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INVESTIGATIONS ON ORGANOANTIMONY COMPOUNDS

XVII *. PREPARATION AND PROPERTIES OF HETEROCYCLIC *trans*-DICHLORO-β-DIKETONATO-*cis*-DIORGANOANTIMONY(V) COMPOUNDS. INFLUENCE OF STEREOCHEMISTRY ON β-DIKETONATE LIGAND EXCHANGE REACTIONS IN OCTAHEDRAL DICHLORO-β-DIKETONATODIORGANOANTIMONY(V) COMPOUNDS

H.A. MEINEMA and J.G. NOLTES

Institute for Organic Chemistry TNO, Utrecht (The Netherlands)

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Summary

A series of heterocyclic *trans*-dichloro-β-diketonato-*cis*-diorganoantimony(V) compounds of the type R_2SbCl_2X (R_2 = $(CH_2)_4$, $(CH_2)_5$, *o,o'*-$C_6H_4C_6H_4$, *o,o'*-$C_6H_4CH_2C_6H_4$; X = Acac, Dpm) has been synthesized. The stereochemistry of these compounds has been deduced from PMR spectroscopic and molecular dipole moment data. Since the *cis*-dichloro-β-diketonato-*trans*-diorganoantimony(V) compounds R_2SbCl_2Acac (R = Me, Et, Ph) were known previously, a set of both *cis*- and *trans*-diorgano main group organometallic complexes has thus been made available, which allows a comparative study of the influence of stereochemistry on the strength of metal—ligand interactions in this type of octahedral d^{10} metal complex. β-Diketonate—ligand exchange reactions have been studied by PMR spectroscopy, and a marked influence of stereochemistry observed. *trans*-Dichloro-β-diketonato-*cis*-diorganoantimony(V) compounds undergo ligand exchange only slowly, if at all, whereas *cis*-dichloro-β-diketonato-*trans*-diorganoantimony(V) compounds react instantaneously. Both PMR chemical shift data and IR spectroscopic data point to the occurrence of a stronger antimony-β-diketonate interaction in *trans*-dichloro-β-diketonato-*cis*-diorganoantimony than in *cis*-dichloro-β-diketonato-*trans*-diorganoantimony compounds. This can be understood in terms of the hybridization of the antimony valence orbitals. The results are in line with the assumption that Sb—O bond rupture is the rate-determining step in β-diketonate ligand exchange.

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* For Part XVI, see ref. 1.

Introduction

The stereochemistry of hexacoordinate β-diketonatoorganoantimony(V) compounds of the type $R_nSbCl_{4-n}X$ (n = 1—4, X = β-diketonate ligand) has been much studied in recent years ([2,3] and references cited therein) and a marked influence of geometric configuration on the antimony-β-diketonate ligand interaction has been observed in the octahedral dichloro-β-diketonato-diorganoantimony(V) compounds (R_2SbCl_2X). This phenomenon has been studied by PMR spectroscopy with isomeric *cis*-dichloro-β-diketonato-*trans*-diphenyl- and *trans*-dichloro-β-diketonato-*cis*-diphenyl-antimony(V) compounds and with heterocyclic dichloro-β-diketonato-*cis*-diarylantimony(V) compounds [4,5]. Dichloro-β-diketonatodialkylantimony(V) compounds (R_2SbCl_2X, R = Me, Et) have the *cis*-dichloro-*trans*-dialkyl configuration [2,3,6] and compounds R_2SbCl_2X in which the alkyl groups occupy *cis*-positions have not previously been reported. In continuation of a study on heterocyclic *cis*-"dialkyl"antimony (V) compounds [1,7] we have prepared dichloro-β-diketonato-*cis*-"dialkyl"antimony(V) compounds in which the antimony—carbon bonds are in a heterocyclic ring. The compounds have been included in our study of the influence of geometrical configuration on antimony-β-diketonate ligand interaction in R_2SbCl_2X compounds. Some of the results has been reported in preliminary form [4,5] and full details are now given below.

Results and discussion

Preparation of dichloro-β-diketonatodiorganoantimony(V) compounds

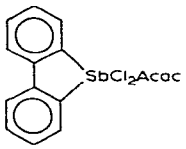
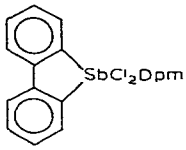
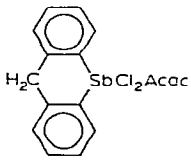
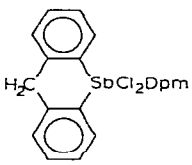
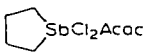
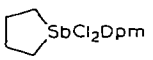
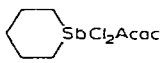
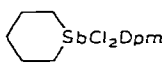
Dichloro-β-diketonatodiorganoantimony(V) compounds (R_2SbCl_2X, R = Me, Et, Ph; X = Acac, Dpm) are easily prepared by the 1/1 molar reaction of the corresponding trichlorodiorganoantimony(V) compounds (R_2SbCl_3) with acetylacetone (HAcac) and dipivaloylmethane (HDpm), respectively [4—6,8]. This procedure has been applied successfully to the synthesis of heterocyclic dichloro-β-diketonato-*cis*-diorganoantimony compounds. Reaction of 5,5,5-trichlorodibenzostibole [9], 5,5,5-trichloro-5,10-dihydrodibenz[*b*,*e*]-antimonin [1], 1,1,1-trichlorostibolane [1] and 1,1,1-trichloroantimonane [1] with acetylacetone or dipivaloylmethane gives the corresponding dichloro-β-diketonato derivatives in fairly good yields. Melting points and analytical data are presented in Table 1. These compounds are monomeric in benzene, as shown by vapour pressure osmometric molecular weight determinations.

IR data

For each of the dichloro-β-diketonato-*cis*-diorganoantimony(V) compounds compiled in Table 1 the positions of the infrared absorption bands connected with the β-diketonate ligand are very similar to those reported for corresponding dichloroacetylacetonatodiorganoantimony(V) compounds (R_2SbCl_2Acac, R = Me, Et, Ph), in which the β-diketonate ligand is known to be bidentate [6]. Very strong absorption bands due to coupled ν(C=O), ν(C=C) stretching vibrations are observed in the region 1600—1500 cm^{-1}. Antimony—carbon, antimony—oxygen, antimony—chlorine and ring-skeletal vibrations are observed in the region 600—250 cm^{-1} but have not been individ-

TABLE 1

MELTING POINTS AND ANALYTICAL DATA FOR SOME HETEROCYCLIC DICHLORO-β-DIKETONATO-*cis*-DIORGANOANTIMONY (V) COMPOUNDS

Compound	M.p. (°C)	Analysis (found (calcd.) (%))			
		Sb	Cl	C	H
	198—204		15.76 (15.97)	46.16 (46.00)	3.45 (3.40)
	245—247		13.18 (13.43)	52.44 (52.31)	5.21 (5.15)
	220—230		16.52 (15.50)	46.47 (47.16)	3.72 (3.17)
	278—280		13.48 (13.10)	53.02 (53.14)	5.43 (5.35)
	134	35.05 (35.00)	20.50 (20.38)	31.05 (31.05)	4.50 (4.34)
	140	28.34 (28.18)	16.62 (16.41)	41.70 (41.70)	6.41 (6.30)
	120	33.36 (33.64)	19.44 (19.59)	33.47 (33.19)	4.87 (4.73)
	125—135	29.16 (27.29)	16.79 (15.90)	42.42 (43.08)	6.71 (6.55)

ually assigned. IR spectral data recorded in the region 2000—250 cm^{-1} are given in the Experimental section.

PMR data

In Tables 2 and 3 β-diketonate ligand PMR chemical shift data are listed for the various dichloro-β-diketonatoantimony(V) compounds discussed in this paper. These data allow the assignment of the stereochemistry of these complexes. The heterocyclic diorganoantimony(V) compounds, 1,1-dichloro-1-

(continued on p. 440)

TABLE 2

PMR CHEMICAL SHIFT DATA FOR DICHLOROACETYLACETONATODIORGANOANTIMONY(V) COMPOUNDS, R_2SbCl_2Acac

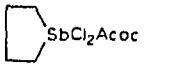
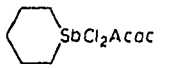
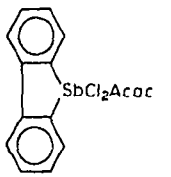
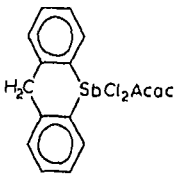
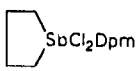
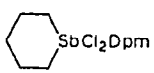
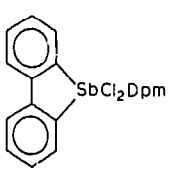
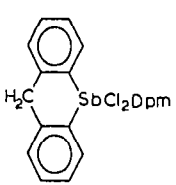
Compound	Chemical shifts Acac ligand protons (ppm)						Solvent shifts (ppm)				Reference
	$\delta(CCl_4)$		$\delta(CDCl_3)$		$\delta(C_6D_6)$		$\Delta^{CCl_4}_{C_6D_6}$		$\Delta^{CDCl_3}_{C_6D_6}$		
	CH	CH_3	CH	CH_3	CH	CH_3	CH	CH_3	CH	CH_3	
Me_2SbCl_2Acac	5.50	2.11	5.62	2.15	4.65	1.39	0.85	0.72	0.97	0.76	6, 8, 10
Et_2SbCl_2Acac	5.52	2.10	5.56	2.10	4.85	1.52	0.67	0.58	0.71	0.58	6, 10
	5.68	2.16	5.76	2.15	5.00	1.50	0.68	0.66	0.76	0.65	[a]
	5.62	2.08	5.68	2.08	4.96	1.47	0.66	0.61	0.72	0.61	[a]
Ph_2SbCl_2Acac	5.23 5.72	1.99 2.16	5.38 5.83	2.02 2.17	4.57 5.05	1.37 1.47	0.66 0.67	0.62 0.69	0.81 0.78	0.65 0.70	4–6, 8, 10
	5.86 5.71	2.36 2.36;1.94	5.93 5.77	2.32 2.34;1.90	5.08 4.94	1.58 1.67;1.08	0.78 0.77	0.78 0.69;0.86	0.85 0.83	0.74 0.67;0.82	4, 11
	5.83	2.30	5.92	2.29	5.10	1.56	0.73	0.74	0.82	0.73	5 [a]

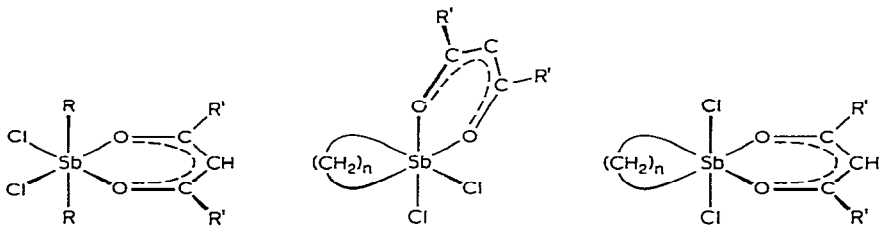
TABLE 3

PMR CHEMICAL SHIFT DATA FOR DICHLORODIPIVALOYLMETHANATODIORGANOANTIMONY(V) COMPOUNDS, N_2SbCl_2Dpm

Compound	Chemical shifts Dpm ligand protons (ppm)				Solvent shifts (ppm)		Reference
	$\delta(CDCl_3)$		$\delta(C_6D_6)$		$\Delta^{CDCl_3}_{C_6D_6}$		
	CH	*t*-Bu	CH	*t*-Bu	CH	*t*-Bu	
Me_2SbCl_2Dpm	5.96	1.18	5.65	0.93	0.31	0.25	5 [a]
Et_2SbCl_2Dpm	5.88	1.16	5.72	1.06	0.16	0.12	[a]
	6.02	1.22	5.97	1.06	0.05	0.16	[a]
	5.97	1.18	5.89	1.03	0.08	0.15	[a]
Ph_2SbCl_2Dpm	5.64 6.08	1.11 1.22	5.45 6.00	0.89 1.06	0.19 0.08	0.22 0.16	4
	6.22 6.12	1.38 1.39; 0.94	6.07 6.01	1.15 1.24; 0.69	0.15 0.11	0.23 0.15; 0.25	4 [a]
	6.18	1.35	6.07	1.12	0.11	0.23	[a]

[a] This paper.

acetylacetonatostibolane, 1,1-dichloro-1-dipivaloylmethanatostibolane, 1,1-dichloro-1-acetylacetonatoantimonane and 1,1-dichloro-1-dipivaloylmethanato-antimonane all show only one singlet due to the β-diketonate ligand CH proton, indicating the presence of only one configuration. The *trans*-diorgano structure (I) is excluded because of the constraints of the heterocyclic $(CH_2)_4Sb$ ring. The appearance of only one singlet due to Acac- or Dpm-CH_3 protons excludes the asymmetric configuration (II) (cf. ref.4) leaving the *trans*-dichloro-*cis*-diorgano configuration (III) for these compounds.



(I) (II) (III)

In agreement with this assignment 1,1-dichloro-1-acetylacetonatostibolane (III, R′ = Me, n = 4) and 1,1-dichloro-1-acetylacetonatoantimonane (III, R′ = Me, n = 5) have been found to possess a low dipole moment (2.1 ± 0.2 and 1.8 ± 0.2 Debye, respectively). For comparison , Me_2SbCl_2Acac, which is known to possess the *trans*-diorgano configuration (I), has a relatively high dipole moment (6.4 Debye) [6].

PMR spectrocopic study of β-diketonate ligand exchange reactions in compounds R_2SbCl_2X

The availability of various types of dichloro-β-diketonato-*cis*- and -*trans*-diorganoantimony(V) compounds offers the opportunity of studying the influence of geometric configuration on the strength of the antimony-β-diketonate ligand interaction in compounds R_2SbCl_2X (X = β-diketonate ligand).

Dichloro-β-diketonatodiphenylantimony compounds are present in solution in two isomeric forms. In the PMR spectra a "high-field" set of β-diketonate ligand proton signals belongs to the *cis*-dichloro-*trans*-diphenyl isomer and a "low-field" set to the *trans*-dichloro-*cis*-diphenyl isomer [6]. In the systems Ph_2SbCl_2Acac + HDpm and Ph_2SbCl_2Dpm + HAcac the β-diketonate ligand exchange process has been followed by PMR spectroscopy on chloroform and benzene solutions. As shown in Fig.1 initially a fast ligand exchange process takes place between the *trans*-diphenyl isomer and the free ligand, whereas the *cis*-diphenyl-*trans*-dichloro isomer appears to be inert. These results clearly demonstrate the remarkable influence of stereochemical configuration on antimony β-diketonate ligand interactions in octahedral dichloro-β-diketonatodiorganoantimony(V) compounds. After a longer period the occurrence of a much slower isomerization process leads to the formation of a mixture of isomers, as shown by a decrease of the amount of *trans*-dichloro-*cis*-diphenyl isomer initially present and the appearance of the β-diketonate ligand exchanged product. However, the occurrence of a very slow ligand exchange process between the

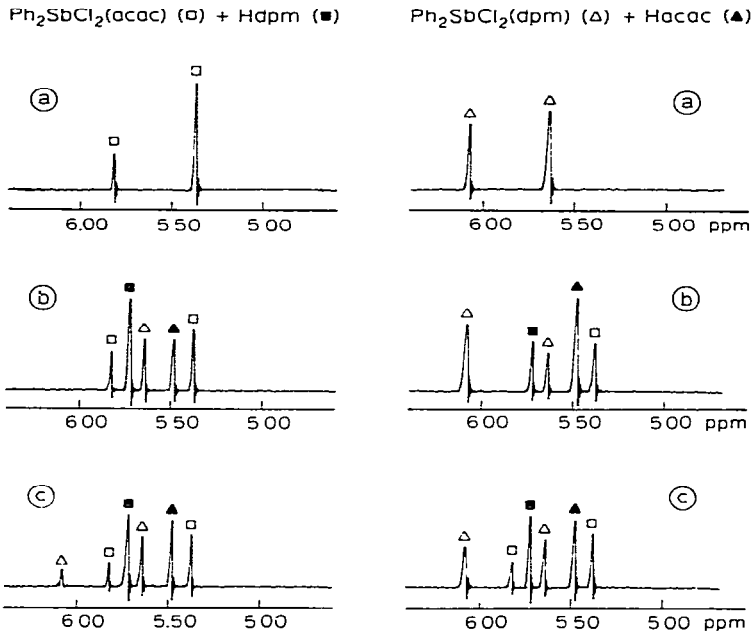
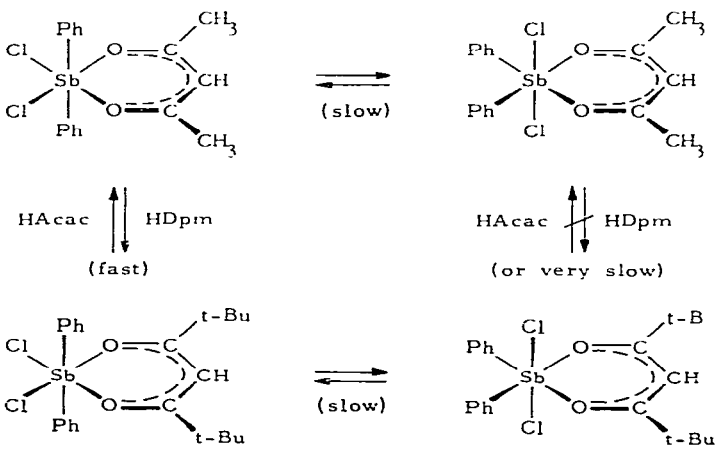


Fig. 1. CH = PMR spectra of mixtures of Ph_2SbCl_2Acac □ + HDpm ■, and of Ph_2SbCl_2Dpm △ + HAcac ▲ in $CDCl_3$ solution at 25°C: (a) equilibrium mixture of the two isomers; (b) 10 min after addition of HDpm of HAcac; (c) after 1 h.

cis-diphenyl isomer and the free ligand cannot be excluded. The various processes are summarized in Scheme 1.

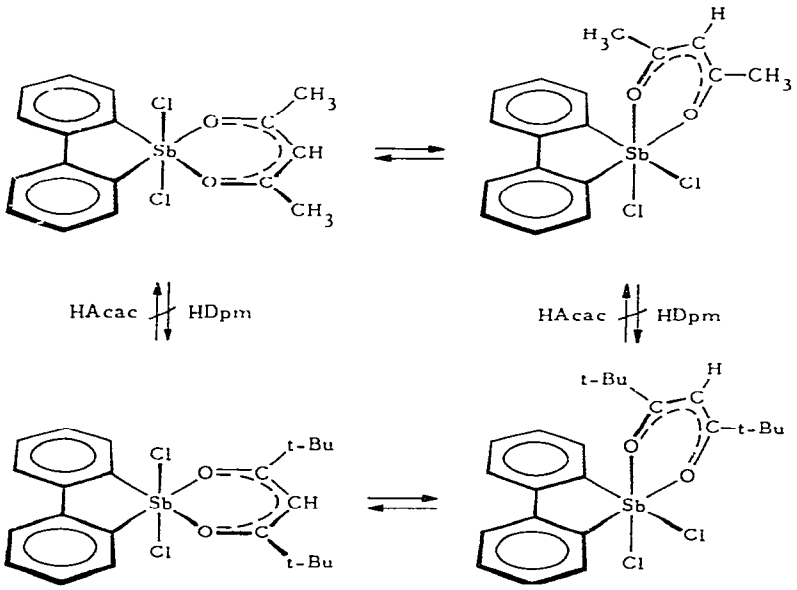
SCHEME 1



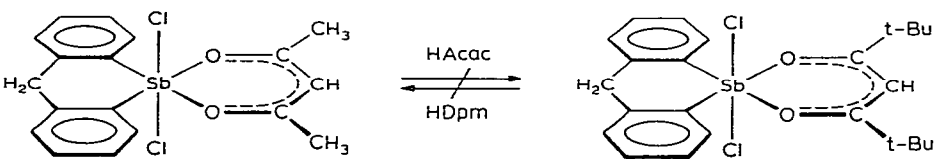
5,5-Dichloro-5-β-diketonatodibenzostiboles are present in solution as two slowly interchanging geometrical isomers [4]. In freshly prepared solutions only the *trans*-dichloro-*cis*-diaryl isomer is present, and at room temperature this slowly isomerizes to an equilibrium mixture with the *cis*-dichloro-*cis*-diaryl isomer. In the presence of free β-diketone ligand, neither of the two isomers

undergoes β-diketonate ligand exchange as demonstrated by PMR spectroscopy (Scheme 2).

SCHEME 2



5,5-Dichloro-5-β-diketonato-5,10-dihydrodibenz[*b*,*e*]antimonins according to the PMR data exist in solution only in the *trans*-dichloro-*cis*-diaryl configuration. One single set of β-diketonate CH and CH_3 signals is present. These compounds are also inert towards β-diketonate ligand exchange.

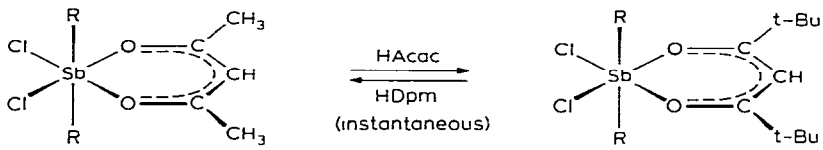


These results indicate that the presence of the organic ligands in mutual *trans*-positions and in *cis*-position with respect to the β-diketonate ligand is required for ligand exchange. Inverting this line of argument, it seems that the β-diketonate ligand is more strongly bonded in compounds having the organic ligands in *cis*-disposition than in those having them in *trans*-disposition.

In order to explore further the apparent influence of stereochemistry of the dichloro-β-diketonatodiorganoantimony(V) compounds on the occurrence of ligand exchange we have investigated β-diketonate ligand exchange reactions with dichloroacetylacetonatodialkylantimony compounds (R_2SbCl_2Acac, R = Me, Et), which are known to possess exclusively the *trans*-dialkyl configuration [2,3,6], and with 1,1-dichloro-1-β-diketonato-stibolanes and -antimonanes ($(CH_2)_nSbCl_2X$, n = 4, 5; X = Acac, Dpm), in which the "alkyl"—antimony bonds are forced into a *cis*-configuration.

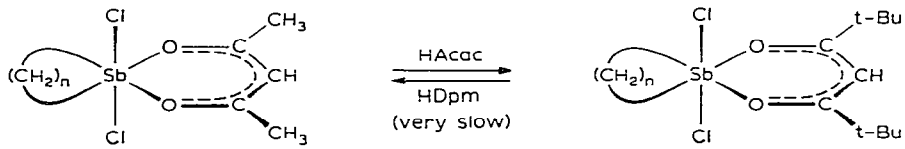
Upon addition of an equimolar amount of dipivaloylmethane (HDpm) to a solution of Me_2SbCl_2Acac or Et_2SbCl_2Acac in $CDCl_3$ instantaneous β-diketonate

ligand exchange occurs to give an equilibrium mixture of the compounds R_2SbCl_2Acac, R_2SbCl_2Dpm (R = Me, Et), HAcac and HDpm.



(R = Me, Et)

In contrast, 1,1-dichloro-1-acetylacetonato-stibolane and -antimonane ($(CH_2)_nSbCl_2Acac$, n = 4, 5), appear to be rather inert towards to β-diketonate ligand exchange. At room temperature (22° C) ligand exchange proceeds very slowly. At 55° C equilibrium mixtures of compounds $(CH_2)_nSbCl_2X$ (n = 4, 5; X = Acac, Dpm) and free ligands, HAcac and HDpm, are reached only after a period of 20—30 min.



(n = 4, 5)

These results are in line with the observation for dichloro-β-diketonatodiaryl-antimony compounds, in which the *cis*-diaryl configurations fail to undergo ligand exchange.

Antimony-β-diketonate ligand interaction

The position of the Acac γ-CH proton resonance signals in the PMR spectra of compounds $R_nSbCl_{4-n}Acac$ has been taken as a measure for the strength of the Sb—Acac interaction [6]. Likewise, the magnitude of Acac—proton solvent shifts $\Delta^{CCl_4}_{C_6D_6}$ ($\delta(CCl_4) - \delta(C_6D_6)$) and $\Delta^{CDCl_3}_{C_6D_6}$ ($\delta(CDCL_3) - \delta(C_6D_6)$) has been related to the strength of the Sb—Acac interaction in compounds $R_nSbCl_{4-n}Acac$ [10]. At present the availability of a series of dichloro-β-diketonatodiorganoantimony(V) compounds (R_2SbCl_2X) allows a more detailed study of these phenomena. The higher field position of the Acac γ-CH proton signals for the *cis*-dichloro-*trans*-dialkyl compounds (R_2SbCl_2Acac, R = Me, Et) compared with those for the *trans*-dichloro *cis*-"dialkyl" derivatives ($(CH_2)_nSbCl_2Acac$, n = 4, 5) (see Table 2) points to a stronger Sb—Acac interaction in the latter compounds. Based on the somewhat stronger antimony—acetylacetonate bonding in compounds $(CH_2)_nSbCl_2Acac$ than in Et_2SbCl_2Acac one would expect a somewhat larger benzene solvent shift for the Acac γ-CH protons in the former compounds. That this is not observed may be the result of repulsive forces exerted by the two chlorine atoms, which in $(CH_2)_nSbCl_2 \cdot$ Acac reside in nearby axial positions, on the benzene molecules solvating the Acac ligand. Apparently, in addition to the inductive effects of the substituents present at antimony [10], steric factors are also involved in benzene—Acac ligand interactions. Compounds Me_2SbCl_2X (X = Acac or Dpm) show benzene solvent

shift values Δ(CH) and Δ(CH_3 or t-Bu) substantially greater than those calculated by assuming that only inductive effects of the chlorine and methyl substituents govern the benzene—β-diketonate ligand interaction. We previously reported that Acac γ-CH benzene solvent shifts ($\Delta^{CCl_4}_{C_6D_6}$) are almost the same for both isomers of Ph_2SbCl_2Acac (0.66 ppm for the *trans*-dichloro-*cis*-diphenyl isomer and 0.67 ppm for the *cis*-dichloro-*trans*-diphenyl isomer) (see ref.10). The presence of ring-current effects exerted by the phenyl groups at antimony on the Acac γ-CH proton chemical shifts of the isomeric Ph_2SbCl_2Acac compounds [6] implies that these chemical shift data cannot be taken as a measure of the strength of the Sb—Acac interaction. However, the β-diketonate ligand exchange studies suggest that these interactions are strongest in the *trans*-dichloro-*cis*-diphenyl isomer, but this is not reflected in the benzene solvent shift values. Again any effect on the solvent shift caused by a stronger antimony—acetylacetonate bonding in the *trans*-dichloro isomer is likely to be counterbalanced by a reduced solvation of the acetylacetonate ligand as a result of the repulsive forces exerted by the nearby chlorine atoms on the benzene molecules.

In principle the strength of the Sb—Acac ligand interaction in compounds R_2SbCl_2Acac will be reflected in the IR spectroscopic data, in particular in the position of the Sb—O_2 stretching absorption band. Comparison of the IR spectra of Me_2SbCl_2Acac (ν(Sb—O_2) 433, 416 cm^{-1}) and Et_2SbCl_2Acac (ν(Sb—O_2) 433, 416 cm^{-1}) with those of the corresponding stibolanes and antimonanes, $(CH_2)_4SbCl_2Acac$ (ν(Sb—O_2) 450, 424 cm^{-1}), $(CH_2)_5SbCl_2Acac$ (ν(Sb—O_2) 446, 427 cm^{-1}), indicates a stronger Sb—Acac bonding interaction in the latter compounds. These data are in accord with the observed ligand-exchange behaviour.

Earlier statements that no marked differences exist in Sb—Acac ligand bonding in *cis*- and *trans*-Ph_2SbCl_2Acac were based amongst others on the observation of only one Sb—O_2 stretching absorption band in the IR spectra of Ph_2SbCl_2Acac both as a solid in KBr or Nujol suspension in solution [6]. A reexamination of these spectra has drawn our attention to an originally neglected change in the envelope of the phenyl-*y*-vibration band at 469 cm^{-1} in the $CHCL_3$ solution spectrum compared with the solid state spectra. Solid *trans*-diphenyl Ph_2SbCl_2Acac shows a strong phenyl-*y*-vibration band at 469 cm^{-1} together with a medium strong Sb—O_2 vibration band at 429 cm^{-1}. In $CHCl_3$ a mixture of *cis*-dichloro-*trans*-diphenyl and *trans*-dichloro-*cis*-diphenyl isomers is known to be present. As compared with the solid state spectra, the IR spectrum in $CHCl_3$ solution contains an additional absorption band λ_{max} 464 cm^{-1} overlapping the phenyl-*y*-vibration band at λ_{max} 469 cm^{-1}. This band is tentatively assigned to the Sb—O_2 vibration band of *trans*-dichloroacetylacetonato-*cis*-diphenylantimony. Again, the higher value of ν(Sb—O_2) pointing to a stronger Sb—Acac interaction in this geometric configuration, is in accordance with the observed ligand-exchange behaviour.

Discussion

The availability of a series of *cis*- and *trans*-diorgano main group organometallic complexes allows a study of the influence of stereochemistry on the

strength of metal—ligand interactions in this type of d^{10} metal complex. In accordance with a model described by Tobias [12], we assume that the strength of the antimony—β-diketonate ligand interaction will be markedly influenced by the hybridization state of the antimony valence orbitals. If *d*-orbitals are not regarded as contributing to the antimony—ligand bonding in a major way, it can be assumed that in *trans*-diorgano-R_2SbCl_2-β-diketonates two *sp*-hybridized orbitals of antimony are used for covalent bonding of the organic groups R, leaving the remaining two *p*-valence orbitals for binding two chlorine and two oxygen atoms by means of hypervalent three-center four-electron bonds [13]. In the *trans*-dichloro-*cis*-diorganoantimony-β-diketonates the two organic groups R are suggested to be covalently bonded to antimony either by two *p*-orbitals or by two sp^2-orbitals of antimony. The bonds to the β-diketonate ligand are then formed by hypervalent three-center four-electron bonds using σ-orbitals of oxygen and an antimony *s*- or sp^2-orbital, whereas the two chlorine atoms are bonded to antimony by hypervalent three-center four-electron bonds involving an antimony *p*-orbital. While these models are extreme descriptions of the antimony—ligand bonding in compounds R_2SbCl_2X (X = β-diketonate ligand), they are useful in indicating that the Sb—O bonds in *trans*-dichloro-*cis*-diorganoantimony-β-diketonates possess more *s*-character than the Sb—O bonds in *cis*-dichloro-*trans*-diorganoantimony-β-diketonates and therefore are likely to be stronger. In *trans*-diorgano (R_2SbCl_2X, R = Me, Et, Ph) compounds, which by the above reasoning, contain a weaker Sb—β-diketonate ligand interaction, ligand exchange proceeds instantaneously. The *cis*-diorgano compounds (R_2SbCl_2X, R_2 = $(CH_2)_4$, $(CH_2)_5$, Ph_2, *o*,*o*′-C_6H_4-C_6H_4, *o*,*o*′-C_6H_4-CH_2-C_6H_4), in which the antimony—β-diketonate interactions are stronger, appear to be less reactive in β-diketonate-ligand exchange. These results can be understood in terms of the mechanism for β-diketonate-ligand exchange reported by Glass and Tobias [14], in which metal—oxygen bond cleavage is considered to be the rate-determining step. The observation that some of our complexes undergo ligand exchange but do not undergo isomerization (e.g. R_2SbCl_2X; R = Me, Et), whereas others isomerize but do not undergo ligand exchange (e.g. R_2SbCl_2X; R_2 = *o*,*o*′-C_6H_4-C_6H_4) suggests that a twist mechanism rather than an antimony—oxygen bond rupture mechanism is involved in the isomerization.

While this paper was being completed Aslanov et al. [15] discussed metal—ligand bonding in octahedral organotin complexes, $Me_nSnX_{(4-n)} \cdot 2D$ (*n* = 0—2; X = Cl, Br; D = a donor ligand). These authors explain the observed tin—ligand bond lengths on the basis of valence orbital hybridization arguments similar to those used in the present paper. Evidently the hypervalent bond model is suitable for the interpretation of metal—ligand interactions in octahedral main group element (organo)metallic complexes.

Experimental

General

PMR chemical shifts (δ) were measured with a Varian HA-100 spectrometer in dilute solutions at a magnet temperature of 22° C, with TMS as an internal standard. IR spectra were recorded on a Perkin—Elmer model 577 instrument

on solids in KBr pellets, unless indicated otherwise. Dipole moments were determined in benzene with the aid of a Wissenschaftlich-Technische Werkstätten dipole meter DM 01 and a measuring cell DFL 2 in benzene at 20°C, as described by Doron and Fischer [16].

Elemental analyses were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO under the supervision of Mr. W.J. Buis. Analytical data are presented in Table 1.

Ph_2SbCl_2Acac has been prepared as described in ref. 8. The preparation of dichloroacetylacetonatodimethylantimony and dichloroacetylacetonatodiethylantimony given in ref. 8 has been modified as follows.

Preparation of dichloro-β-diketonatodiorganoantimony compounds

Dichloroacetylacetonatodimethylantimony. Trichlorodimethylantimony [17] (2.6 g, 10.0 mmol) was dissolved in a mixture of 25 ml of chloroform and 2 ml of acetylacetone. The mixture was kept at room temperature for 1 h. Subsequently the solvent was evaporated at reduced pressure. Recrystallization of the solid residue from methanol afforded 0.8 g of Me_2SbCl_2Acac as a colourless crystalline solid (m.p. >160°C (dec.), yield 25%) (cf. ref. 8).

Dichloroacetylacetonatodiethylantimony. Trimethoxodiethylantimony [18] (1.7 g, 6.2 mmol) was dissolved in 50 ml of methanol containing 1.0 g (10 mmol) of acetylacetone and 1 ml of concentrated HCl (12 mmol). The mixture was concentrated at reduced pressure. Recrystallization of the semi-solid residue from chloroform/light petroleum (b.p. 60—80°C), afforded 1.8 g of pale-yellow, almost colourless Et_2SbCl_2Acac (m.p. 100—102°C (dec.), yield 83%) (cf. ref. 8).

Dichlorodipivaloylmethanatodiphenylantimony. Trichlorodiphenylantimony (3.0 g, 8 mmol) was dissolved in 50 ml of methanol containing 1.5 g (8 mmol) of dipivaloylmethane. After 15 min reflux the solution was concentrated to dryness by evaporation at reduced pressure. The solid residue was recrystallized from methanol to give 2.6 g of Ph_2SbCl_2Dpm (colourless leaves, m.p. 185—187°C), yield 61.4%). Analysis. Found: C, 52.09; H, 5.49; Cl, 13.49. $C_{23}H_{27}Cl_2OSb$ calcd.: C, 52.11; H, 5.51; Cl, 13.37%. IR spectrum: 1530vvs, 1510vvs, 1479m, 1453w, 1436(sh), 1434s, 1365m, 1337s, 1329s, 1302w, 1289w, 1272w, 1248m, 1221s, 1182w, 1160w, 1142s, 1061w, 1021w, 1018w, 997m, 954m, 936w, 873s, 848w, 834w, 820w, 812m, 742vs, 736vs, 691s, 685m, 620m, 505m, 488m, 473s, 461w, 430m(br), 307(sh), 296vs(br), 285(sh) cm^{-1}.

5,5-Dichloro-5-acetylacetonatodibenzostibole. 5,5,5-Trichlorodibenzostibole [9] (1.0 g, 2.6 mmol) was dissolved in 50 ml of chloroform containing 1.0 g (10 mmol) of acetylacetone. The mixture was refluxed for 15 min and subsequently concentrated to 15 ml. At reflux temperature 20 ml of light petroleum (b.p. 60—80°C) was added to give a clear solution which on cooling gave 1.0 g of a colourless crystalline solid. Recrystallization from 75 ml of benzene/light petroleum (b.p. 60—80°C) (1/1) gave 0.95 g of 5,5-dichloro-5-acetylacetonatodibenzostibole (m.p. 198—204°C, yield 82%). IR spectrum: 1580(sh), 1560(sh), 1550vs(br), 1535vs, 1460w 1435m, 1420(sh), 1360m, 1330vs, 1290m, 1060w, 1020s, 938s, 810w, 758s, 749s, 710w, 680w, 638w, 612w, 585m, 485s, 455s, 470s, 307vs cm^{-1}.

5,5-Dichloro-5-dipivaloylmethanatodibenzostibole. 5,5,5-Trichlorodibenzostibole [9] (0.76 g, 2.0 mmol) was dissolved in 20 ml of methanol containing 1 ml of dipivaloylmethane. The mixture was refluxed for 15 min. Subsequently methanol was evaporated at reduced pressure to give a pale-yellowish solid, which upon recrystallization from chloroform/pentane afforded 0.7 g of 5,5-dichloro-5-dipivaloylmethanatodibenzostibole as a colourless crystalline solid (m.p. 245—247°C, yield 66%). IR spectrum: 1583m, 1550(sh), 1522vvs(br), 1480(sh), 1460m, 1436m, 1386m, 1329s, 1300w, 1280w, 1250m, 1222s, 1148s, 1060w, 1040w, 1030w, 1020w, 982w, 958s, 943m, 878s, 865w, 818s, 745vs, 710w, 668w, 638s, 615w, 520m, 490s, 485m, 420m, 308vs(br) cm^{-1}.

5,5-Dichloro-5-acetylacetonato-5,10-dihydrodibenz[b,e]antimonin. 5,5,5-Trichloro-5,10-dihydrodibenz[*b*,*e*]antimonin [1] (0.6 g, 1.5 mmol) was dissolved in 25 ml of chloroform containing 1.0 g of acetylacetone. The mixture was refluxed for 15 min. Evaporation to dryness afforded a brownish solid residue, which was recrystallized twice from a $CCl_4/CHCl_3$ mixture to give 0.3 g of 5,5-dichloro-5-acetylacetonato-5,10-dihydrobenz[*b*,*e*]antimonin, as a colourless crystalline solid (m.p. 220—230°C (dec), yield 44%). IR spectrum: 1560vs(br), 1540vs(br), 1460m, 1437m, 1420m, 1333s, 1291m, 1272w, 1260w, 1022s, 939s, 917w, 816m, 750s, 677m, 616m, 572m, 486m, 450m, 437s, 370m, 315vs cm^{-1}.

5,5-Dichloro-5-dipivaloylmethanato-5,10-dihydrodibenz[b,e]antimonin. 5,5,5-Trichloro-5,10-dihydrobenz[*b*,*e*]antimonin [1] (0.8 g, 2.0 mmol) was dissolved in 25 ml of chloroform containing 1.5 g of dipivaloylmethane. After 15 min reflux the mixture was evaporated to dryness. The pale-brown residue was recrystallized from chloroform/methanol to give 0.6 g of 5,5-dichloro-5-dipivaloylmethanato-5,10-dihydrodibenz[*b*,*e*]antimonin as a colourless crystalline solid (m.p. 178—280°C, yield 55%). IR spectrum: 1580(sh), 1550(sh), 1530(br), 1490(sh), 1480(sh), 1460m, 1438m, 1420w, 1366m, 1322vs, 1280w, 1270w, 1258w, 1250m, 1224s, 1150s, 1045w, 1030w, 960s, 940w, 915w, 875s, 832w, 816s, 749s, 658w, 630m, 620m, 585w, 512m, 500w, 490(sh), 483m, 431m, 371m, 305vs cm^{-1}.

1,1-Dichloro-1-acetylacetonatostibolane. Freshly prepared 1,1,1-trichlorostibolane [1] (1.05 g, 3.7 mmol) was dissolved in 10 ml of methylene chloride containing 0.5 g (5 mmol) of acetylacetone. The solution was kept at room temperature for 1 h and subsequently evaporated to dryness. The pale-yellow residue was recrystallized from light petroleum (b.p. 60—80°C) to give 0.8 g of 1,1-dichloro-1-acetylacetonatostibolane ($(CH_2)_4SbCl_2Acac$) as a colourless crystalline solid (m.p. 134°C, yield 61%). IR spectrum: 1560 vs(br), 1535vs(br), 1430m(br), 1420m(br), 1400m, 1360m(sh), 1339s, 1308m, 1285m, 1247w, 1175w, 1020s, 940s, 812m, 782ms, 718w, 678w, 578w(sh), 568m, 450m, 424w, 322w(sh), 300vs cm^{-1}.

1,1-Dichloro-1-dipivaloylmethanatostibolane. Freshly prepared 1,1,1-trichlorostibolane [1] (2.15 g, 7.6 mmol) was dissolved in 30 ml of methylene chloride containing 1.5 g (8 mmol) of dipivaloylmethane. After 1 h at room temperature the mixture was evaporated to dryness. Recrystallization of the pale-brown residue from light petroleum (b.p. 60—80°C) afforded 1.8 g of 1,1-dichloro-1-dipivaloylmethanatostibolane ($(CH_2)_4SbCl_2Dpm$) as a colourless crystalline solid (m.p. 140°C, yield 54%). IR spectrum: 1530—1510vs(br),

1460w, 1400m, 1383w, 1364s, 1328s, 1310s, 1295m(sh), 1254m, 1220s, 1170w, 1149s, 1105w, 1056w, 1026m, 1012m, 960s, 950w, 938m, 900w, 876s, 851w, 831w, 828w, 810s, 790s, 742m, 721m, 631s, 567m, 510ms, 490m, 450m, 305vs, 280vs cm^{-1}.

1,1-Dichloro-1-acetylacetonatoantimonane. Freshly prepared 1,1,1-trichloroantimonane [1] (0.50 g, 1.7 mmol) was dissolved in 10 ml of methylene chloride containing 0.2 g of acetylacetone. After 1 h at reflux temperature the mixture was evaporated to dryness. Recrystallization of the pale-yellow residue from light petroleum (b.p. 60—80°C) afforded 0.27 g of 1,1-dichloro-1-acetylacetonatoantimonane ($(CH_2)_5SbCl_2Acac$) as a colourless crystalline solid (m.p. 120°C, yield 44%). IR spectrum: 1562vs(br), 1537vs(br), 1440m, 1420m(br), 1400m, 1364m, 1341s, 1330s, 1289m, 1279m, 1229m, 1179m, 1159w, 1100w, 1021s, 984m, 940(sh), 933s, 914m, 812s, 762s, 676m, 640w, 572mw, 555w, 541m, 465m, 446m, 427m, 300vs(br) cm^{-1}.

1,1-Dichloro-1-dipivaloylmethanatoantimonane. Freshly prepared 1,1,1-trichloroantimonane [1] (1.94 g, 6.5 mmol) was dissolved in 20 ml of methylene chloride containing 1.20 g (6.5 mmol) of dipivaloylmethane. The mixture was refluxed for 1.5 h and then evaporated to dryness. Recrystallization of the pink coloured residue from pentane (100 ml) afforded 0.8 g of slightly impure 1,1-dichloro-1-dipivaloylmethanatoantimonane ($(CH_2)_5SbCl_2Dpm$, m.p. 125—135°C). Both PMR and analytical data pointed to the presence of traces of 1,1,1-trichlorostibocyclohexane starting material as a contaminant. Yield 27.6%. IR spectrum: 1532vs(br), 1512vs(br), 1448m, 1404w, 1365m, 1340(sh), 1328vs, 1297w, 1249m, 1223s, 1180w, 1150s, 1030w, 984m, 962s, 932w, 918m, 875s, 830w, 810s, 778w, 763s, 744m, 631s, 559w, 544w, 510m, 490m, 460w, 425vw, 305vs, 280s, 250s cm^{-1}.

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