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Coordinatively stabilized antimony(I) chelates

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Abstract

The iodostibinidene complex, $ISb[Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4)]_2$ (**1**) reacts with XH functional chelating ligands HXB (X = O, S) such as 2,4-pentanedione, tropolone, 8-hydroxyquinoline, or 8-mercaptoquinoline to form the antimony(I) chelate complexes $\underbrace{BXSb}[Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4)]_2$ (**2a–2d**).

Introduction

Stibinidene complexes $[L_nM]_2SbR$ [1] (L_nM = 16-electron transition metal fragment, R = univalent residue), like other "-inidene" complexes [2] show a strong tendency to form adducts with Lewis bases |B in which the trigonal planar coordination of the heavy main group element present in $[L_nM]_2SbR$ is replaced by the tetrahedral coordination of $[L_nM]_2Sb(R) \leftarrow B$. For phosphinidene and arsinidene complexes it had been shown that such adducts are especially stable when the Lewis base is part of a chelating ligand [3,4]. We have found that this generalization applies also to the coordinatively stabilized antimony(I) chelates obtained from $ISb[Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4]_2$ (**1**) and various chelating ligands.

Results and discussion

The antimony(I) chelate compounds are formed by treating an n-pentane solution of the stibinidene compound **1** with the appropriate amount of an n-pentane/CH_2Cl_2 solution containing the chelating ligand $H\overline{XB}$ and 1,4-diazabicyclo[2.2.2]octane (DABCO) in a 1/1 ratio (eq. 1). The reactions are carried out at $-20\,^\circ C$, and the less soluble chelates **2** precipitate under these conditions. This procedure gives the coordinatively-stabilized antimony(I) chelates **2** in yields of between 40 and 80%. The compounds **2** are generally more easily handled than the very labile stibinidene complexes themselves (e.g. **1**), but are far less stable than the many known arsenic(I) or phosphorus(I) chelate compounds [3,4]. They are espe-

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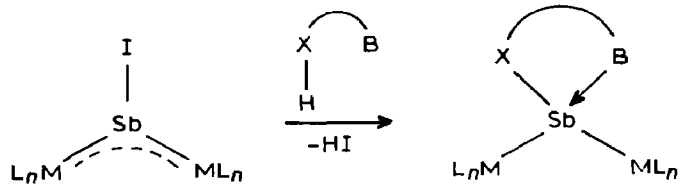
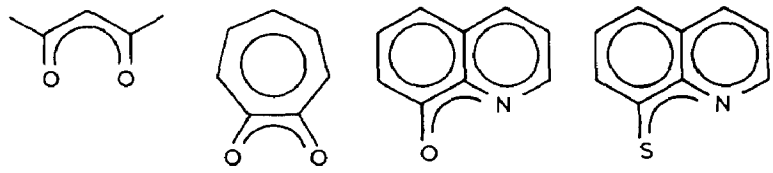


(1)

(1) (2)

$L_nM = \eta^5\text{-}CH_3C_5H_4(CO)_2Mn$

XB:



(2a) (2b) (2c) (2d)

cially unstable in solution; recrystallization at low temperatures is possible, but chromatography (on diatomaceous earth or silica gel) inevitably leads to complete decomposition. It is noteworthy that for $L_nM = \eta^5\text{-}CH_3C_5H_4Mn(CO)_2$ or $\eta^5\text{-}C_5H_5Mn(CO)_2$, neither arsinidene complexes $[L_nM]_2AsHal$ nor phosphinidene complexes $[L_nM]_2PHal$ have been reported to yield analogous chelate derivatives. The higher reactivity of the stibinidene compounds, $[L_nM]_2SbHal$, may be attributed to the greater degree of coordinative unsaturation at the trigonally planar coordinated antimony centre of the stibinidene starting compounds. The longer Mn–Sb compared with Mn–P or Mn–As distances and a weaker Mn–Sb π-interaction may provide an explanation for this phenomenom.

Compounds **2** form orange coloured solids, which are well soluble in CH_2Cl_2 but, except for **2a**, insoluble in n-pentane. As expected, the strong $\pi\text{–}\pi^*$ transition characteristic of "-inidene" complexes such as **1** [2,5] (longer wavelength $\pi\text{–}\pi^*$ transition for **1**: 17270 cm^{-1} [6]) is absent in the chelate complexes **2**. The ν(CO) (IR) spectra of **2** (Table 1) indicate the presence of more than one rotameric form (rotation about the Mn–Sb axis) for the compounds **2**. Because of solubility problems, for **2b–2d** the spectra could be recorded only in CH_2Cl_2 and so the bands are not as well resolved as for **2a** (the spectrum of which could be recorded in n-pentane). Compound **2a** shows a total of five ν(CO) bands compared with the expected six bands for the three possible rotameric forms [2]. The spectra of **2b–2d** still show three, relatively broad, bands, indicating rotamerism for these compounds as well. The rotamerization is too rapid to be detected on the NMR time scale, and so the ^1H NMR spectra (Table 1) display the expected time-averaged patterns. The EI mass spectra (Table 2) in all cases but **2d** show weak but clear signals for the molecular ion M^+; weak signals are also observed for $M^+ - n$CO ($n = 2,4$). Stronger signals are observed for $M^+ - \overline{XB}$, $CH_3C_5H_4(CO)_2MnSb^+$ and their decarbonylation products.

The straightforward formation of **2d** sheds some light on to the mechanism of the reaction of **1** with sulfanes RSH. Whereas PhSH will react with **1** under oxidative

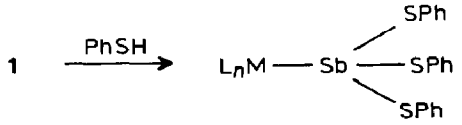
Table 1

Spectroscopic data for the compounds **2a–2d**

Compound	IR [a] (CO) (cm^{-1})	^1H NMR [b] (ppm)
$(C_5H_7O_2)Sb[Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4)]_2$ [c] (**2a**)	1951m, 1934s, 1895s, 1887m, 1855w	1.90 (S, 6H), 2.17 (S, 6H), 4.3–4.6 (M, 8H), 5.56 (S, 1H)
$(C_7H_5O_2)Sb[Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4)]_2$ [d] (**2b**)	1948m, 1926s, 1884s	1.87 (S, 4H), 4.4–4.6 (M, 8H), 7.2–7.6 (M, 5H)
$(C_9H_6NO)Sb[Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4)]_2$ [d] (**2c**)	1942m, 1919s, 1877s	1.80 (S, 6H), 4.2–4.4 (M, 8H), 7.3–8.7 (M, 6H)
$(C_9H_6NS)Sb[Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4)]_2$ [d] (**2d**)	1947m, 1916s, 1874s	1.77 (S, 6H), 4.2–4.4 (M, 8H) 7.5–8.9 (M, 6H)

[a] w = weak, m = medium, s = strong. [b] In $CDCl_3$ solution, 25 °C; S = singulet M = multiplet. [c] In n-pentane solution. [d] In CH_2Cl_2 solution.

addition to yield the stibane complex **3** [6] (eq. 2), there is no indication of an



(2)

(3)

analogous oxidative addition reaction of 8-mercaptoquinoline, which forms exclusively **2d**. This difference can be accounted for in terms of the proposed mechanism for the formation of **3** [6], which involves nucleophilic addition of PhSH to the primary substitution product $[L_nM]_2SbSPh$ as an essential step [6]. The antimony coordination site is blocked towards adduct formation by the nitrogen function of **2d**, thus preventing further nucleophilic attack by RSH on antimony and subsequent oxidative addition processes.

Table 2

EI Mass spectra for the compounds $\underline{\overline{XB}Sb}[Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4)]_2$ (**2a–2d**)

Fragment	$\overline{XB} = C_5H_7O_2$ (**2a**)		$C_7H_5O_2$ (**2b**)		C_9H_6NO (**2c**)		C_9H_6NS (**2d**)	
	m/e	I_r	*m/e*	I_r	*m/e*	I_r	*m/e*	I_r
M^+	600	16	622	2	645	3		
$M^+ - 2CO$	544	2	566	1	589	1	605	1
$M^+ - 4CO$	488	4	510	1	561	1		
$(CH_3C_5H_4(CO)_2Mn)_2Sb^+$	501	9	501	1	501	8	501	2
$(CH_3C_5H_4(CO)Mn)_2Sb^+$	445	5	445	1	445	2	445	1
$(CH_3C_5H_4Mn)_2Sb^+$	389	7	389	3	389	6	389	2
$CH_3C_5H_4(CO)_2MnSb^+$	311	62	311	13	311	23	311	3
$CH_3C_5H_4(CO)MnSb^+$	283	49	283	10	283	14	283	2
$CH_3C_5H_4MnSb^+$	255	22	255	14	255	8	255	7
$(CH_3C_5H_4)_2Mn^+$	213	74	213	14	213	51	213	31
$MnSb^+$	176	3	176	9	176	5	176	3
$CH_3C_5H_4Mn^+$	134	100	134	73	134	92	134	98
$CH_3C_5H_4^+$	79	97	79	100	79	87	79	91
Mn^+	55	98	55	54	55	100	55	100

Table 3

Analytical data for the antimony(I) chelate complexes $\overline{XB}Sb[Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4)]_2$ (**2a–2d**)

$H\overline{XB}$	Chelate (g (mmol))	Yield [a] (g (%))	M.p. [b] (°C)	Analysis (Found (calcd.) (%))		
				C	H	N
$C_5H_8O_2$ (**2a**)	0.10(1.00)	0.251(46)	110–112	42.17 (41.97)	3.50 (3.52)	
$C_7H_6O_2$ (**2b**)	0.13(1.07)	0.442(78)	163–164	44.29 (44.34)	3.14 (3.07)	
C_9H_7NO (**2c**)	0.15(1.03)	0.358(62)	154–157	46.53 (46.48)	3.25 (3.12)	2.12 (2.17)
C_9H_7NS (**2d**)	0.17(1.06)	0.279(42)	163–165	45.24 (45.35)	3.30 (3.04)	2.21 (2.11)

[a] Based on antimony. [b] With decomposition.

Experimental

All reactions and manipulations were carried out under dinitrogen, and dried and freshly distilled solvents were used. Mass spectra: Varian MAT-112S/372. IR spectra: Perkin–Elmer 938G. ^1H NMR spectra: Bruker AC 200.

Synthesis of the antimony(I) chelate complexes **2a–2d**

In a typical experiment 0.06 g (0.50 mmol) 1,4-diazabicyclo[2.2.2]octane (DABCO) was added to a solution of 1.0 mmol of the chelating ligand (see Table 3) in 30 ml of n-pentane/CH_2Cl_2 (1/1). The mixture was added dropwise to a cooled (−20 °C) solution of 0.57 g (0.90 mmol) $ISb[Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4)]_2$ (**1**) [6] in 30 ml n-pentane, upon which a mixture of **2a–2d** and DABCO · HI separated immediately as an orange precipitate. The suspension was stirred for 0.5 h at −20 °C then 20 ml of CH_2Cl_2 was added. This resulted in the dissolution of **2a–2d** leaving DABCO · HI as a colourless residue. After removal of the solvent, the orange residue was recrystallized from n-pentane/CH_2Cl_2 (−30 °C). Yields, melting points and analytical data for the compounds **2a–2d** are given in Table 3.

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