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Inorganic Chemistry Communications 9 (2006) 82-85

INORGANIC CHEMISTRY COMMUNICATIONS

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## First ferrocenylstibines and their molecular structures

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> Received 8 August 2005; accepted 29 September 2005 Available online 15 November 2005

## Abstract

Stibines Ph<sub>2</sub>SbFc containing the pendant arm [2-(Me<sub>2</sub>NCHR)] [where R = H(1) or Me(2)] on ferrocenyl ring were synthesized, and reaction of (1) with CH<sub>3</sub>I was carried out to obtain the monoammonium salt {[2-(Me<sub>3</sub>N<sup>+</sup>CH<sub>2</sub>)Fc]} SbPh<sub>2</sub>[I]<sup>-</sup>. All new stibines have been characterized by various physicochemical techniques. The structures of all these 1,2-disubstituted ferrocenylstibines were determined by X-ray diffraction analyses. This is the first report on the stibines containing disubstituted ferrocenyl group and it is worth mentioning that even monosubstituted ferrocenylstibines are virtually unknown. Heterobimetallic stibine (1) does not show intramolecular Sb–N interactions while the stibine (2) is stabilized by intramolecular Sb–N interactions. © 2005 Elsevier B.V. All rights reserved.

Keywords: Ferrocene; Stibines; Hypervalent; Heterobimetallic; X-ray structure

1,2-Disubstituted ferrocenylphosphines are important catalytic precursors for many different types of reaction, e.g., hydrogenation, carbonylation and hydrosilylation [1–3]. To best of our knowledge, few examples associated with ferrocene bonded directly to a bismuth atom have appeared in organobismuth chemistry [4–6], but still ferrocene bonded antimony is unknown. In 1984, a report appeared mentioning the  $R_{\rm f}$  value of one ferrocenylstibine, while its synthesis and characterization data have not been mentioned in the report [7].

Ligands with the potential for supplemental Lewis base interactions are finding increasing utility. 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 [8–12]. Recently, our group has reported some new stibines containing  $CH(R)NMe_2$  (where R = H, Me) pendant arm at the *ortho* position showing these interactions [13].

Considering the vast number of ferrocene ligands and the unique stereoelectronic properties of the ferrocene framework and in view of the nonexistence of ferrocene bonded antimony in the literature and our interest in stibine ligands [13–17], some novel diphenylstibines containing ferrocenyl group having pendant arm [2-(Me<sub>2</sub>NCHR)] on ferrocenyl ring were synthesized and their structures were determined.

The yellowish orange colored crystalline stibines 1[18] and 2 [19] were prepared via a salt elimination reaction of 2-lithiated (*N*,*N*-dimethylamino) methylferrocene or (*N*,*N*-dimethylamino) ethylferrocene, respectively, with Ph<sub>2</sub>SbCl in ether at -20 °C, while the orange compound 3[20] was prepared by salt formation reaction of amine with CH<sub>3</sub>I. It is to be noted that phosphorus analogue of (1) reacts with one equivalent of MeI and give an unstable *N*-methylated product while with an excess of MeI yields the respective P,N-dimethylated salt [21,22], which in different to the case of antimony where with one or more

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<sup>1387-7003/\$ -</sup> see front matter @ 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2005.09.029

equivalent of MeI, a very stable *N*-methylated product was obtained.

All the compounds are soluble in  $CH_2Cl_2$  and  $CHCl_3$ . These stibines are stable and melt without decomposition. These compounds were analyzed by  $FAB^+$  mass spectrometry. For compounds **1** and **2** molecular ion peaks were observed along with fragments corresponding to the successive loss of organic entities attached to antimony atom. In the  $FAB^+$  mass spectra of compound **3**, dimerization of two stibine cations was observed but the X-ray structure of **3** shows its monomeric nature. In the far IR spectra of these compounds, Sb–C vibrations have been observed.

In all of the compounds the assignment of individual protonic signals in the <sup>1</sup>H NMR spectra was based on  $J_{\rm HH}$  coupling constant values and was confirmed by COSY and HETCOR. The chemical shifts due to the proton adjacent to the antimony atom in C<sub>5</sub>H<sub>3</sub> ring of (2) appeared at upfield region (3.79 and 3.84 ppm, respectively) compared with those due to the other two protons in the ring. This may be due to the ring current of the aryl groups attached to antimony. A similar observations was made in homologous ferrocenylbismuth compounds [5,6]. All proton signals of the ammonium compound 3 appear downfield of those of compound 1.

The molecular structures of (1), (2) and (3) have been confirmed by X-ray crystallography [23] as shown in Figs. 1–3. All these compounds are monomeric in nature and no significant intermolecular interactions were observed. The ammonium salt (3) crystallizes with one molecule of ethanol as solvent of crystallization. Further, crystallographic structure of **3** does not show significant cation–anion interactions. It is to be mentioned here that X-ray structure of *N*-alkylated salt of disubstituted ferrocene is only the second reported in the literature as molecular structure of only *rac*-benzyldimethyl {2-(diphenylphosphinoferrocenyl) methyl} ammonium bromide is known [24]. Intramolecular interactions between the Sb atom and N atom of amine side chain is present in stibine **2**.

The average Sb–C<sub>(ferrocenyl)</sub> bond length found in these ferrocenylstibines is 2.123 Å, which is slightly shorter than that found in other known tertiary stibines. The shortest Sb–C<sub>(ferrocenyl)</sub> bondlength is ascribable to the effect of bidentate and electron donating. This may be due to the  $p\pi$ –d $\pi$  bonding to a greater extent and thus shortening of Sb–C bond ferrocenyl group in all the compounds.

Stibine (1) and its ammonium salt (3) are pyramidal. The average C–Sb–C angle is  $97.42^{\circ}$  and  $95.62^{\circ}$ , respectively, which is slightly higher than found in PH<sub>3</sub>Sb or tris



Fig. 1. Molecular structure of diphenyl(*N*,*N*-dimethylaminomethylferrocenyl)stibine; Sb(1)-C(2) = 2.122(3) Å, Sb(1)-C(18) = 2.141(3) Å, Sb(1)-C(12) = 2.147(3) Å,  $C(2)-Sb(1)-C(18) = 95.17(11)^{\circ}$ ,  $C(2)-Sb(1)-C(12) = 97.58(11)^{\circ}$ ,  $C(12)-Sb(1)-C(18) = 95.17(12)^{\circ}$ .



Fig. 2. Molecular structure of diphenyl(*N*,*N*-dimethylaminoethylferrocenyl)stibine; Sb(1)–C(6) = 2.124(2) Å, Sb(1)–C(15) = 2.142(2) Å, Sb(1)–C(21) = 2.162(2) Å, Sb(1)–N(1) = 3.042(2) Å, C(6)–Sb(1)–C(15) = 96.76(9)^\circ, C(6)–Sb(1)–C(21) = 94.97(9)°, C(15)–Sb(1)–C(21) = 96.12(9)°, C(6)–Sb(1)–N(1) = 66.32(7)°.

(2-thienyl)stibine. In stibine 2, a distance between nitrogen atom of NMe<sub>2</sub> group and the central antimony atom is 3.041(2) Å, which is much shorter (80%) than the sum of

their Van der waals radii (3.74 Å) [25]. These distances are slightly longer than the covalent bond length of 2.11 Å [25]. This result indicates hypervalent bond formation between antimony and nitrogen. The geometry about antimony atom is distorted pseudotrigonal bipyramid where the two carbon atoms bound to antimony atom (1Ph and 1Fc) occupy the equatorial plane. The apical positions are occupied by nitrogen atom and carbon atom of phenyl group with an C-Sb-N angle 158.7°. The lone pair of electrons can be considered to occupy the equatorial position. The C21-Sb bond [2.162(2) Å] trans to the nitrogen atom is slightly longer than the other Sb–C bonds, 2.142(2) Å. A similar structure and lengthening of one of the Sb-C bond length were reported earlier in similar compounds  $Tol_2Sb[2-(Me_2NCH_2)C_6H_4]$  and  $Tol_2$   $Sb\{1-[8 (Me_2NCH_2)C_{10}H_6$  [7]. This tendency, also observed in these stibines, is considered to be the hypervalent effect on the central antimony. The two phenyl groups in stibine 1 and 2 are at an angle of 68.1° and 68.9°, respectively, to each other.

In conclusion, the paper presents the first well-characterized ferrocenylstibines and their crystal structures. The existence of strong interactions between antimony and nitrogen, transcending the octet theory, and classified as the hypervalent bonding, was shown not only in tri aryl stibines but also in ferrocenylstibines. This hypervalent Sb–N bonding was demonstrated by single crystal X-ray analysis. The synthesis of other triferrocenylstibines and their platinum and palladium complexes are in progress.



Fig. 3. Molecular structure of diphenyl[(*N*,*N*-trimethylammoniomethylferrocenyl)iodide]stibine Sb(1)-C(2) = 2.123(4) Å, Sb(1)-C(15) = 2.141(4) Å, Sb(1)-C(21) = 2.160(4) Å,  $C(2)-Sb(1)-C(15) = 96.17(15)^{\circ}$ ,  $C(2)-Sb(1)-C(21) = 94.78(14)^{\circ}$ ,  $C(15)-Sb(1)-C(21) = 95.93(16)^{\circ}$ .

## Acknowledgment

Authors are thankful to DGAPA UNAM for financing the project IN 210905.

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- [18] In a Schlenk tube a solution of Ph<sub>2</sub>SbCl (1.0 mmol) in anhydrous THF (10 ml) was added dropwise under a nitrogen atmosphere to 2-FcNLi (1.1 mmol) which was synthesized in situ according to reported method [26] at -20 °C with continuous stirring. The mixture was further stirred for 24 h at room temperature (r.t.) and then reaction was quenched with ice. After extraction with dichloromethane  $(3 \times 10 \text{ ml})$  and drying over sodium sulfate, solvent was removed under vacuum. Slow concentration from chloroform solution gives the orange crystalline compound. Yield: 60%; m.p.: 90-91 °C; IR (m cm<sup>-1</sup>): 458 (Sb–C), 3057 (C–H aromatic) FAB<sup>+</sup> m/z 517 (95%)  $[M]^+$ , 473(36%)  $[M - NMe_2]^+$ , 440 (17%)  $[M - Ph]^+$ , 397 (29%)  $[M - Ph - NMe_2]^+$ , 275(9%)  $[SbPh_2]^+$ , 242(18%)  $[FcCH_2NMe_2]^+$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm) 1.91 (s, 6H, NMe<sub>2</sub>), 3.03 (d<sup>2</sup> J<sub>HH</sub>, 12.7 Hz, 1H, CH<sub>2</sub>), 3.66 (d<sup>2</sup> J<sub>HH</sub>, 12.9 Hz, 1H, CH<sub>2</sub>), 3.79 (m, 1H, C<sub>5</sub>H<sub>3</sub>), 3.98 (s, 5H,  $C_5H_5$ ), 4.20 (t, 1H,  $C_5H_3$ ), 4.31 (m, 1H,  $C_5H_3$ ), 7.19–7.59 (m, 10H, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) 44.78 (NMe<sub>2</sub>), 59.91 (CH<sub>2</sub>), 69.28 (C, C<sub>5</sub>H<sub>5</sub>), 69.97 (CH, C<sub>5</sub>H<sub>3</sub>), 71.96 (CH, C<sub>5</sub>H<sub>3</sub>), 72.48 (CH, C<sub>5</sub>H<sub>3</sub>),

74.0 (C–Sb, C<sub>5</sub>H<sub>3</sub>), 91.12 (C, C<sub>5</sub>H<sub>3</sub>), 127.91 (C, Ph), 128.28 (C, Ph), 135.93 (C, Ph), 136.81 (C–Sb).

- [19] Compound **2** was synthesized as compound **1**, Fc(Me)NLi was used in place of FcNLi. Yield 55%; m.p.: 60-61 °C; IR (m cm<sup>-1</sup>): 453 (Sb-C), 3060 (C–H aromatic) FAB<sup>+</sup> (m/z): 531(100%) [M]<sup>+</sup>, 502(6%) [M – Me<sub>2</sub>]<sup>+</sup>, 487 (62%) [M – NMe<sub>2</sub>]<sup>+</sup>, 454 (28%) [M – Ph]<sup>+</sup> 410 (16%) [M – Ph – NMe<sub>2</sub>]<sup>+</sup>, 275(14%) [SbPh<sub>2</sub>]<sup>+</sup> , 257(13%) [FcCHMeNMe<sub>2</sub>]<sup>+</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm) 1.15 (d, 3H, CH<sub>3</sub>), 1.73 (s, 6H, NMe<sub>2</sub>), 3.84 (q, 1H, CH), 4.00 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.12 (t, 1H, C<sub>5</sub>H<sub>3</sub>), 4.20 (m, 1H, C<sub>5</sub>H<sub>3</sub>), 4.30 (m, 1H, C<sub>5</sub>H<sub>3</sub>), 7.23–7.58 (m, 10H, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) : 7.50 (Me), 38.66 (NMe<sub>2</sub>), 59.30 (CH), 68.89 (C, C<sub>5</sub>H<sub>5</sub>), 68.99 (CH, C<sub>5</sub>H<sub>3</sub>), 69.31 (CH, C<sub>5</sub>H<sub>3</sub>), 72.06 (CH, C<sub>5</sub>H<sub>3</sub>), 74.68 (C–Sb, C<sub>5</sub>H<sub>3</sub>), 96.04 (C, C<sub>5</sub>H<sub>3</sub>), 127.84 (C, Ph), 128.09 (C, Ph), 128.17 (C, Ph), 136.57 (C–Sb).
- [20] In a schlenk tube, to a solution of stibine 1 (1.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml), was added CH<sub>3</sub>I (8.03 mmol) with continuous stirring. The reaction was stirred for 24 h and the solution was concentrated under vacuum to obtain a orange product which was isolated by filtration. The compound was recrystallized from ethanol. Yield: 93%; m.p.: 120 °C; IR (m cm<sup>-1</sup>): 462 (Sb–C), 3058 (C–H aromatic); FAB<sup>+</sup> m/z:  $1064(6\%) \hspace{0.2cm} [2M]^{+}, \hspace{0.2cm} 946(16\%) \hspace{0.2cm} [2M-2NMe_{3}]^{+}, \hspace{0.2cm} 532(95\%) \hspace{0.2cm} [M]^{+}, \hspace{0.2cm} 473$ (36%) [M - NMe<sub>3</sub>]<sup>+</sup>, 454 (21%) [M - Ph]<sup>+</sup>, 397 (29%)  $[M - Ph - NMe_2]^+$ , 275 (31%)  $[SbPh_2]^+$ ; 242(12%)  $[FcCH_2NMe_2]^+$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm) 3.12 (s, 9H, NMe<sub>3</sub>), 4.05(d<sup>2</sup> J<sub>HH</sub>, 12.5 Hz, 1H, CH<sub>2</sub>), 4.30 (d<sup>2</sup> J<sub>HH</sub>, 12.4 Hz, 1H, CH<sub>2</sub>), 4.58 (m, 1H, C<sub>5</sub>H<sub>3</sub>), 4.20 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 5.05 (t, 1H, C<sub>5</sub>H<sub>3</sub>), 5.53 (m, 1H, C<sub>5</sub>H<sub>3</sub>), 7.29–7.56 (m, 10H, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) 52.87 (NMe<sub>3</sub>), 68.08 (CH<sub>2</sub>), 70.40 (C, C5H5), 74.29 (CH, C5H3), 76.02 (CH, C5H3), 76.98 (CH, C5H3), 78.28 (C-Sb C<sub>5</sub>H<sub>3</sub>), 93.28 (C, C<sub>5</sub>H<sub>3</sub>) 128.92 (C, Ph), 129.35 (C, Ph), 135.79 (C,Ph), 136.57 (C-Sb).
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- [23] Crystal data. Compound 1: crystal dimensions  $0.368 \times 0.178 \times$  $0.034 \text{ mm}^3$ , empirical formula =  $C_{25}H_{26}FeNSb$ , Fw = 518.07, triclinic, space group  $P\bar{1}$ , a = 7.7115(4), b = 10.3465(5), c = 14.6537(7),  $\alpha = 70.184(1), \beta = 82.810(1), \gamma = 83.632(1), V = 1088.35(9) \text{ Å}^3, Z = 2,$  $D_c = 1.581 \text{ mg/m}^3$ ,  $\mu = 1.917$ , F(000) = 520, independent reflections = 7761,  $R_{[I>2\sigma(I)]} = 0.0456$ .  $\Delta/\sigma = 1.123/-0.379 \text{ e} \text{ Å}^{-3}$ , GOF = 0.999. CCDC No. = 280195; Compound 2: crystal dimensions  $0.346 \times 0.322 \times 0.142 \text{ mm}^3$ , empirical formula =  $C_{26}H_{28}FeNSb$ , Fw = 532.09, triclinic, space group P1, a = 8.0351(4), b = 10.8605(6),  $c = 13.7936(8), \quad \alpha = 74.648(1), \quad \beta = 89.276(1), \quad \gamma = 81.366(1) \quad V =$ 1147.0(1) Å<sup>3</sup>, Z = 2,  $D_c = 1.541 \text{ mg/m}^3$ ,  $\mu = 1.917$ , F(000) = 536, independent reflections = 8168,  $R_{[I>2\sigma(I)]} = 0.0445$ ,  $\Delta/\sigma = 1.000/$  $-0.507 \text{ e} \text{ Å}^{-3}$ , GOF = 0.990. CCDC No. = 280196; Compound 3: crystal dimensions  $0.214 \times 0.192 \times 0.078 \text{ mm}^3$ , empirical formula =  $C_{28}H_{35}FeINOSb$ , Fw = 706.07, monoclinic, space group  $P2_1/n$ , a =15.3782(8),  $b = 13.2581(7), c = 15.7316(8), \alpha = 90, \beta = 118.975(1),$  $\gamma = 90$ , V = 2806.0(3) Å<sup>3</sup>, Z = 4,  $D_c = 1.671$  mg/m<sup>3</sup>,  $\mu = 2.600$ , F(000) = 1392, independent reflections = 10163,  $R_{[I>2\sigma(I)]} = 0.0456$ .  $\Delta/\sigma = 1.612/-0.733$  e Å<sup>-3</sup>, GOF = 1.009, CCDC No. = 280197.
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