

Tertiary stibines containing aromatic heterocycles and their silver complexes: synthesis and X-ray structures

J. Vela, P. Sharma *, A. Cabrera, C. Álvarez, N. Rosas, S. Hernández, A. Toscano

Instituto de Química, UNAM, AP 70-213, Circuito Exterior, 04510 México D.F., Mexico

Received 1 March 2001; received in revised form 16 May 2001; accepted 18 May 2001

Abstract

The work presents the synthesis of tertiary stibines containing heterocyclic aromatic groups of general formula $(2-C_4H_3X)_3Sb$ where $X = S$ (**1**), O (**2**) or NMe (**3**). These stibines were brominated to give corresponding dibromide and were complexed with silver(I) nitrate. The stibines, dibromides and their silver complexes were characterized by elemental analyses, IR, UV, mass, 1H , ^{13}C , COSY, HETCOR NMR spectroscopy. Molecular structures of $(2-C_4H_3S)_3Sb$ (**1**); $(2-C_4H_3S)_3SbBr_2$ (**4**) and $\{Ag[(2-C_4H_3S)_3Sb]_2\}NO_3$ (**6**) were determined by X-ray spectroscopy. This is the first X-ray crystallographic report on stibines containing heterocyclic aromatic groups and their silver complexes. The stibine (**1**) is pyramidal while its dibromide has trigonal bipyramidal structure. The silver complex (**6**) has a polymeric nature with NO_3^- acting as a bridging ligand. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Stibines; Aromatic heterocycles; Tripodal ligands; Silver complex

1. Introduction

Tertiary stibines R_3Sb (where $R =$ alkyl or aryl) are very well known but there exist only few reports on tertiary stibines where antimony is directly attached to an aromatic heterocycle. To the best of our knowledge, the very first report appeared in early 1940s regarding the synthesis of tris-thienylstibine, tris-furylstibine or tris-pyridylstibine, and characterization was done by elemental analyses only [1]. In 1981, Schewhuk and Wild reported [2] the synthesis and properties of three tertiary stibines, viz. dimethyl(α -picolyl)stibine, dimethyl(8-quinolyl)stibine and methylphenyl(8-quinolyl)stibine. All these stibines were well characterized by proton NMR and mass spectroscopy. These stibines readily formed the expected neutral Pt(II) and Pd(II) complexes. A report [3] appeared later describing the synthesis of diphenyl(pyridyl)stibines after reducing Ph_3Sb . Recently our group [4] has characterized some

new tetrachloropyridylstibines but their ligation properties were not discussed.

Studies on organometallic compounds containing thienyl, furyl or *N*-methylpyrrolyl with Si, Ge, Sn or Hg and even with lighter pnictogens (P, As) are known [5]. In addition to this, it was also observed that 2-thienyl or 2-furyl phosphines are better ligands in palladium catalyzed Stille reaction than triphenylphosphine [6,7].

So in view of the applications of trisfuryl or tris-thienyl phosphines and since only a couple of reports exist on the tertiary stibines containing heterocyclic aromatic groups and no structural report is available on these type of stibines — not even arsines — or their complexes, this work was undertaken.

2. Results and discussion

The color, m.p., percent yield and elemental analyses of the synthesized compounds reported in this work are presented in Table 1. The three tertiary stibines remain unaffected by water thus the Sb–C bonds in the above compounds are not hydrolyzed by water alone. These

* Corresponding author. Tel./fax: +52-5-622-4515.

E-mail address: pankajsh@servidor.unam.mx (P. Sharma).

Table 1
Elemental analyses and physical properties of triheteroarylstibines and derivatives

No.	Colour	m.p. (°C)	Yield (%)	C (%)	H (%)	S (%)	N (%)	Br (%)
1	White	40.0–41.1	74	37.18 ^a (38.83) ^b	2.42 (2.44)	26.10 (25.92)	–	–
2	Light yellow	38.8–40.7	82	44.07 (44.62)	2.82 (2.79)	–	–	–
3	White	98.2–100.9	37	49.98 (49.76)	5.06 (4.98)	–	12.76 (11.61)	–
4	Light green	173.7–178.1	59	27.08 (27.15)	1.68 (1.71)	17.57 (18.12)	–	31.14 (30.10)
5	Light green	141.3–145.9 _{dec}	84	30.12 (29.86)	2.01 (1.88)	–	–	34.25 (33.10)
6	Bright white	144.8–147.3 _{dec}	76	30.94 (31.60)	1.84 (1.98)	–	1.61 (1.54)	–
7	Bright white	141.7–146.3 _{dec}	29	–	–	–	–	–

^a Observed value.

^b Calculated value in parentheses.

tertiary stibines behave like other triarylstibines and one of the dibromides, tris(2-thienyl)stibine dibromide (**4**) is thermally stable and melts without decomposition. Silver complexes **6** and **7** obtained are sensitive to moisture, light and air to a varying degree, even these complexes show some decomposition in solution. The decomposition product could not be characterized because of its insolubility in common solvents.

The three stibine ligands were nonconducting while their silver complexes show 1:1 conductance in acetonitrile solution.

On the basis of the structure of other tertiary stibines [4,8] a pyramidal structure may be assigned to **1–3**. For the dibromides R_3SbBr_2 , the stretching vibration of the Sb–Br bond occurs at higher frequency when increasing the electron-withdrawing capacity of the substituent R: thienyl 195 cm^{-1} , furyl 210 cm^{-1} , tetrachloropyridyl [4] 218 cm^{-1} . The replacement of the heterocycle by a more electron-withdrawing one leads to an increase in partial positive charge on the antimony atom and strengthens the Sb–Br band.

The same correlation is found for the two silver(I) complexes, in which the highest frequency for the Sb–Ag vibration is observed when the heterocycle is furyl.

UV spectra of these stibines and their dibromides were studied. The principal band observed in UV spectra of these compounds can be assigned to a $\pi-\pi^*$ transition in the heterocycle. In the spectrum of **2** a bathochromic shift was observed in comparison to its phosphorus analogue $(2-C_4H_3O)_3P$; because of unavailability of the data in literature we could not make comparison for the other two analogues but these also show a bathochromic shift with respect to the corresponding phosphine oxides $(2-C_4H_3X)_3P=O$ where X = S or NMe.

These spectroscopic comparisons are particularly important for determining the $p\pi-d\pi$ interaction. Redmore [5e] has noted that the higher the $p\pi-d\pi$ interaction, the higher the bathochromic shift in relation to the maximum of unsubstituted heterocyclic ring; $\Delta\lambda_{max}$ in these stibines **1**, **2** and **3** are 10.8, 39.0, and

46.5 nm, respectively, showing the increasing order of $p\pi-d\pi$ interaction in the order **1** < **2** < **3**. The bathochromic shifts are summarized in Table 2 and are higher in comparison to phosphorus analogues indicating higher $p\pi-d\pi$ interaction in stibines than in phosphines bearing these heterocycles.

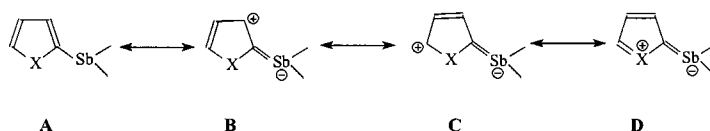
EI mass spectral analyses of stibines $(2-C_4H_3X)_3Sb$, where X = S, O or NMe show some common decomposition patterns. The fragmentation peaks observed for the heterocyclic part are not of much importance and are according to those reported in literature [9]. In the case of their dibromides, a molecular ion peak could not be observed either in EI or in CI but the presence of $[(C_4H_3X)_3SbBr]^+$ ion in EI and $[(C_4H_3X)_nSbBr_2]^+$ in CI (where X = S or O, and $n = 1$ or 2) confirms the assigned molecular formula. Both silver complexes were characterized by FAB⁺ spectra giving a well defined peak for complex cationic unit $\{Ag[(2-C_4H_3X)_3Sb]_2\}^+$ (where X = S or O).

The proton NMR spectra of all these compounds show a characteristic pattern of three multiplets in the aromatic proton region. In all the cases assigning individual protonic signal was based on J_{HH} coupling constant values [10] and was confirmed by COSY.

Table 2
Bathochromic shifts for triheteroarylstibines and phosphines

Compound	λ_{max} (nm)	$\Delta\lambda_{max}$ (nm) ^a	Reference
$(2-C_4H_3S)_3Sb$	241.8	10.8	This work
$(2-C_4H_3S)_3SbBr_2$	270.5	39.5	This work
$(2-C_4H_3S)_3PO$	238.0	≈0	5e
C_4H_4S (thiophene)	231.0	–	5e
$(2-C_4H_3O)_3Sb$	244.0	39.0	This work
$(2-C_4H_3O)_3SbBr_2$	239.4	34.4	This work
$(2-C_4H_3O)_3P$	243.0	38.0	5e
$(2-C_4H_3O)_3PO$	238.0	33.0	5e
C_4H_4O (furan)	205.0	–	5e
$(2-C_4H_3NMe)_3Sb$	259.5	46.5	This work
$(2-C_4H_3NMe)_3P$	243.0	30.0	5e
C_4H_4 NMe (<i>N</i> -methylpyrrole)	213.0	–	5e

^a Values relative to corresponding parent heterocycle.



Scheme 1.

Proton coupling constants for tris(1-methyl-2-pyrrolyl)stibine could not be determined accurately as H_4 and H_3 appeared very close ($\Delta\nu/J < 8$) and it was found that H_4 and H_3 appeared interchanged in position in comparison to their appearance in the other two ligands **1** and **2**. This phenomenon was also found in oxides of the phosphine analogues [5c].

For five-membered heterocycle substituted at the second position by antimony, it was observed that H_3 and H_5 are more deshielded compared to parent unsubstituted heterocycle, which may be due to $p\pi-d\pi$ bonding and can be explained by the contribution of canonical form B and C, respectively in Scheme 1. The increase of deshielding of H_3 and H_5 (in **1** and **2**, Table 3) by increasing the polarity of solvent from $CDCl_3$ to acetone d_6 supports the previous statements. Similarly to proton NMR, the ^{13}C C_3 and C_5 carbons show a more pronounced downfield shift in comparison to C_4 or C_2 carbons also supporting the $p\pi-d\pi$ bonding concept in these compounds.

In contrast to UV data analyses, from 1H -NMR one can observe that in thienyl and furylstibines $p\pi-d\pi$ bonding is more pronounced than in pyrrolylstibine. However and as noted previously [5e], both UV and NMR data should be considered as complementary since they describe measurements in the excited and ground states of molecules, respectively. In dibromides, the protonic signals appeared more downfield because of the presence of electronegative bromine.

At ambient temperature, four ^{13}C -NMR signals were observed for these compounds in the aromatic region. With the intention to get more information on the influence of antimony directly attached at the second position of the heterocyclic ring, the carbon-carbon coupling constant for compound **1** has been measured using INADEQUATE. The experimental value of $^1J_{C_{2C_3}}$ is 54.23 Hz for tris(2-thienyl)antimony while the theoretically calculated value is 53.17 Hz [11]. This $^1J_{C_{2C_3}}$ value depends on the electronegativity of the atom attached to the 2nd position and for the more electropositive Li atom it is 27.3 Hz.

A downfield shift is observed in the proton NMR spectra of the silver complexes in comparison to the corresponding stibine ligands. The high sensitivity of these complexes in solution did not allow us to measure J_{35} in **6** and C_2 in ^{13}C -NMR for **7** or to complete COSY and HETCOR experiments.

Selected bond lengths and angles for structures of **1**, **4** and **6** are listed in Table 4 and X-ray diffraction parameters are shown in Table 5. The molecular structures of **1**, **4** and **6** are shown in Figs. 1–3, respectively.

Stibine (C_4H_3S) $_3$ Sb (**1**) is pyramidal. The unit cell contains two different crystallographically independent

Table 3

1H -NMR chemical shifts ($\Delta\delta$ /ppm) for triheteroarylstibines and dibromides relative to parent heterocycle^a

Compound	Solvent	H_3	H_4	H_5
(2- C_4H_3S) $_3$ Sb	$CDCl_3$	+0.34	+0.19	+0.46
(2- C_4H_3S) $_3$ Sb	Acetone d_6	+0.42	+0.23	+0.62
(2- C_4H_3S) $_3$ SbBr $_2$	$CDCl_3$	+1.39	+0.34	+0.65
(2- C_4H_3O) $_3$ Sb	$CDCl_3$	+0.49	+0.20	+0.41
(2- C_4H_3O) $_3$ Sb	Acetone d_6	+0.55	+0.27	+0.55
(2- C_4H_3O) $_3$ SbBr $_2$	$CDCl_3$	+1.49	+0.42	+0.60
(2- C_4H_3NMe) $_3$ Sb	$CDCl_3$	-0.11	-0.07	+0.14
(2- C_4H_3NMe) $_3$ Sb	Acetone d_6	-0.14	-0.09	+0.11

^a Values of δ (ppm) for unsubstituted heterocycles are: thiophene (H_2 7.18, H_3 6.99), furan (H_2 7.29, H_3 6.24), 1-Methylpyrrole (H_2 6.74, H_3 6.28) [10].

Table 4

Selected bond lengths (Å) and bond angles ($^\circ$)

Compound 1			
Sb(1)–C(22)	2.126(7)	C(22)–Sb(1)–C(12)	97.9(3)
Sb(1)–C(2)	2.139(7)	C(32)–Sb(2)–C(52)	98.2(3)
Sb(2)–C(32)	2.125(7)	C(52)–Sb(2)–C(42)	95.4(3)
Sb(2)–C(42)	2.131(7)	C(45)–S(5)–C(42)	93.9(5)
S(2)–C(12)	1.730(8)	C(13)–C(12)–S(2)	114.3(5)
S(4)–C(35)	1.673(11)	C(53)–C(52)–Sb(2)	123.0(5)
C(42)–C(43)	1.450(11)	S(4)–C(32)–Sb(2)	127.4(4)
C(53)–C(54)	1.417(13)	C(55)–C(54)–C(53)	117.2(10)
Compound 4			
Sb(1)–C(22)	2.098(10)	C(22)–Sb(1)–C(12)	123.8(4)
Sb(1)–C(2)	2.131(12)	C(12)–Sb(1)–C(2)	120.9(4)
Sb(1)–C(12)	2.102(10)	C(22)–Sb(1)–Br(1)	89.8(3)
Sb(1)–Br(2)	2.6182(16)	C(22)–Sb(1)–Br(2)	89.0(3)
Sb(1)–Br(1)	2.6109(15)	Br(1)–Sb(1)–Br(2)	178.67(6)
Compound 6			
Sb(1)–C(12)	2.10(3)	O(2) # 1–Ag–O(1)	70.6(9)
Ag–O(2) # 1	2.40(2)	O(1)–Ag–Sb(2)	116.0(8)
Sb(1)–Ag	2.694(3)	O(1)–Ag–Sb(1)	101.4(7)
Sb(2)–Ag	2.677(3)	O(2) # 1–Ag–Sb(2)	121.9(11)
Ag–O(1)	2.46(2)	O(2) # 1–Ag–Sb(1)	114.1(12)
O(2)–Ag # 2	2.40(2)	Sb(2)–Ag–Sb(1)	119.80(8)
Sb(1)–C(2)	2.14(3)	C(12)–Sb(1)–Ag	116.8(7)
N(1)–O(1)	1.20(4)	O(1)–N(1)–O(3)	116(3)
N(1)–O(3)	1.29(3)		

Table 5
Crystal data for compounds **1**, **4** and **6**

	Compound		
	1	4	6
Empirical formula	C ₂₄ H ₁₈ S ₆ Sb ₂	C ₁₂ H ₉ Br ₂ S ₃ Sb	C ₂₄ H ₁₈ AgNO ₃ -S ₆ Sb ₂
Formula weight	742.24	498.88	912.12
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> <i>c</i>
<i>a</i> (Å)	9.876(1)	12.753(4)	26.164(3)
<i>b</i> (Å)	11.469(2)	8.913(2)	13.625(1)
<i>c</i> (Å)	13.894(3)	14.548(5)	8.783(1)
α (°)	88.54(2)	90	90
β (°)	72.25(2)	102.56(3)	93.77(1)
γ (°)	67.45(1)	90	90
<i>V</i> (Å ³)	1376.7(6)	1614.1(8)	3124.2(6)
<i>Z</i>	2	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.791	2.053	1.939
μ [Mo-K α] (mm ⁻¹)	2.429	6.986	22.569
Crystal size (mm)	0.32 × 0.28 × 0.20	0.38 × 0.32 × 0.12	0.60 × 0.16 × 0.04
2 θ (°)	1.93–24.99	1.64–25.00	1.50–56.75
Reflections collected	5160	2939	1993
Unique reflections	4851	2810	1993
<i>R</i> _{int}	0.0374	0.0433	0.0000
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0443	0.0502	0.0588
Method of solution	SHELXS-97	SHELXS-97	SHELXS-97
Max/min $\Delta\rho$ (e Å ⁻³)	1.011/–0.764	0.750/–0.706	0.833/–0.976
<i>S</i> [goodness-of-fit]	0.948	0.828	1.036

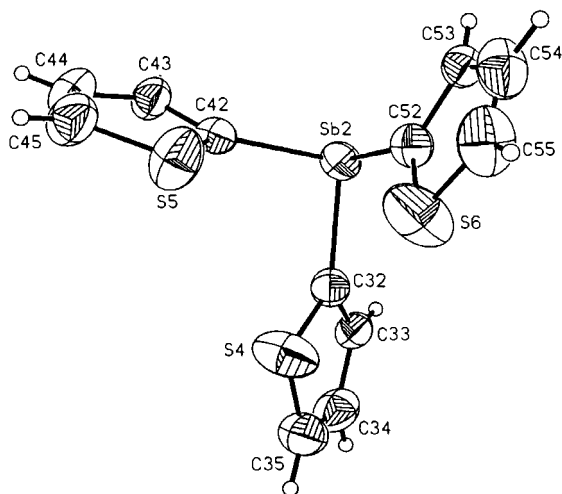


Fig. 1. Molecular structure of compound **1**.

molecules. The average angle C–Sb–C is 96.5°, which is higher than found in Ph₃Sb, 95° [12]. The three sulfur atoms are more or less in a one plane forming three

points of an equilateral triangle. The structure shows that it can act as a tripodal ligand, but unlike tripodal ligand trispyridylphosphine or arsine [13] the molecule does not deviate from C_{3v} symmetry.

The average Sb–C bond length found in **1** is 2.129 Å, which is slightly shorter than that found in other known tertiary stibines [14] e.g. Ph₃Sb 2.155; 2.190 in tris(2,6-dimethylphenyl)stibine; 2.158 in tris(2-methylphenyl)stibine. This may be due to the p π –d π bonding to a greater extent and thus shortening of Sb–C bond length. Intramolecular distances are greater than normal van der Waals interactions.

Tris(2-thienyl)stibine dibromide (**4**) proved to be monomeric in the solid state and in the molecule, the antimony atom is pentacoordinated, two Br atoms being in the apical positions with three C(thienyl) atoms in the equatorial trigonal plane. In this compound, the mean Sb–C is 2.110(1) Å.

Considering the axial angle Br(1)–Sb–Br(2), 178.67° and the equatorial/axial bond angles with a maximum deviation of 4.8 and 1.3°, respectively from the ideal mean values of 120 and 90°, it can be inferred that there is a slight distortion around the antimony polyhedron. There are two Sb–Br distances, 2.611(1) and 2.619(2) Å, which are different from the single type, found in Ph₃SbBr₂, 2.632(1) Å.

The structure determination of complex **6** is consistent with the stoichiometry Ag[Sb(2-thienyl)₃]₂NO₃, the asymmetric unit comprising a polymeric unit of the complex. The silver atom is four-coordinated by two Sb atoms from the two Sb(2-thienyl)₃ moieties with Ag–Sb bond distances 2.694(2) and 2.677(3) Å and by two O atoms from two symmetry related NO₃[–] ions [Ag–O(1) 2.46(2), Ag–O(2') 2.40(2) Å]. The nitrate ligand is bidentate with an oxygen atom bridging symmetrically to two Ag atoms. The nitrate plane also seems to be negligibly twisted to place the oxygen closer to the second silver atom.

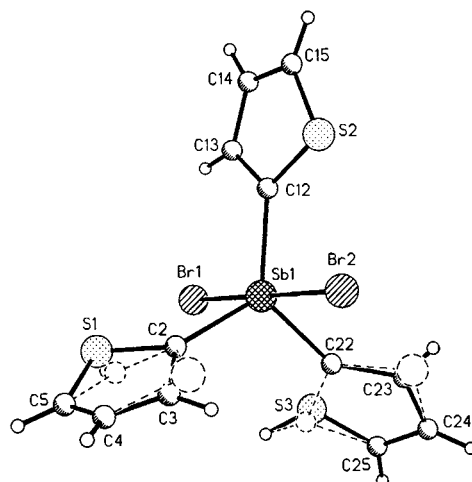


Fig. 2. Molecular structure of compound **4**.

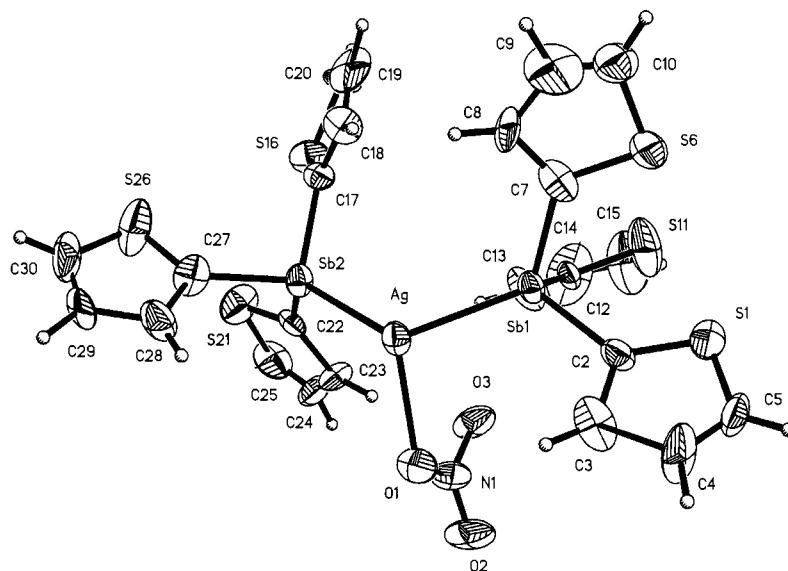


Fig. 3. Molecular structure of compound 6.

In the complex, the angle sum $\text{Sb}(1)\text{--Ag--Sb}(2) + \text{Sb}(1,2)\text{--Ag--O}(1)$ is 336° , perhaps indicative that a very large distortion from trigonal planar description of the coordination environment is to be preferred in terms of the more complex regular array.

3. Experimental

All the solvents were distilled immediately prior to use. All the reactions were performed under an atmosphere of oxygen-free, dry nitrogen. Melting points were obtained in a MEL-TEMP II Fisher and are uncorrected. Elemental analyses were performed by Galbraith Laboratory at Knoxville, TN. Far IR spectra were recorded in polyethylene on a Nicolet-Magna 750 spectrometer. For UV spectra, λ_{max} was measured in methylene chloride (**1–5**) or acetonitrile (**6** and **7**) in a Pharmacia Biotech Ultraspec 3000 UV/Vis. EI, CI and FAB^+ mass spectra were recorded on a JEOL SX102 double focusing mass spectrometer with reverse geometry using a 6-kV Xenon beam (10 mA); nitrobenzyl alcohol was used as matrix for recording the mass spectra. Conductimetry measurements of 10^{-3} M solutions of complexes **6** and **7** in acetonitrile were made with a Metrohm 644 Conductometer, with $\text{kc}^{-1} = 2.07$ cm.

3.1. Crystal X-ray structure determination

Data were collected on a Siemens P4/Pc diffractometer at 293 K using monochromated Mo--K_α radiation ($\lambda = 0.7107 \text{ \AA}$) for compounds **1** and **4**; Cu--K_α radiation ($\lambda = 1.5418 \text{ \AA}$) was used for **6**. The system used for calculations was Siemens SHELXTL PLUS (PC Version)

and structure determination was done by direct methods with refinement by a full matrix least-squares procedure.

3.2. Synthesis of $(2\text{-C}_4\text{H}_3\text{S})_3\text{Sb}$ (**1**)

A solution of antimony trichloride (3.22 g, 14.1 mmol) in ether (10 ml) was added drop-wise and under a nitrogen atmosphere to 2-thienyllithium (3.81 g, 42.3 mmol) (Aldrich, 1 M in THF) at -20°C with continuous stirring. The mixture was further stirred for 30 min at room temperature (r.t.) and then quenched with ice. After extraction with hexane (3×5 ml) and drying over sodium sulfate, solvent was removed under vacuum. Slow concentration from chloroform solution afforded single crystals suitable for X-ray analysis. Yield: 3.86 g (74%); $\lambda_{\text{max}} = 241.8$; $\text{IR}(\text{cm}^{-1})$: (Sb–C) 474, 464, 296, 270, 248; $^1\text{H-NMR}$ (CDCl_3 , δ in ppm): 7.64 (m, $J_{45} = 4.95$, H_5), 7.33 (m, $J_{35} = 0.90$, H_3), 7.18 (m, $J_{34} = 3.30$, H_4). $^{13}\text{C-NMR}$ (CDCl_3 , δ in ppm): 137.14 (C_3), 132.62 (C_2), 132.54 (C_5), and 128.20 (C_4). MS (EI) m/z (%): 370 (10) [M^+], 287 (5) [$\text{M}-(2\text{-C}_4\text{H}_3\text{S})^+$], 204 (100) [$\text{M}-(2\text{-C}_4\text{H}_3\text{S})^+$].

3.3. Synthesis of $(2\text{-C}_4\text{H}_3\text{O})_3\text{Sb}$ (**2**)

The compound was synthesized by a similar procedure to **1**. 2-Furyllithium was prepared according to the literature procedure [15]. Yield: 3.73 g; $\lambda_{\text{max}} = 244.0$; $\text{IR}(\text{cm}^{-1})$: (Sb–C) 622, 595, 298, 275, 243 $^1\text{H-NMR}$ (CDCl_3 , δ in ppm): 7.70 (m, $J_{45} = 4.89$, H_5), 7.41 (m, $J_{35} = 0.83$, H_3), 7.22 (m, $J_{34} = 3.44$, H_4). $^{13}\text{C-NMR}$ (CDCl_3 , δ in ppm): 150.70 (C_2), 148.04 (C_5), 122.86 (C_3), and 110.37 (C_4). MS (EI) m/z (%): 322 (25) [M^+], 255 (6) [$\text{M}-(2\text{-C}_4\text{H}_3\text{O})^+$], 188 (100) [$\text{M}-(2\text{-C}_4\text{H}_3\text{S})^+$].

3.4. Synthesis of (2-C₄H₃NMe)₃Sb (3)

The compound was synthesized by a similar procedure to **1**. 1-Methyl-2-pyrrolyllithium was prepared according to the literature procedure [15]. Yield: 1.89 g; λ_{\max} = 259.5; IR(cm⁻¹): (Sb–C) 421, 409, 387, 283, 261; ¹H-NMR (CDCl₃, δ in ppm): 7.70 (m, J_{45} = 4.89, H₅), 7.41 (m, J_{35} = 0.83, H₃), 7.22 (m, J_{34} = 3.44, H₄). ¹³C-NMR (CDCl₃, δ in ppm): 126.80 (C₅), 124.14 (C₂), 120.99 (C₃), 109.17 (C₄), 37.27 (NCH₃). MS (EI) m/z (%): 361 (30) [M⁺], 281 (5) [M-(2-C₄H₃NMe)⁺], 201 (61) [M-(2-C₄H₃NMe)⁺].

3.5. Synthesis of (2-C₄H₃S)₃SbBr₂ (4)

A titration-like procedure was followed. Bromine in hexanes was added at 0 °C to stibine **1** (1.11 g, 3.0 mmol) in hexane–methylene chloride until complete precipitation of dibromide was attained and a permanent red color was observed in solution. Light crystals suitable for X-ray analysis were obtained by evaporation of solvent at r.t. Yield: 0.94 g; λ_{\max} = 270.5; IR(cm⁻¹): (Sb–C) 455, 290, 239, 222, 162; ν (Sb–Br) 195; ¹H-NMR (CDCl₃, δ in ppm): 8.38 (m, J_{35} = 1.20, H₃), 7.83 (m, J_{45} = 5.10, H₅), 7.33 (m, J_{34} = 3.90, H₄). ¹³C-NMR (CDCl₃, δ in ppm): 140.21 (C₃), 136.55 (C₅), 135.64 (C₂), and 128.44 (C₄). MS (EI) m/z (%): 364 (1) [M-2(2-C₄H₃S)⁺], 451 (100) [M–Br⁺], 285 (10) [(2-C₄H₃S)SbBr⁺]; (CI) 451 (21) [M–Br⁺], 287 (56) [(2-C₄H₃S)SbBr–H₂⁺].

3.6. Synthesis of (2-C₄H₃O)₃SbBr₂ (5)

The compound was synthesized by a similar procedure to **4** from corresponding furyl stibine **2**. Yield: 1.22 g; λ_{\max} = 239.4; IR(cm⁻¹): (Sb–C) 592, 459, 316, 268, 219; ν (Sb–Br) 210; ¹H-NMR (CDCl₃, δ in ppm): 7.89 (m, J_{35} = 0.55, H₅), 7.73 (m, J_{34} = 3.58, H₃), 6.66 (m, J_{45} = 1.65, H₄). ¹³C-NMR (CDCl₃, δ in ppm): 150.34 (C₅), 143.62 (C₂), 126.16 (C₃), and 112.24 (C₄). MS (EI) m/z (%): 415 (1) [M-(2-C₄H₃O)⁺], 349 (1) [M-2(2-C₄H₃O)⁺], 403 (41) [M–Br⁺], 269 (5) [(2-C₄H₃O)SbBr⁺]; (CI) 416 (7) [M-(2-C₄H₃O)–H⁺], 349 (1) [M-2(2-C₄H₃O)⁺], 403 (100) [M–Br⁺], 269 (16) [(2-C₄H₃O)SbBr⁺].

3.7. Synthesis of {Ag[(2-C₄H₃S)₃Sb]₂}NO₃ (6)

To a solution of ligand **1** (742 mg, 2.0 mmol) in methylene chloride in a Schlenk flask was added silver(I) nitrate (169 mg, 0.5 equiv.) in methanol under a constant flux of dry nitrogen. Bright white crystals precipitated immediately, and the solvent was removed by filtration. Single crystals for X-ray studies were grown from acetonitrile solution at –70 °C. Yield: 1.39 g (76%). IR(cm⁻¹): (Sb–C) 470, 262, 231, 222, 187,

ν (Sb–Ag) 151; ¹H-NMR (Acetone d_6 , δ in ppm): 7.87 (m, J_{35} = 1.10, H₅), 7.52 (m, J_{34} = 3.30, H₃), 7.25 (m, J_{45} = 4.68, H₄). ¹³C-NMR (Acetone d_6 , δ in ppm): 138.18 (C₃), 133.54 (C₅), 128.48 (C₄), C₂ not resolved. MS (FAB⁺) m/z (%): 850 (16) [AgL₂⁺], 479 (100) [AgL⁺], 107 (15) [Ag⁺], (L = **1**). Molar conductance in acetonitrile: 143.14 S cm² mol⁻¹.

3.8. Synthesis of {Ag[(2-C₄H₃O)₃Sb]₂}NO₃ (7)

The complex was obtained by a similar procedure to that of **6**. Yield: 473 mg (29%). IR(cm⁻¹): (Sb–C) 594, 289, 261, 247, 215; ν (Sb–Ag) 163; ¹H-NMR (Acetone d_6 , δ in ppm): 7.70 (m, H₅), 6.80 (m, J_{34} = 3.30, H₃), 6.44 (m, J_{45} = 1.65, H₄). ¹³C-NMR (Acetone d_6 , δ in ppm): 149.20 (C₂), 148.25 (C₅), 122.78 (C₃), and 110.17 (C₄). MS (FAB⁺) m/z (%): 752 (7) [AgL₂⁺], 431 (38) [AgL⁺], 107 (17) [Ag⁺], (L = **2**). Molar conductance in acetonitrile: 135.21 S cm² mol⁻¹.

4. Conclusions

Three new potentially multidentate tripodal ligands, their bromides and silver complexes have been synthesized. A number of such types of ligands containing one or two heterocyclic atoms and their ligation properties can be studied in view of the great applicability of their phosphorus congeners. Work is in progress to study the ligand effects in hydroformylation and amidocarbonylation of alkenes using rhodium and cobalt catalysts.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC no. 159579, 159580 and 159581 for compounds **1**, **4** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors are grateful to DGAPA-UNAM (IN 204199) for financial support.

References

- [1] (a) H.E. Ramsden, Br. Patent 824,944, Dec. 9, 1959; (b) A. Étienne, Bull. Soc. Chim. (1946) 50.
- [2] E. Schewhuk, S.B. Wild, J. Organomet. Chem. 210 (1981) 181.

- [3] A.R. Al-Soudani, A.G. Massey, *Appl. Organomet. Chem.* 2 (1988) 553.
- [4] P. Sharma, N.K. Jha, *J. Organomet. Chem.* 506 (1996) 19.
- [5] (a) É. Lukevits, O.A. Pudova, Y. Popelis, N.P. Erchak, *Zh. Obshch. Khim.* 51 (1981) 115;
(b) A.P. Ebdon, T.N. Huckerby, F.G. Thorpe, *Tetrahedron Lett.* (1971) 2971;
(c) E. Niwa, H. Aoki, H. Tanaka, K. Munakata, *Chem. Ber.* 99 (1966) 712;
(d) R.H. Kemp, W.A. Thomas, M. Gordon, C.E. Griffin, *J. Chem. Soc. (B)* (1969) 527;
(e) D. Redmore, *Chem. Rev.* 71 (1971) 334;
(f) D.W. Allen, B.F. Taylor, *J. Chem. Soc. Dalton Trans.* (1982) 51;
(g) S.S. Moore, G.M. Whitesides, *J. Org. Chem.* 47 (1982) 1489.
- [6] V. Farina, B. Krishnan, *J. Am. Chem. Soc.* 113 (1991) 9585.
- [7] R. Rossi, F. Bellina, M. Biagetti, L. Martínez, *Tetrahedron Lett.* 39 (1998) 7599.
- [8] (a) J.H.S. Green, W. Kynaston, H.M. Paisley, *Spectrochim. Acta A* 19 (1963) 549;
(b) J.H.S. Green, D.J. Harrison, *Spectrochim. Acta A* 33 (1977) 75.
- [9] C.W. Bird, G.W.H. Cheeseman, *Structure of Five-Membered Rings with One Heteroatom in Comprehensive Heterocyclic Chemistry*, Pergamon, Oxford, 1984, pp. 21–24.
- [10] A.A. Bothner-by, Proton–proton coupling constants, in: *Advances in Magnetic Resonance*, Academic Press, New York, 1965, pp. 295–301.
- [11] A. Dabrowski, K. Kamienska-Trela, J. Wojcik, *Spectrochim. Acta Part A* 56 (2000) 91.
- [12] E.A. Adams, J.W. Collis, W.T. Pennington, *Acta Crystallogr. Sect. C* 46 (1990) 917.
- [13] L.F. Szczepura, L.M. Witham, K.J. Takeuchi, *Coord. Chem. Rev.* 174 (1998) 5.
- [14] (a) A. Ates, H.J. Breunig, K.H. Ebert, R. Kaller, M. Drager, U. Behrens, *Z. Naturforsch., B Chem. Sc.* i. 47 (1992) 503;
(b) A.N. Sobolev, I.P. Romm, V.K. Belsky, O.P. Syufina, E.N. Guryanova, *J. Organomet. Chem.* 209 (1979) 49;
(c) A.N. Sobolev, I.P. Romm, V.K. Belsky, O.P. Syufina, E.N. Guryanova, *J. Organomet. Chem.* 179 (1979) 153;
(d) E.A. Adams, J.W. Collis, W.T. Pennington, *Acta Crystallogr. Sect. C* 46 (1990) 917;
(e) P. Sharma, N. Rosas, A. Rama Shankar, A. Toscano, S. Hernandez, A. Cabrera, *Main Group Met. Chem.* 19 (1996) 21;
(f) P. Sharma, N. Rosas, G. Espinosa, A. Cabrera, *Acta Crystallogr. Sect. C* 52 (1996) 889;
(g) P. Sharma, A. Cabrera, N. Rosas, R. Le Lagadec, S. Hernandez, J. Valdes, J.L. Arias, C.V. Ambrose, *Main Group Met. Chem.* 21 (1998) 303.
- [15] B.J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon, Oxford, 1976, pp. 44–48.