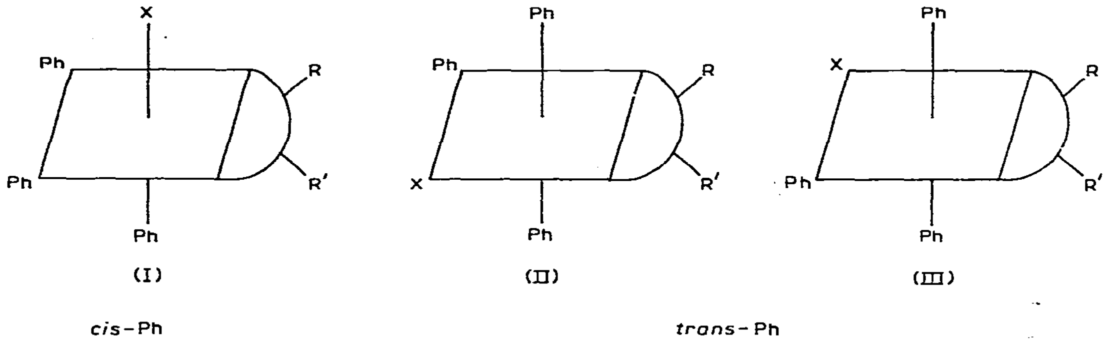

Fig. 1. Structure of compounds I—III.

of only one signal due to the methine and terminal alkyl groups in the PMR spectra of triphenylantimony complexes with symmetrical ligands (Ph_3SbBr-Acac and $Ph_3SbBrDpm$) at first sight might suggest the symmetrical configuration in which bromo substituent occupies the axial position at the ambient temperatures (Fig. 1, I, $R = R' = CH_3$ and $C(CH_3)_3$). However, at room temperature the possibility of a configuration in which bromo substituent occupies the equatorial position can not be ruled out completely, and a low temperature PMR spectra of $Ph_3SbClAcac$ [1] unequivocally points to a configuration in which chlorine atom occupies an equatorial position (Fig. 1, II, $R = R' = CH_3$ and $X = Cl$). These complexes may also have a similar configuration (Fig. 1, II, $R = R' = CH_3$ or $C(CH_3)_3$ and $X = Br$). This accidental degeneracy of terminal alkyl groups in these derivatives at ambient temperature might be due to the non-rigid configuration of these molecules.

In case of complexes with unsymmetrical ligands ($Ph_3SbBrBzac$, Ph_3SbBr4'-MeBzac and $Ph_3SbBrTtfac$) three geometrical isomers are possible (Fig. 1, I, II, III, $R \neq R'$; $X = Br$). Since PMR spectra of these complexes at room temperature also exhibit one methine and methyl resonances, it is difficult to assign a definite configuration. Similarly ^{19}F NMR spectrum of $Ph_3SbBrTtfac$ show only one signal due to CF_3 group at 0.5 ppm.

The presence of two methine protons in the PMR spectra of $Ph_3Sb(OMe)Acac$ and $Ph_3Sb(OMe)Bzac$ suggest that both the geometric forms (*cis*-Ph and *trans*-Ph) exists at room temperature.

Experimental

Triphenylantimony dibromide [9], triphenylantimony dimethoxide [10,11], 1-(4'-methylphenyl) butane-1,3-dione [12], 1-(4'-methoxyphenyl) butane-1,3-dione [13], 1-(4'-chlorophenyl)butane-1,3-dione [14] and 1-(4'-bromophenyl)-butane-1,3-dione [15] have been prepared by the reported methods. Solvents and other materials were dried and purified before use. All reactions were carried out under anhydrous conditions. Antimony and bromine were estimated by iodometric and Volhard's methods respectively [16,17]. Carbon and hydrogen were analysed with a Colman—Carbon Hydrogen Analyzer.

IR spectra were measured in Nujol mulls between KBr plates in the range

TABLE 2

REACTIONS OF TRIPHENYLANTIMONYDIBROMIDE WITH SODIUM SALT OF 1,3-DIKETONES AND TRIPHENYLANTIMONYDIMETHOXIDE WITH 1,3-DIKETONES

Reactants (g)			Product and (%) yield of recrystallized compound	M.p. (°C)	Analysis Found (calcd.) (%)				IR assignments $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ (cm^{-1})
Ligand	sodium	Ph_3SbBr_2			C	H	Br	Sb	
AcacNa		2.10	$Ph_3SbBrAcac$	168	52.24	4.63	15.19	22.64	1560–70vs
0.52			(~68)	(dec.)	(51.92)	(4.17)	(15.02)	(22.88)	
DpmH	0.12	2.48	$Ph_3SbBrDpm$	222	55.20	5.51	13.07	19.17	1560–75vs
0.91			(~51)		(56.54)	(5.56)	(12.97)	(19.76)	
BzacH	0.10	2.18	$Ph_3SbBrBzac$	169–70	56.86	4.86	13.07	20.27	1590vs
0.69			(~73)	(dec.)	(56.62)	(4.07)	(13.45)	(20.49)	
4'-MeBzacH	0.09	2.03	Ph_3SbBr-4'-MeBzac	175	57.64	4.66	12.75	20.54	1587vs
0.70			(~60)	(dec.)	(57.27)	(4.31)	(13.14)	(20.02)	
4'-MeOBzacH	0.11	2.35	Ph_3SbBr-4'-MeOBzac	218	55.28	4.71	13.24	19.47	1605vs
0.88			(~36)	(dec.)	(55.80)	(4.20)	(12.80)	(19.51)	
4'-MeBzacH	0.07	1.51	Ph_3SbBr-4'-ClBzac	235	52.98	4.21	12.69	19.80	1585vs
0.58			(~60)	(dec.)	(53.50)	(3.69)	(12.71)	(19.37)	
4'-BrBzacH	0.09	1.97	Ph_3SbBr4'-BrBzac	242	50.05	4.02	11.72	18.95	1584vs
0.92			(~64)		(49.96)	(3.44)	(11.87)	(18.09)	
TtfacH 0.94	0.10	2.19	$Ph_3SbBrTtfac$	139–40	47.29	3.46	11.73	19.09	1595vs
			(~58)		(47.74)	(2.93)	(12.21)	(18.61)	
	$Ph_3Sb(OMe)_2$								
AcacH		1.48	$Ph_3Sb(OMe)Acac$	142–3	58.11	5.86		25.33	1555–65vs
0.36			(~62)		(59.65)	(5.22)		(25.20)	
BzacH		1.98	$Ph_3Sb(OMe)Bzac$	145	64.21	5.48		22.14	1583vs
(0.76)			(~66)	(dec.)	(63.88)	(4.99)		(22.33)	

4000—400 cm^{-1} and in CsI plates in the range 600—200 cm^{-1} with a Perkin—Elmer Model 577 Spectrophotometer. The PMR spectra were determined on a Perkin—Elmer $R_{12}B$ Spectrometer (60 MHz) in $CDCl_3$ solutions using TMS as an external standard. The ^{19}F NMR spectrum was recorded, with the same spectrometer working at 56.4 MHz, in $CHCl_3$ solution using TFA as an external standard. Molecular weights have been determined with a semi-micro ebulliometer (Gallenkamp) using thermistor sensor.

Reaction of triphenylantimonydibromide with sodium salt of 1-phenylbutane-1,3-dione in 1 : 1 molar ratio

A benzene solution of triphenylantimonydibromide (2.18 g) was added to a suspension of sodium salt of 1-phenylbutane-1,3-dione (prepared from 0.10 g sodium and 0.69 g ligand) in benzene. The mixture was refluxed for 2 h. The sodium bromide formed was filtered off and the filtrate was evaporated under vacuum. Recrystallization from benzene—hexane mixture gave a white crystalline solid (yield ~73%). M.p. 169—170°C (dec.). Anal. Found: C, 56.86; H, 4.86; Br, 13.07; Sb, 20.27. $Ph_3SbBrBzac$ calcd.: C, 56.62; H, 4.07; Br, 13.45; Sb, 20.49%.

Reaction of triphenylantimonydimethoxide with pentane-2,4-dione in 1 : 1 ratio ratio

A mixture of triphenylantimonydimethoxide (1.48 g) and pentane-2,4-dione (0.36 g) was refluxed in anhydrous benzene for 2 h. A methanol—benzene mixture was fractionated out on a fractionation column. Excess benzene was removed under vacuum, giving a cream coloured solid. Recrystallization from benzene—light petroleum mixture gave a white crystalline solid (yield 62%). M.p. 142—143°C. Anal. Found: C, 58.11; H, 5.86; Sb, 25.33. $Ph_3Sb(OMe)Acac$ calcd.: C, 59.65; H, 5.22; Sb, 25.20%.

All other reactions are summarized in Table 2.

Acknowledgement

One of the authors (V.K.J.) is grateful to the University Grants Commission, New Delhi for the award of a Junior Research Fellowship under the Special Assitance Programme.

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