Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 689 (2004) 2593–2600
Journal of Organo metallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and structures of organoantimony compounds containing intramolecular Sb–N interactions

P. Sharma *, D. Castillo, N. Rosas, A. Cabrera, E. Gomez, A. Toscano, F. Lara, S. Hernández, G. Espinosa

Instituto De Quimica, UNAM, Quimica Inorganica, Circuito Exterior Coyoacan, Mexico D.F. 04510, Mexico

Received 1 March 2004; accepted 14 May 2004

Abstract

Stibines R'_3Sb containing the pendant arm [2-(Me_2NCHR)C_6H_4] (where R = H or Me) were synthesized, and their reactions with CH3I and HBr have been carried out to obtain the diammonium salt {[2-(Me_2NCHR)C_6H_4] [2-(Me_3N^+CHR)C_6H_4]}Sb 2[I]$^-$ (where R = H **3**; Me **4**) and triammonium salt {2-[($Me_2HN^+CH_2$)C_6H_4]$_3$}Sb 3[Br]$^-$ **5**, respectively. A novel platinum complex **6** [$PtCl_2 \cdot$ **1**] containing stibine **1** as a bidentate ligand has also been prepared. All these compounds show Sb–N interactions. A good conjunction was observed between semi-empirical method and ^{1}H and ^{13}C NMR (at different temperature) data for the diammonium salts of compounds **3** and **4**. The structures of all the synthesized compounds were determined by X-ray diffraction analyses. This appears to be the second molecular structure of a Pt stibine complex containing a Pt–Cl bond *trans* to stibine ligand, as few Pt–Sb X-ray structures are known.

Keywords: Hypervalent; Antimony; Intramolecular; Platinum; X-ray structures

1. Introduction

Ligands with the potential for supplemental Lewis base interactions are finding increasing utility for the stabilization of electrophilic main group species such as group 13 hydrides and intermetallics. A noteworthy development in this regard is the isolation of higher coordinate main group compounds in which the customary coordination number is expanded by virtue of an intermolecular dative interaction. This interaction, which is categorized as hypervalent bonding, is of interest because of the effect it may have on the structure, chemical properties and biological activities [1–5].

Most of the interactions involving group 15 elements were observed in compounds with cyclic structures. Recently articles have appeared that describe the origin of this interaction in compounds bearing an aryl substitutent with NMe_2 or CH_2NMe_2 in the ortho position [6–12].

Here, we wish to report the preparation, structural characterization of stibines containing the pendant arm [2-(Me2NCHR)C6H4] and their complexes containing hypervalent Sb–N bonding. The pendant arm [2-(Me_2NCHR)C_6H_4] (where R = H or Me) group was used to stabilize unusual organoantimony derivatives in a low oxidation state through intramolecular Sb–N coordination.

2. Results and discussion

The colorless crystalline stibines **1** and **2** were prepared via a salt elimination reaction of *o*-lithiated dimethylbenzylamine or dimethyl-1-phenethyl amine, respectively, with $SbCl_3$ in ether at −78 °C, while the compounds **3**–**5** were prepared by salt formation reaction of amine. Even with an excess of CH_3I, only two

---

* Corresponding author. Tel.: +525556224556; fax: +525556162217.
E-mail address: pankajsh@servidor.unam.mx (P. Sharma).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.05.016

amine groups of stibines **1** and **2** form the ammonium cation, yielding **3** and **4**, respectively. When stibine **1** was allowed to react with HBr, a triprotonated ammonium species **5** was obtained. This difference may be due to the bulkiness of methyl group to occupy at all the three positions. Stibine **1** forms complex $PtCl_2 \cdot L$ **6** after reacting with $[PtCl_4]^{2-}$.

Compounds **1, 2** and **6** (the platinum complex of stibine **1**) are soluble in CH_2Cl_2 and $CHCl_3$. Compounds **1**, **2** and **6** are stable in solution, in contrast to, compounds **3, 4** and **5** which are unstable and decompose in solution. Compounds **4–6** decompose during melting. Compounds **3–5** are moderately soluble in water and highly soluble in methanol. Compound **3** was used as a modifying ligand in the $RhHCO(PPh_3)_2$ catalyzed hydroformylation reaction of 1-pentene in water. Preliminary results show that at 100 °C, 600 psi of H_2 and 200 psi of CO pressure, L:Rh in 1:1, a total yield of 95% of aldehyde (*n*/*i* 2.59) was obtained. These results are in accordance with the earlier reports on the use of stibine ligands in the carbonylation reactions [13–15]. In the FAB^+ mass spectra of compounds **3**, **4** and **5,** dimerization of two stibine cations was observed. X-ray structures of these compounds show their monomeric nature. Their molar conductance values in methanol are 139.5, 82.18 and 141.5 $\Omega/S\,cm^2\,mol^{-1}$ for **3**, **4** and **5**, respectively, which indicate the conductance for two ions (dimer) rather than three ions (monomer) on dissolution in methanol.

In all of the cases the assignment of individual protonic signals in the ^1H NMR spectra was based on J_{HH} coupling constant values and was confirmed by COSY and HETCOR. For compounds **3** and **4,** proton NMR spectra were also recorded at 5, 40 and 60 °C, respectively.

Though Sb–N interactions were observed in the structural characterizations, evidence for such interactions could not be detected in ^1H NMR spectra of these compounds. The compound **1** has already been reported in the literature [12], so its NMR spectrum is not discussed in this report.

In the ^1H NMR spectrum of compound **4**, the two Me_3N^+CHR side chains present two different chemical shifts, which implies that these ammonium groups have different electronic environments. In accordance with this, a distorted trigonal bipyramidal structure may be proposed for this compound where one of the ammonium groups is at the axial position, while the other is on an equatorial site. The proton NMR spectra at 40 and 60 °C also show the similar result suggesting the restriction of free rotation (axial to equatorial) even at higher temperatures. It is suggested that the Sb–N interactions present in the molecule put an end to the free rotation. This type of separation of signals was not observed in compound **3** indicating unrestricted free rotation at room temperature. When the ^1H NMR spectrum of **3** was recorded at 5 °C, broadening of signals was observed and a complex spectrum was obtained.

^{13}C NMR spectra of these compounds show a similar trend as observed in the ^1H NMR spectra. It is important to note that in ^{13}C NMR spectra of **4**, C4 and C6; C7 and C9 show different chemical shifts, while carbon C3 and C5 of the ammonium salt are the same.

Semi-empirical methods (PM3) using SPARTAN' 02 win program on the crystallographic data of compound **4**, energy and its electrostatic potential surface were calculated at a single point ($H_f = -93$ kcal/mol). In compound **4**, the four different chemical shifts for CH and CH_3 groups of the side chain of the apparently similar ammonium salt are due to the fact that the side chain of one of the ammonium groups is at a shorter distance from the two iodide ions than of the other ammonium group. This makes the CH and CH_3 group of one ammonium side chain more protected than the CH and CH_3 group of other ammonium side chain, as shown in Fig. 1. It is interesting to note that the compound attains the same structure in solid and solution state. In the far IR spectra of these compounds, Sb–C vibrations have been observed.

The molecular structures of **1–6** have been confirmed by X-ray crystallography. All these compounds are monomeric in nature and no significant intermolecular interactions were observed. Intramolecular interactions between the Sb atom and N atoms of amine side chain are present in all the compounds. Further, crystallographic structures of **3** and **4** do not show significant cation/anion interactions. Compound **5** crystallizes with water as a solvent of crystallization and shows the ionic interactions.

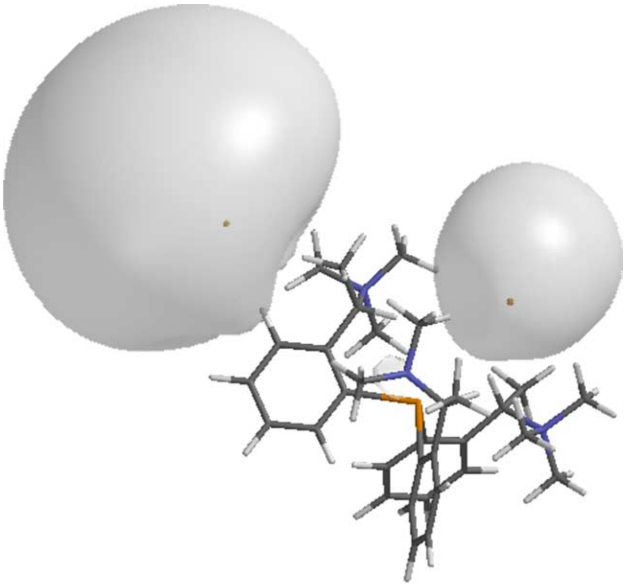


Fig. 1. View of Electrostatic potential surface of compound **4**.

Compound **1** crystallizes in the space group $P2_1/n$ with two independent molecules per asymmetric unit, see Fig. 2. The metrical parameters and stereochemical features of the two independent molecules are very similar. The crystal structure of this compound has already been reported in the $P2_1$ space group [12]. To best of our knowledge, there exist a very few examples in organoantimony compounds showing polymorphism [16]. In the crystal structures of the two polymorphs, three Sb–N intramolecular interactions were observed. The average intramolecular Sb–N bond length (averaged over both the molecules) is 3.00 Å. The primary coordination sphere consists of a trigonal pyramidal SbC_3 skeleton, and including the three Sb–N interactions the antimony can be described as heptacoordinate with one position occupied by a lone pair of electrons. It is to be noted that heptacoordinate antimony is not very common.

Compound **2** contains two intramolecular Sb–N interactions in comparison to compound **1**, which may be due to the bulkiness in the molecule because of the presence of three methyl groups, see Fig. 3. The two Sb–N bond lengths differ slightly [2.988(5) and 2.920(4) Å] and both are shorter than the Sb–N distance in compound **1**. Similar to compound **1,** the primary coordination sphere consists of a trigonal pyramidal SbC_3 skeleton but if Sb–N interactions are included, the overall geometry at antimony is that of a ψ octahedron where one of the vertices is occupied by a lone pair of electrons. In this geometry, the bond angles C(21)–Sb(1)–N(2) and C(11)–Sb(1)–N(1) (160.99 and 159.90 Å, respectively) present the high degree of distortion in the molecule.

Compound **3**. The molecule contains only one Sb–N intramolecular interaction as the other two nitrogen atoms are in ammonium form, see Fig. 4. The Sb–N interaction is much shorter than in compounds **1** and **2** (2.817 Å). This may be due to the absence of competition from other nitrogen atoms for a dative interactions with Sb atom and also may be due to the increased Lewis acidity at the antimony center due to the presence of two ammonium groups. The molecule is highly distorted from its trigonal pyramidal geometry with a lone pair.

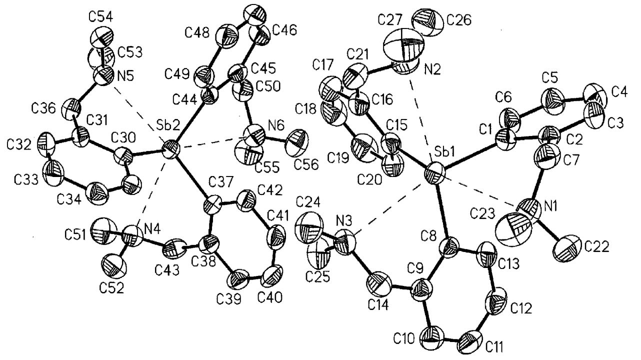


Fig. 2. Molecular Structure of Compound **1**.

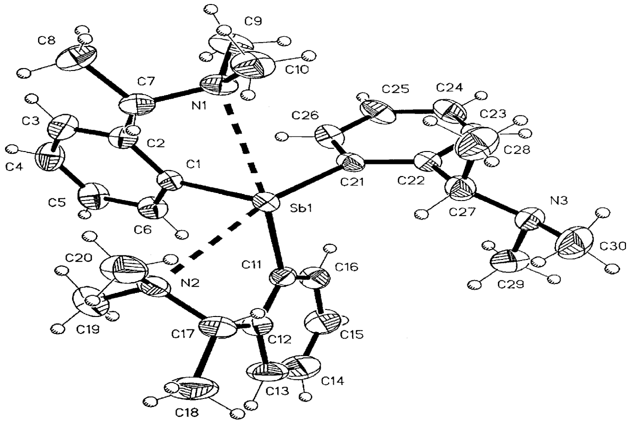


Fig. 3. Molecular structure of compound **2**.

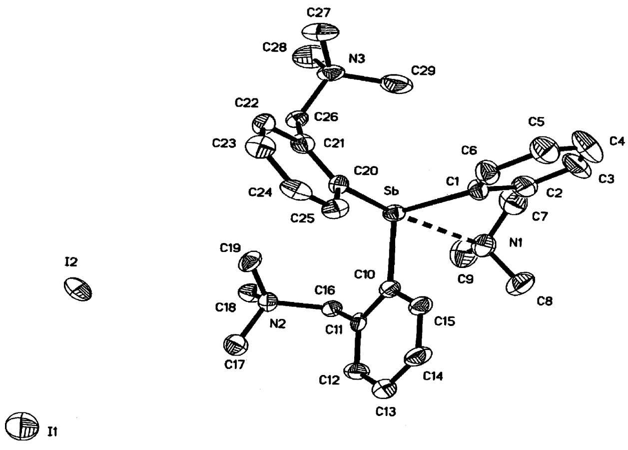


Fig. 4. Molecular structure of compound **3**.

Compound **4**. Similar to compound **3**, there exists only one Sb–N intramolecular interaction (2.804 Å), see Fig. 5. The molecule is highly distorted from its trigonal pyramidal geometry with a lone pair. As concluded by ^1H and ^{13}C NMR also, one of the ammonium groups containing a carbon atom is at the axial position, while the other is equatorial. The other equatorial position is

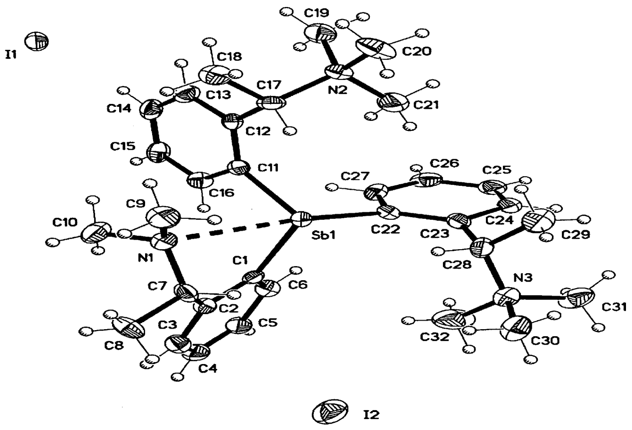


Fig. 5. Molecular structure of compound **4**.

occupied by a nitrogen atom of the amine group and the C(22)–Sb(1)–N(1) bond angle is 164.8°.

Compound **5**. The geometry around the antimony atom is distorted tetrahedral, see Fig. 6. The molecule is situated on a C_3 axis and has a pyramidal geometry. The average Sb–C distances fall within the limits found in related organoantimony structures. The molecule does not show any significant Sb–N intramolecular interactions. There is residual electron density around the antimony atom with the largest peak 2.209 at 0.05 Å from the antimony atom.

Compound **6**. This is the second structure of determination of a Pt stibine complex containing a Pt–Cl bond *trans* to stibine ligand. To best of our knowledge very few structures of platinumstibine complexes are reported in literature. In this molecule the stibine ligand **1** acts as a bidentate chelating Sb,N-type ligand. Platinum is in square planar geometry, and the two chlorine atoms lie in a *cis* configuration, see Fig. 7. The Pt–Cl bond *trans* to antimony is 2.360 Å and is longer than the Pt–Cl bond length reported in *cis*-[$PtCl_2(SbPh_3)_2$] (2.338 Å) [17]. The Pt–Sb bond length (2.494 Å) found in compound **6** is similar to the Pt–Sb bond length observed in reported *cis*-[$PtCl_2(SbPh_3)_2$] complex (2.502 Å) [17].

In this compound, the geometry around antimony is distorted trigonal bipyramidal where the two organic groups, carbon atom and platinum atom, occupy equatorial positions while N2 and the carbon atom C10 occupy axial positions. This molecule contains a weaker Sb–N intramolecular interaction.

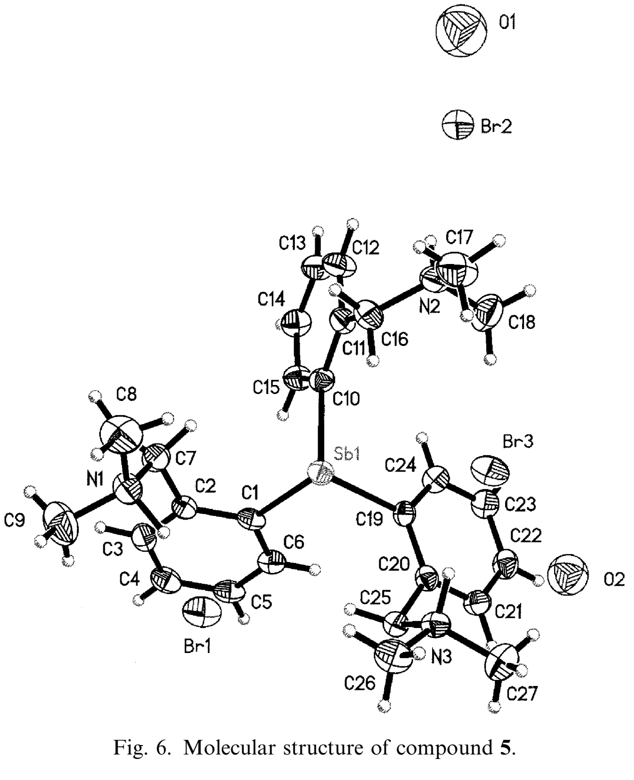


Fig. 6. Molecular structure of compound **5**.

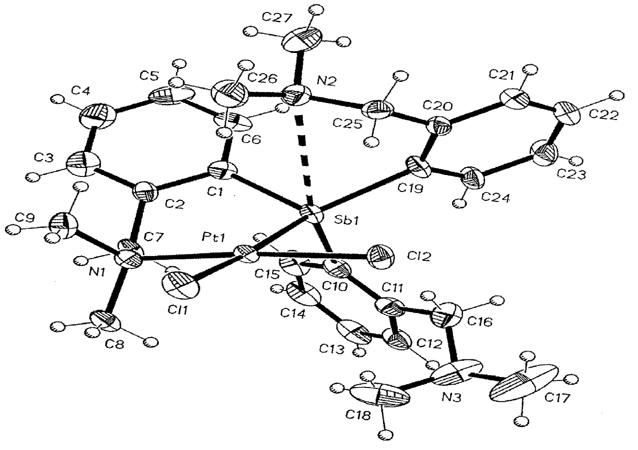
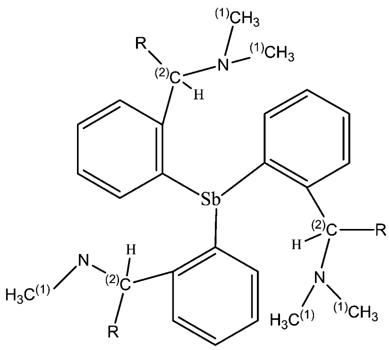
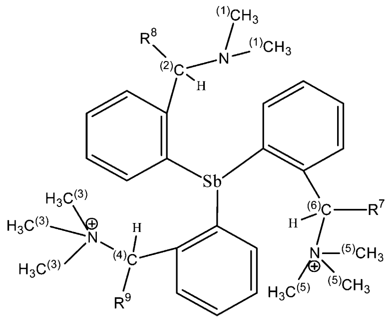


Fig. 7. Molecular structure of compound **6**.

In each case, it was found that the amine arms are weakly coordinated, which is in contrast to the observation that the structures of conventional triarylantimony derivatives exhibit only weak Lewis acidity. It was also confirmed that the degree of hypervalent interaction strongly depends on the Lewis acidity of the central atom. The Sb–N distances for these compounds were 74–85% of the sum of van der Waals radii of 3.74 Å. No short intermolecular contacts involving an antimony atom were observed in any of the crystals.



Compounds
1 and **6** ; R = H
2 ; R = Me



Compounds:
3 : $R^7, R^8, R^9 = H$
4 : $R^7 = {}^{(7)}CH_3$; $R^8 = {}^{(8)}CH_3$
$R^9 = {}^{(9)}CH_3$

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 on a MEL-TEMP II Fisher and are uncorrected. The C, H and N analyses were carried out with a Perkin–Elmer elemental analyzer 240 C. Far IR spectra were recorded in polyethylene on a Nicolet-Magna 750 spectrometer. EI and FAB$^+$ mass spectra were recorded on a JEOL SX102 double-focusing mass spectrometer with reverse geometry using a 6-kV Xenon beam (10 am); nitrobenzyl alcohol was used as matrix for recording the mass spectra. Conductance measurements of 10^{-3} M solutions of complexes **3**–**5** in acetonitrile were made with a Metrohm 644 Conductometer, with k_c=1.0 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded in $CHCl_3$ or CD_3OD on JEOL ECLIPSE 300 (^{1}H: 300.5311 MHz; ^{13}C: 75.5757) spectrometer.

3.1. Crystal X-ray structure determination

Diffraction data were collected on a Siemens P4/Pc diffractometer at 293 K using monochromated Mo Kα radiation (λ = 0.7107 Å). The system used for calculation was Siemens SHELXTL PLUS (PC Version). The complete indexing of the diffraction pattern of compound **5** required two orientation matrices [18]. The relationship between the component orientations could be described with the matrix (−1.00 0.00 0.00 0.00 −1.00 0.00 0.851 0.586 1.00) which approximates to a 180°-rotation about [0 0 1]. Such "twinning" conditions may give rise to refinement difficulties because reflections from different domains partially overlap, but such problems were avoided by simultaneous integration of both components, which ensures that fully and partially overlapping reflections are treated correctly [19]. Crystal data for all structural analyses are given in Table 1. Selected bond lengths and angles for all compounds are listed in Table 2.

3.2. *Tris(2-N,N-dimethylaminomethyl)phenylstibine (**1**)*

A solution of $SbCl_3$ (2.36 mmol) in 20 ml ether was added dropwise to a stirred slurry of 2-(Me_2NCH_2)-C_6H_4Li (7.0 mmol) [prepared according to literature method] in 20 ml of ether at −20 °C with continuous stirring. The mixture was further stirred for 6 h at room temperature and then the reaction was quenched with ice. After extraction with hexane (3×15 ml) and drying over sodium sulfate, solvent was removed under vacuum. The solid was washed 3–4 times with cold acetone. Slow concentration at low temperature of a solution in (90:10) dichloromethane–acetone solvent afforded single crystals suitable for X-ray analysis. Yield: 60%; m.p. 133 °C; Anal. Found: C, 61.32; H, 6.54; N, 7.89%; Calc. for $C_{27}H_{36}N_3Sb$: C, 61.95; H, 6.88; N, 8.03; IR(cm^{-1}): (Sb–C),461, 221; ^{1}H NMR ($CDCl_3$, δ in ppm): δ_1 1.93(s); δ_2 3.50(s); δ_{phenyl} 7.00–7.25(m); ^{13}C NMR ($CDCl_3$, δ in ppm): 44.34 (δ_{C1}), 65.96 (δ_{C2}), 127.13, 129.28, 137.76, 138.95, 145.16, 146.98 (δ_C aromatic); MS(EI) *m/z* (%): 523(4.4) [M$^+$], 389(100) [M − L]$^+$, 254(2.5) [M − 2L]$^+$, 134(12.6) [L]$^+$.

3.3. *Tris-[(S)-2-N,N-Dimethylaminoethyl)phenylstibine (**2**)*

A mixture of (*S*)-*N*,*N*,-dimethyl-1-phenylethylamine (18.1 mmol) and *n*-butyl lithium (2.5 M in hexane,

Table 1
Crystal data for compounds **1**–**6**

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{54}H_{72}N_6Sb_2$	$C_{30}H_{42}N_3Sb$	$C_{29}H_{42}I_2N_3Sb$	$C_{32}H_{48}I_2N_3Sb$	$C_{27}H_{41}Br_3N_3OSb$	$C_{27}H_{36}Cl_2N_3PtSb$
Formula weight	1048.68	566.42	808.21	850.28	785.09	790.33
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$Fdd2$
Crystal size	0.40×0.20×0.20	0.60×0.24×0.14	0.60×0.26×0.12	0.40×0.34×0.28	0.26×0.22×0.18	0.48×0.28×0.24
a (Å)	8.942(2)	11.361(1)	10.596(2)	10.427(1)	11.331(2)	32.384(4)
b (Å)	16.965(2)	7.394(1)	13.330(3)	13.309(1)	12.557(2)	36.583(5)
c (Å)	35.085(4)	17.470(2)	24.337(4)	13.023(1)	12.695(2)	9.832(1)
α (°)	90	90	90	90	102.511(4)	90
β (°)	90.098(11)	93.09(1)	102.40(11)	104.02(11)	108.895(4)	90
γ (°)	90	90	90	90	101.147(4)	90
Volume (Å^3)	5322.3(12)	1465.4(3)	3357.1(11)	1753.4(3)	1599.1(5)	1164.8(3)
Z	4	2	4	2	2	16
D_{calc} (Mg/cm^3)	1.309	1.284	1.599	1.611	1.626	1.803
μ	1.054	0.962	2.681	2.571	4.633	5.930
Reflections collected	10,021	5874	5826	3418	31,284	5448
Independent reflections	9373	5176	5571	3235	31,286	5119
R	0.037	0.0367	0.0632	0.0366	0.0781	0.0409
Goodness-of-fit	0.816	1.033	1.003	1.039	0.961	1.046
Δ/σ (e/Å^3)	0.802/−0.400	0.244/−0.548	0.742/−0.725	0.716/−0.629	0.2.209/−0.831	1.099/−1.007

Table 2
Selected bond lengths and bond angles for compounds **1**–**6**

1	
Sb(1)–C(1)	2.186(4)
Sb(1)–C(8)	2.185(4)
Sb(1)–C(15)	2.180(5)
Sb(1)–N(1)	3.022(4)
Sb(1)–N(2)	2.974(4)
C(15)–Sb(1)–C(8)	96.09(18)
C(15)–Sb(1)–C(1)	95.50(18)
C(8)–Sb(1)–C(1)	94.93(17)
C(1)–Sb(1)–N(1)	68.42(15)
C(8)–Sb(1)–N(1)	79.42(14)
C(15)–Sb(1)–N(1)	162.61(15)
C(1)–Sb(1)–N(2)	83.30(15)
C(15)–Sb(1)–N(2)	67.91(16)
C(1)–Sb(1)–N(3)	161.27(16)
C(15)–Sb(1)–N(3)	79.33(15)
N(2)–Sb(1)–N(3)	110.73(12)
N(2)–Sb(1)–N(1)	114.65(12)
N(1)–Sb(1)–N(3)	113.71(12)
2	
Sb(1)–C(1)	2.169(5)
Sb(1)–C(21)	2.182(5)
Sb(1)–C(11)	2.172(5)
Sb(1)–N(1)	2.988(5)
Sb(1)–N(2)	2.920(4)
C(1)–Sb(1)–C(11)	94.9(2)
C(1)–Sb(1)–C(21)	97.8(2)
C(11)–Sb(1)–C(21)	93.4(2)
C(1)–Sb(1)–N(1)	67.51(2)
C(11)–Sb(1)–N(1)	159.90(2)
C(21)–Sb(1)–N(1)	80.03(2)
C(1)–Sb(1)–N(2)	80.71(2)
C(11)–Sb(1)–N(2)	68.01(2)
C(21)–Sb(1)–N(1)	160.99(2)
3	
Sb–C(1)	2.156(12)
Sb–C(20)	2.223(11)
Sb–C(10)	2.176(11)
Sb–N(1)	2.817(12)
C(1)–Sb–C(10)	101.9(5)
C(10)–Sb–C(20)	94.5(4)
C(1)–Sb–C(20)	94.7(4)
C(1)–Sb–N(1)	69.8(4)
C(10)–Sb–N(1)	83.5(4)
C(20)–Sb–N(1)	163.5(4)
C(8)–N(1)–C(7)	109.9(14)
C(8)–N(1)–C(9)	110.3(4)
C(8)–N(1)–Sb	120.3(11)
4	
Sb(1)–C(1)	2.130(10)
Sb(1)–C(22)	2.217(8)
Sb(1)–C(11)	2.180(10)
Sb(1)–N(1)	2.804(7)
C(10)–N(1)	1.459(13)
C(1)–Sb(1)–C(11)	98.8(3)
C(11)–Sb(1)–C(22)	93.5(4)
C(22)–Sb(1)–C(1)	96.5(4)
C(1)–Sb(1)–N(1)	69.7(3)
C(11)–Sb(1)–N(1)	82.8(3)
C(22)–Sb(1)–N(1)	164.8(3)
5	
Sb(1)–C(1)	2.159(5)
Sb(1)–C(19)	2.143(5)
Sb(1)–C(10)	2.175(5)
C(19)–Sb(1)–C(1)	94.74(18)
C(19)–Sb(1)–C(10)	96.60(18)
C(1)–Sb(1)–C(10)	95.44(18)
6	
Sb–C(1)	2.097(11)
Sb(1)–C(19)	2.121(11)
Sb(1)–C(10)	2.155(12)
Sb(1)–N(2)	3.237(11)
Pt(1)–N(1)	2.126(9)
Pt(1)–Cl(2)	2.310(3)
Pt(1)–Cl(1)	2.360(3)
Pt(1)–Sb(1)	2.4949(7)
C(1)–Sb(1)–C(10)	99.7(5)
C(1)–Sb(1)–C(19)	109.7(4)
C(19)–Sb(1)–C(10)	101.9(5)
C(19)–Sb(1)–N(2)	65.3(4)
C(10)–Sb(1)–N(2)	160.4(4)
C(1)–Sb(1)–N(2)	72.9(4)
N(1)–Pt(1)–Cl(2)	174.9(3)
N(1)–Pt(1)–Cl(1)	89.9(3)
Cl(1)–Pt(1)–Cl(2)	87.88(11)
Sb(1)–Pt(1)–Cl(2)	89.59(8)
Sb(1)–Pt(1)–Cl(1)	173.03(8)

18.3 mmol) in ether (60 ml) was stirred for 24 h at room temperature. To the resulting yellow solution which contains 2-[(*S*)-(1-dimethylamino)ethyl]phenyllithium, a solution of $SbCl_3$ (6.02 mmol) in ether (15 ml) was added dropwise and under a nitrogen atmosphere at −20 °C with continuous stirring. The mixture was further stirred for 6 h at room temperature and then quenched with ice. After extraction with hexane (3×15 ml) and drying over sodium sulfate, solvent was removed under vacuum. The solid was washed 3–4 times with cold acetone. Slow concentration at low temperature from dichloromethane–acetone (90:10) afforded single crystals suitable for X-ray analysis. Yield: 64%; m.p. 151 °C; Anal. Found: C, 62.98; H, 6.92; N, 7.13%; Calc. for $C_{30}H_{42}N_3Sb$: C, 63.71; H, 7.43; N, 7.43; IR(cm^{-1}): (Sb–C),464, 219; ^1H NMR ($CDCl_3$, δ in ppm): δ_1 1.8046; δ_2 3.9048(q); δ_3 1.3184(d); δ_{phenyl} 6.97–7.2916(m) $J_{23}=6.61$; ^{13}C NMR ($CDCl_3$,): 41.01 (δ_{C1}), 64.11 (δ_{C2}), 13.03 (δ_{C3}), 127.07, 129.54, 137.12, 139.08, 145.86, 146.57 (δ_C aromatic); MS(EI) *m*/*z* (%): 565(1.6) [M^+], 417(100) $[M-L]^+$, 269(5.6) $[M-2L]^+$, 148(10) $[L]^+$.

3.4. [Bis-(2-N,N,N–trimethylammoniummethyl)phenyl(2-N,N-dimethylaminomethyl) phenyl stibine] diiodide (**3**)

In a schlenk tube, to a solution of tris(*N*,*N*-dimethylaminomethyl)stibine (1.9 mmol) in CH_2Cl_2 (30 ml), was added CH_3I (8.03 mmol) with continuous stirring. The reaction was stirred for 24 h and the solution was concentrated under vacuum to obtain a white product which was isolated by filtration. The compound was recrystallized from methanol–ethanol mixture (70:30). Yield: 45%; m.p. 135(dec) °C; Anal. Found: C, 42.87; H, 5.63; N, 4.95%; Calc. for $C_{29}H_{42}I_2N_3Sb$: C, 43.12; H, 5.22; N, 5.22; IR(cm^{-1}): (Sb–C) 462, 222; ^1H NMR ($CDCl_3$, δ in ppm): δ_1 1.83(s); δ_2 3.58(s); δ_3 3.13(s); $\delta_{4a,5a}$ 4.84(d) $\delta_{4b,5b}$ 5.01(d), δ_5 3.13(s); $J_{44} = J_{66} = 13.34$; δ_{phenyl} 7.22–7.74(m); ^{13}C NMR ($CDCl_3$, ppm): 43.27 (δ_{C1}), 64.80 (δ_{C2}), 52.83 ($\delta_{C3,C5}$), 70.91 ($\delta_{C4,C6}$); 127.27, 128.87, 137.14, 138.03, 145.10, 146.85 (δ_C aromatic); MS(FAB$^+$) *m*/*z* (%): 1489(1.3) $[2M-I]^+$, 680(11.1) $[M-I]^+$, 531(2.0) $[M-L-I]^+$, 382(2.0) $[M-2L-I]^+$, 255(26.5) $[M-2L-2I]^+$.

3.5. [Bis-(S)(2-N,N,N–trimethylammoniumethyl)phenyl(S)(2-N,N-dimethylaminoethyl phenyl)stibine] diiodide (**4**)

In a schlenk tube, to a solution of tris(*o*-(S)-*N*,*N*-dimethyl-1-phenethyl) stibine (0.88 mmol) in CH_2Cl_2 (30 ml), was added CH_3I (3.30 mmol) with continuous stirring. The reaction was stirred for 24 h and the solvent was removed under vacuum. Methanol (30 ml) was added, and a white product was formed and removed by filtration. The compound was recrystallized from methanol–ethanol mixture (70:30). Yield: 45%; m.p. 211(dec) °C; Anal. Found: C, 45.66; H, 5.73; N, 4.97%; Calc. for $C_{32}H_{48}I_2N_3Sb$: C, 45.22; H, 5.65; N, 4.94; IR(cm^{-1}): (Sb–C) 473, 226; ^1H NMR ($CDCl_3$, δ in ppm): δ_1 1.84(s); δ_2 4.00(q); δ_3 2.95(s); δ_4 5.14(q) δ_5 3.04(s), δ_6 5.48(q) δ_7 1.92 (d), δ_8 1.44 (d), δ_9 1.80(d); $J_{28} = J_{49} = J_{67} = 6.61$; δ_{phenyl} 7.19–8.12(m); ^{13}C NMR ($CDCl_3$, δ in ppm): 39.97 (δ_{C1}), 63.84 (δ_{C2}), 51.64 (δ_{C3}), 76.50 (δ_{C4}), 51.64 (δ_{C5}), 75.45 (δ_{C6}), 16.46 (δ_{C7}), 10.93 (δ_{C8}), 15.94 (δ_{C9}); 127.22, 128.62, 136.99, 138.16, 145.21, 146.82 (δ_C aromatic); MS(FAB$^+$) *m*/*z* (%): 1573(2.2) $[2M-I]^+$, 722(70.4) $[M-I]^+$, 559(100) $[M-L-I]^+$, 396(13.8) $[M-2L-I]^+$, 269(90.2) $[M-2L-2I]^+$.

3.6. [Tris-(2-N,N,N–trimethylammonium methyl)phenyl stibine] tribromide (**5**)

In a schlenk tube, to a solution of tris (*N*,*N*-dimethylbenzyl)stibine (1.9 mmol) in acetone (30 ml), was added HBr (6.0 mmol, 40% solution) with continuous stirring. The reaction was stirred for 4 h and the solution was concentrated under vacuum and extracted with dichloromethane. The extracted dichloromethane solution was dried over anhydrous sodium sulfate and concentrated to obtain a white product. The compound was recrystallized from ethanol–hexane mixture (70:30). Yield: 65%; m.p. 267(dec) °C; Anal. Found: C, 41.89; H, 5.02; N, 5.06%; Calc. for $C_{27}H_{39}Br_3N_3Sb$: C, 42.29; H, 5.09; N, 5.48; IR(cm^{-1}): (Sb–C) 458, 225; ^1H NMR (CD_3OD, δ in ppm): δ_1 1.93(s); δ_2 3.50(s); δ_{phenyl} 7.00–7.25(m); MS(FAB$^+$) *m*/*z* (%): 1451(2.1) $[2M-Br]^+$, 1237(2.6) $[2M-Br-L]$, 526(5.3) $[M]^+$, 524(10.1) $[M-2H]^+$, 390(17.0) $[M-L-2H]^+$, 382(2.0) $[M-2L-I]^+$, 255(16.1) $[M-2L-3H]^+$.

3.7. cis-Dichloro [(tris(2-N,N-dimethylaminomethyl)phenylstibino-N,Sb)]platinum(II) (**6**)

To a solution of (**1**) (0.19 mmol) in acetone (20 ml) was added K_2PtCl_4 in water. The mixture was stirred for 12 h. The resultant mixture was filtered to remove any undissolved material and filtrate was concentrated to obtain a yellow powder, which was recrystallized from dichloromethane–acetone mixture (70:30). Yield: 40%; m.p. 210–212 (dec) °C; Anal. Found: C, 42.14; H, 4.78; N, 5.86%; Calc. for $C_{27}H_{36}Cl_2N_3PtSb$: C, 41.06; H, 4.56; N, 5.33; IR(cm^{-1}): (Sb–C),428, 220; ^1H NMR (CDCl3, δ in ppm): δ_1 2.23(s); δ_2 3.43(s); δ_{phenyl} 7.12–7.47 (m); ^{13}C NMR ($CDCl_3$, δ in ppm): 45.30 (δ_{C1}), 64.32 (δ_{C2}), 127.28, 128.92, 137.14, 138.29, 145.10, 146.79 (δ_C aromatic); MS(FAB$^+$) *m*/*z* (%): 790(11.3)$[M]^+$, 754(8.1) $[M-Cl]^+$, 718(2.1) $[M-2Cl]^+$, 718(2.1) $[M-L-Cl-H]^+$, 583(5.6) $[M-L-Cl-H]^+$, 389(67.4) $[M-Pt-2Cl-L]^+$, 255(11.9) $[M-2L]^+$.

4. Supplementary materials

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 229888–229893 for compounds **1**–**6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK [fax. (int code) +44(1223)336-033, or e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk].

Acknowledgement

Authors are thankful to DGAPA for financing project (IN218901 and IX204004). One of the author

(P.S.) is thankful DGAPA,UNAM for his sabbatical stay at IITD.

References

[1] A. David, A.H. Cowley, J. Ruiz, Inorg. Chim. Acta 198 (1992) 271.

[2] T. Murafuji, T. Mutoh, K. Satoh, K. Tsunenari, N. Azuma, H. Suzuki, Organometallics 14 (1995) 3848.

[3] M. Weinmann, A. Gehrig, B. Schiemenz, G. Huttner, B. Nuber, G. Reinwald, H. Lang, J. Organomet. Chem. 563 (1998) 61.

[4] Y. Takaguchi, A. Hosokawa, S. Yamada, J. Motoyoshishya, H. Aoyama, J. Chem. Soc., Perkin. Trans. I (1998) 3147.

[5] M. Ikowa, S. Tomoda, J. Org. Chem. 60 (1995) 5299.

[6] H.J. Breunig, I. Ghesner, M.E. Ghesner, E. Lork, Inorg. Chem. 42 (2003) 1751.

[7] T. Tokunaga, H. Seki, S. Yasuike, M. Ikoma, J. Kurita, K. Yamaguchi, Tetrahedron 56 (2000) 8833.

[8] T. Tokunaga, H. Seki, S. Yasuike, M. Ikoma, J. Kurita, K. Yamaguchi, Tetrahedron Lett. 41 (2000) 1031.

[9] C.J. Carmalt, D. Waslsh, A.H. Cowley, N.C. Norman, Organometallics 16 (1997) 3597.

[10] C.J. Carmalt, A.H. Cowley, R.D. Culp, R.A. Jones, S. Kamepalli, N.C. Norman, Inorg. Chem. 36 (1997) 2770.

[11] L.M. Opris, A. Silvestru, C. Silvestru, H.J. Breunig, E. Lork, J. Chemical Soc., Dalton Trans. (2003) 4367.

[12] S. Kamepalli, C.J. Carmalt, R.D. Culp, A.H. Cowley, R.A. Jones, N.C. Norman, Inorg. Chem. 35 (1996) 6179.

[13] A. Cabrera, P. Sharma, J.L. Arias, J.F. Perez, L. Velasco, R.M. Gomez, J. Mol. Catal. 212 (2004) 19.

[14] P. Sharma, A. Cabrera, R. Lagadec, R. Manzo, J.L. Arias, M. Sharma, Main Group Met. Chem. 22 (1999) 95.

[15] A. Cabrera, P. Sharma, J.L. Arias, J.F. Perez, L. Velasco, R.M. Gomez, J. Mol. Catal. 170 (2001) 271.

[16] P. Sharma, A. Cabrera, N. Rosas, S. Hernandez, R. Lelagadec, J. Valdes, J.L. Arias, Main Group Met. Chem. 21 (1998) 303.

[17] O.F. Wendt, A. Scodinu, L.I. Elding, Inorg. Chim. Acta 277 (1998) 237.

[18] R.A. Sparks, GEMINI: Program for Indexing X-ray Diffraction Patterns Derived from Multiple or Twinned Crystals, Bruker-AXS, Madison, WI, 2000.

[19] SAINT, version 6.33, Bruker-Nonius, Madison, WI, 2002.