

Organometallics for metal organic chemical vapour deposition (MOCVD) processes

I. Cyclopentadienyl antimony halides: syntheses and ^{121}Sb Mössbauer spectroscopy, A systematic approach

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Abstract

Comproportionation of SbCp_3 with SbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in stoichiometric amount yields Cp_2SbX and CpSbX_2 . TlCp does not react with SbX_3 in 1/1 or 2/1 ratios. Of the Group 14 organometallic cyclopentadienyls $\text{Me}_3\text{M}-\sigma\text{-C}_5\text{H}_5$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$), only Me_3SiCp reacts with SbBr_3 to give Cp_2SbBr and CpSbBr_2 . The ^1H and ^{13}C NMR data and mass spectra for selected compounds are reported.

^{121}Sb Mössbauer spectral data for 18 chemically and structurally related antimony(III) derivatives are reported; isomeric shifts are interpreted for two series of compounds by correlating electronegativity differences $\overline{\Delta\chi p}$ for the ligands with their possible π -donation abilities.

Introduction

Triscyclopentadienylantimony ($^1h\text{-C}_5\text{H}_5$) $_3\text{Sb}$ was made by Fischer et al. [1,2] as long ago as 1960 by the reaction shown in eq. 1. The red oil decomposes at elevated



temperatures to “ Cp_4Sb_2 ” tetracyclopentadienyldistibane, by an unknown route (eq. 2).



Becker et al. [3], in an attempt to confirm the identity of “ Cp_4Sb_2 ”, repeated reaction 2 and obtained a rather complex species from the reaction, viz. tetracyclo-

pentadienyltetraadamantane. We have synthesized (¹*h*-C₅H₅)₃Sb [4] as yellow crystalline needles from reaction 3. Its was identified as a monohapto-bonded



species, of trigonal pyramidal shape, with bond angles (C–Sb–C) ca. 96°, considerably smaller than tetrahedral [4].

Efforts to obtain cyclopentadienyl antimony compounds with ligands other than C₅H₅ failed: experiments with MeC₅H₅ resulted in the formation of ill-defined red oils, probably mixtures of isomers of (¹*h*-C₅H₄Me)₃Sb [5]. The use of pentamethylcyclopentadiene (denoted by PcpH) surprisingly yielded (¹*h*-PcpSb)₄, tetrakis(pentamethylcyclopentadienyl)tetraantibetane, the intermediate Pcp₃Sb apparently undergoing elimination of (Pcp)₂ [6] (eq. 4,5).



In order to obtain functionalized cyclopentadienyls of antimony as synthons for further clean reactions we started a systematic search for synthetic pathways leading to cyclopentadienylantimony halides Cp_{3–*n*}SbX_{*n*}. Only one example, viz. CpSbCl₂ had been reported, and this was made by Jutzi et al. [7] by reaction of either LiCp or Me₃SiCp with SbCl₃. Since volatile organometallic antimony derivatives for MOCVD-processes (MOCVD = metal organic chemical vapour deposition) are at present restricted to Me₃Sb or Et₃Sb, volatile cyclopentadienyl antimony compounds must be regarded as of possible potential in this field.

Results and discussion

Cyclopentadienylantimony halides cannot be synthesized like the simple alkyl derivatives, Me₂SbBr or MeSbBr₂, by thermolysis of easily available antimony(V) derivatives (eq. 6). The species Cp₃SbX₂ are unknown, and if formed at all as



intermediates, proceed to give CpSbX₂ (see eq. 9). We examined several possible organometallic routes to the compounds Cp₂SbX and CpSbX₂:

(a) Comproportionation of SbCp₃ with SbX₃ in 2/1 and 1/2 ratios:



(X = Cl, Br, I)

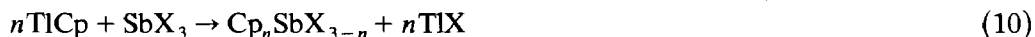
In all cases we obtained the corresponding cyclopentadienylantimony halides (or dihalides) as light-sensitive, moisture sensitive, yellow-to-orange coloured oils or low-melting solids which even at low temperatures and with exclusion of light have short lifetimes. Decomposition yields violet coloured viscous oils or black tars from which no material for identification could be extracted.

Similar redistribution reactions have been investigated in the system Me₃Sb/SbCl₃ in solution by ¹H NMR [8], and for solid state reactions of Ph₃Sb/SbX₃

(X = Cl, Br) in 2/1 or 1/2 molar ratios, which yielded Ph_2SbX and PhSbX_2 , respectively, in quantitative yield [9]. Berlitz examined interesting alternatives to these solution procedures by mixing solid crystalline SbCp_3 with crystalline SbX_3 (purified by vacuum sublimation), and observed exothermic but smooth and clean reactions that gave $\text{Cp}_2\text{SbX}/\text{CpSbX}_2$ cyclopentadienylantimony halides identical to that previously prepared in solution reactions [5]. An unexpected reaction takes place with the halogens X_2 in solution at low temperatures, cyclopentadienylantimony dihalides being formed with reductive elimination of $(\text{Cp})_2$ according to:

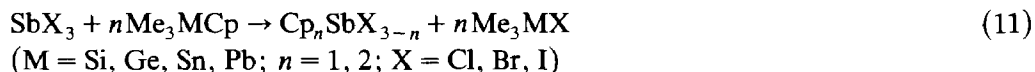


(b) Organometallic synthesis involving TlCp as the cyclopentadienylating reagent:



Various ratios of reactants, solvents, and temperature and reaction times were used, but TlCp was not sufficiently reactive to form cyclopentadienylantimony halides.

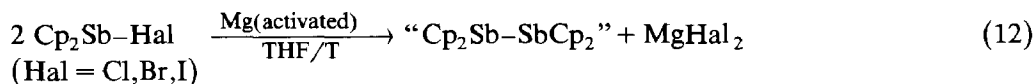
(c) Ligand exchange from organometallic cyclopentadienyls of group 14 elements, viz. $\text{Me}_3\text{M}(\text{}^1h\text{-C}_5\text{H}_5)$ with SbX_3 :



In contrast with the results reported by Jutzi et al. [7], upon trying all the combinations possible in eq. 11, we obtained, Cp_2SbBr and CpSbBr_2 (in moderate yields), only from the reaction of Me_3SiCp and SbBr_3 ; in all other cases the starting materials were recovered unchanged.

Reactivity

Few experiments have been carried out previously on the reactivity of cyclopentadienylantimony halides. Attempts to synthesize " $\text{Cp}_2\text{Sb-SbCp}_2$ " from $\text{Cp}_2\text{Sb-Hal}$ by treatment with activated magnesium in THF (a method successfully exploited by Breunig et al. [10] for distibanes R_4Sb_2) failed, and gave black, intractable tars (eq. 12). However, further experiments are planned, e.g. reactions with $\text{Li}(\text{Na})\text{H}$ or



LiAlH_4 in the hope of making hydridic species " Cp_2SbH " or their decomposition products, perhaps the elusive " $(\text{Cp}_2\text{Sb})_n$ ".

Experimental

Experiments were carried out under argon in dry degassed solvents by Schlenk techniques and vacuum line manipulations when required.

Spectrometers

IR: Perkin-Elmer 557; NMR: Varian T60; Bruker AC300 (at 300 MHz), Bruker WP400 (at 400 MHz). Mass spectrometer: Varian CH7 (low resolution); Varian 711 (high resolution). Mössbauer spectrometer: Mössbauer absorbers containing 7–10

mg cm⁻² of antimony were prepared under dry nitrogen. The source was ca. 200 μ Ci of Ba^{121m}SnO₃. Spectra were obtained with both source and absorber immersed in liquid helium in a bath-cryostat. The spectrometer consisted of a linear-velocity drive unit, a thin NaI(Tl) scintillation counter or a 2at Xe/CO₂ proportional counter, and a 512-channel analyser. The discrimination was set to count the escape peak of the 37 KeV ¹²¹Sb γ -ray. The velocity range scanned was ± 25 mm/s, and was calibrated using a ⁵⁷Co/Rh source and a metallic iron foil absorber at room temperature. From this calibration procedure we found an isomer shift of -8.5 mm/s between BaSnO₃ and InSb as standard. The spectra were folded (256 channels) before being computed. Chemical isomer shift data are quoted with respect to InSb. Satisfactory spectra were obtained during 36 h, with accumulation of 50–100 $\times 10^3$ counts per channel.

The preparation of SbCp₃ from Sb(NMe₂)₃ and CpH has been described elsewhere [4].

Solid state reactions of SbCp₃ with SbX₃ yielding Cp₂Sb-X

A typical procedure is: Finely ground crystals of the two components were mixed under argon; after a short induction period an exothermic reaction started and was complete after several hours. The required cyclopentadienylantimony halides were formed as viscous oils.

Typical run: Cp₂SbCl from 2.2 g (6.9 mmol) SbCp₃ and 0.78 g (3.45 mmol) SbCl₃.
Cp₂SbBr from 1.9 g (6.0 mmol) SbCp₃ and 1.08 g (3.0 mmol) SbBr₃.
Cp₂SbI from 2.0 g (6.3 mmol) SbCp₃ and 1.57 g (3.15 mmol) SbI₃.

Solution chemistry of SbCp₃ with SbX₃ yielding Cp₂SbX and CpSbX₂

Typical procedures were as follows: A suspension of SbCp₃ and SbX₃ in ca. 30 ml dry n-hexane (or ether) was stirred for 12 h at -50°C to -70°C , then allowed to warm to room temperature. The solvent was evaporated in vacuo to leave the corresponding cyclopentadienylantimony halides.

Cp₂SbCl from 2.5 g (7.8 mmol) SbCp₃ and 0.9 g (3.9 mmol) SbCl₃ in 20 ml OEt₂ at -20°C .

CpSbCl₂ from 7.3 g (23 mmol) SbCp₃ and 10.5 g (46 mmol) SbCl₃ in 30 ml OEt₂ at -30°C .

Cp₂SbBr from 2.0 g (6.3 mmol) SbCp₃ and 1.14 g (3.15 mmol) SbBr₃ in 30 ml OEt₂ at -50°C .

CpSbBr₂ from 1.47 g (4.6 mmol) SbCp₃ and 3.35 g (9.3 mmol) SbBr₃ in 30 ml n-hexane at -70°C .

Cp₂SbI from 3.2 g (10 mmol) SbCp₃ and 2.52 g (5 mmol) SbI₃ in 25 ml n-hexane at -70°C .

CpSbI₂ from 1.54 g (4.9 mmol) SbCp₃ and 4.85 g (9.7 mmol) SbI₃ in 30 ml n-hexane at -70°C .

Cp₂SbNMe₂ from 4.6 g (8.3 mmol) Sb(NMe₂)₃ and 2.4 g (18.2 mmol) freshly cracked monomeric cyclopentadiene in 25 ml n-hexane at -50°C .

Reactions of SbCp₃ with halogens X₂ yielding CpSbX₂

Typical experiments were carried out as follows: Usually a solution of the appropriate halogen in ether was added slowly to a cooled solution (-85°C) of SbCp₃ in ether and the mixture was kept for about 2 h at that temperature;

however, in the case of chlorine, the gas was condensed into the cooled reaction mixture. The mixture was allowed to warm to room temperature during 4 h, then the solvent was removed in vacuo to leave the product in quantitative yield.

CpSbCl₂ from 1.65 g (5.2 mmol) SbCp₃ and 0.37 g (5.2 mmol) Cl₂ in 50 ml ether at -85 °C.

CpSbBr₂ from 1.43 g (4.5 mmol) SbCp₃ and 0.72 g (4.5 mmol) Br₂ in 50 ml ether at -78 °C.

CpSbI₂ from 1.62 g (5.1 mmol) SbCp₃ and 1.29 g (5.1 mmol) I₂ in 50 ml ether at -78 °C.

Spectroscopic studies

Cyclopentadienylantimony halides obtained from reactions described above were investigated by several methods:

(¹H, ¹³C) NMR spectra (Table 1) indicate fluxionality of the cyclopentadienyl rings bonded to antimony with only minor variation of chemical shifts, the strongest substituent effect being exerted by chlorine in CpSbCl₂. For both nuclei the singlets observed persist in the temperature range from ambient to -80 °C.

Electron impact (EI) mass spectra were recorded for all compounds but the highly moisture/oxygen sensitive halides did not survive procedures required for field-desorption (FD) mass spectra scanning. A typical mass spectrum, that for Cp₂SbCl, is assigned in Table 2.

IR spectra were very difficult to obtain; in almost all cases decomposition occurred in the light beam of the spectrometer during scanning. It was impossible to record Raman spectra. Only few examples of very poorly resolved spectra were recorded. The spectra of the cyclopentadienylantimony halides were closely similar

Table 1

(¹H, ¹³C) NMR data for cyclopentadienyl antimony halides Cp_{3-n}SbX_n (X = Cl, Br, I) δ in ppm, TMS as internal standard

Compound	δ(C ₅ ¹ H ₅)	δ(¹³ C ₅ H ₅)
Cp ₃ Sb	6.0	116.14
(MeCp) ₃ Sb	6.0/5.4/2.0	140.6/123.26/100.26/15.16
Cp ₂ SbCl	6.30	117.73
Cp ₂ SbBr	6.3	117.68
Cp ₂ SbI	6.0	117.43
CpSbCl ₂	6.73	^a
CpSbBr ₂	6.23	^a
CpSbI ₂	6.20	^a

^a Insufficient solubility in C₆D₆.

Table 2

m/e fragments of Cp₂SbCl, obtained with EI-source at 70 eV energy

<i>m/e</i>	39	65	66	121	130	158	186	221	251
Fragment	C ₃ H ₃	Cp	CpH	Sb	Cp ₂	SbCl	SbCp	CpSbCl	Cp ₂ Sb

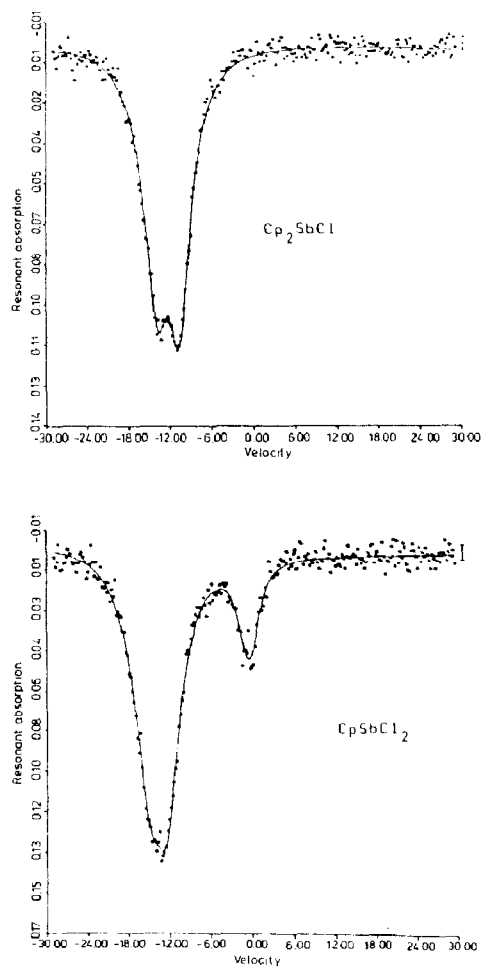


Fig. 1. Typical Mössbauer spectra of Cp_2SbCl and CpSbCl_2 .

Table 3

$^{121}\text{Antimony}$ Mössbauer data (in mm/s) for structurally related derivatives [5]

Compounds	$\delta(\text{IS}(\text{BaSnO}_3))$ isomer shift	$\delta(\text{IS}(\text{InSb}))$ (mm/s)	quadrupol asymmetry line splitting parameter width		
			e^2qQ	r	T
$\text{Sb}(\text{NMe}_2)_3$	-9.66	-1.16	+17.9	0.43	3.5
SbCp_3	-11.17	-2.67	+15.6	-	3.5
$\text{Cp}_2\text{SbNMe}_2$	-10.36	-1.86	+18.6	0.46	4.0
Cp_2SbCl	-12.60	-4.10	+18.9	0.72	3.5
CpSbCl_2	-14.00	-5.50	+14.7	0.77	3.5
Cp_2SbBr	-12.60	-4.10	+17.5	0.75	3.5
Cp_2SbI	-12.40	-3.90	+18.2	0.61	3.5
CpSbI_2	-13.60	-5.10	+13.8	0.79	4.0
SbCl_3	-14.40	-5.90	+13.3	0.20	3.5
$\text{Me}_2\text{SbNMe}_2$	-9.70	-1.20	+20.9	0.80	3.5
Me_3Sb	-8.72	-0.22	+16.3	-	3.5
Me_2SbN_3	-11.17	-2.67	-31.5	-	3.5
Me_2SbBr	-10.36	-1.66	-37.0	0.46	4.0

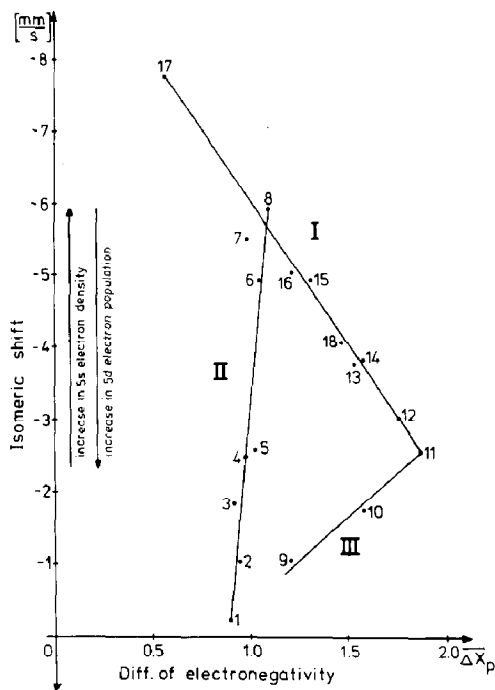


Fig. 2. Plot of isomer shifts $\delta(\text{IS})$ (mm/sec) versus electronegativity differences $\overline{\Delta\chi p}$. Indexing of compounds: 1. SbMe_3 ; 2. $\text{Me}_2\text{SbNMe}_2$; 3. Me_2SbBr ; 4. Me_2SbCl ; 5. Me_2SbN_3 ; 6. MeSbCl_2 ; 7. SbBr_3 , ref. 12; 8. SbCl_3 , ref. 12; 9. $\text{Sb}(\text{NMe}_2)_3$; 10. $\text{Cp}_2\text{SbNMe}_2$; 11. Cp_3Sb ; 12. Sb_2O_3 , ref. 13; 13. Cp_2SbI ; 14. Cp_2SbCl ; 15. CpSbCl_2 ; 16. CpSbI_2 ; 17. SbI_3 ; 18. Cp_2SbBr .

to that of cyclopentadiene itself. As expected, differences were only detectable below the 300 cm^{-1} region, where typical antimony-halide stretching frequencies appear [11], e.g.: $\nu(\text{Sb}-\text{I})$ in SbBr_3I^- : 164 cm^{-1} ; SbI_3 : $187, 147, 74\text{ cm}^{-1}$; $\nu(\text{Sb}-\text{Br})$ in SbBr_3I^- : 204 cm^{-1} ; SbBr_3 : $246, 234\text{ cm}^{-1}$. We observed $\nu(\text{Sb}-\text{I})$ for CpSbI_2 at 154 cm^{-1} and $\nu(\text{Sb}-\text{Br})$ for Cp_2SbBr at 242 cm^{-1} , values which agree satisfactorily with those previously reported [11].

Mössbauer spectroscopy: In order to expand our knowledge of antimony(III) Mössbauer data and on the correlations made to particular structural features we investigated a series of antimony(III) compounds. The Mössbauer parameters are listed in Table 3. Figure 1 shows the spectra of Cp_2SbCl and CpSbCl_2 .

For Fig. 2 Pauling electronegativities were used, viz.: $\overline{\chi p}(\text{I}) = 2.5$; $\overline{\chi p}(\text{Cl}) = 3.0$; $\overline{\chi p}(\text{NMe}_2) = 3.1$; $\overline{\chi p}(\text{Br}) = 2.8$; $\overline{\chi p}(\text{O}) = 3.5$; $\overline{\chi p}(\text{Me}) = 2.8$; $\overline{\chi p}(\text{Cp}) = 3.8$; $\overline{\chi p}(\text{Sb}) = 1.9$. Isomer shifts $\delta(\text{IS})$ are relative to InSb as standard; in Fig. 2 $5s$ -electron density at the antimony atom increases with increasing (negative) velocity; this increase may be due to depopulation of $5p$ -electron spin states, thus diminishing their screening effect.

In trigonal SbX_3 compounds ($X = \text{Cl}, \text{Br}, \text{I}$) and in Sb_2O_3 the effective s -electron densities decreased with an increase in $\overline{\Delta\chi p}$, the difference in electronegativity.

Hartree-Fock-Slater LCAO calculations [14] for SbCl_3 and SbI_3 result in $5s$ -electron population of 1.85 (SbCl_3) respectively 1.94 (SbI_3) and a $5pz$ -population of 0.88 (SbCl_3), respectively 0.96 (SbI_3), values which explain the isomer shifts $\delta(\text{IS})$ for these compounds.

Table 4
¹²¹Antimony Mössbauer data and bond angles in SbX₃ derivatives

Compound	bond angle (X-Sb-X) at antimony	Isomer shift δ (IS)(BaSnO ₃) (mm/s)	Quadrupol splitting (mm/s)	Ref.
SbCl ₃	95°	-14.40	+12.3	12
SbBr ₃	96°	-14.20	+9.4	12
SbI ₃	96°	-7.80		
Me ₃ Sb	96°	-8.72	+16.3	
Ph ₃ Sb	94° ^a	-9.33	+16.8	15
(<i>p</i> -tolyl) ₃ Sb	97.3°	-9.37	+17.0	16
Cp ₃ Sb	96.4°	-11.17	+15.6	

^a From dipole moment: J. Chem. Soc., (1955) 3116.

Figure 2 should be regarded as illustrative, indicating how linear correlations can be discerned for various groups of chemical compounds. Extrapolation of line I in Fig. 2 suggest a value for the electron population of 1.73 for SbCp₃ (ignoring minor influences of the 5*p*-electrons on the δ -values), and indicates an electronegativity for Cp, $\overline{\chi p}(\text{Cp})$, (in SbCp₃) of 3.8.

Two contrasting trends are now observed: in Me_{*n*}SbX_{3-*n*} (X = Cl, Br, I), line II, and in (Me₂N)_{*n*}SbCp_{3-*n*} (*n* = 0-3), line III, the 5*s*-electron densities increase with increase of $\overline{\Delta \chi p}$, whereas upon substitution of a cyclopentadienyl ring by a halide, as in Cp_{*n*}SbX_{3-*n*}, line I, the 5*s*-electron density increases with a decrease of $\overline{\Delta \chi p}$.

A more speculative explanation for the increase in *p*-electron density at antimony can be based on the assumption that antimony uses no hybrid orbitals in its Sb-C bonds (bond angles C-Sb-C: approximately 96°), in which case the π -electrons of the ring carbon atoms can to some extent interact with the vacant *d*-orbitals, thus compensating for the higher *s*-electron density in the σ -bonds.

To summarize, from our Mössbauer data we conclude that ligands with π -systems are potentially able to donate electron density into vacant antimony *d*-orbitals, with consequent effects on some σ -donor π -acceptor properties in organo-antimony(III) derivatives.

Of the 18 compounds mentioned in Fig. 2, molecular structures have been reported as shown in Table 4.

The few data available make it very difficult to account for differences in chemical reactivity in terms of differences in chemical isomer shifts.

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