

# Formation of (vinyl-ferrocenyl)stibines involving $\beta$ -elimination: Hypervalent Sb–N bonding

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Received 17 January 2007; received in revised form 17 April 2007; accepted 17 April 2007

Available online 22 April 2007

## Abstract

Unusual syntheses of vinyl substituted ferrocenylstibines viz. diphenyl(2-vinylferrocenyl) stibine (**2**) and iodo-(*N,N*-dimethylaminoethylferrocenyl)(2-vinylferrocenyl)stibine (**4**) involving  $\beta$ -elimination, are reported. Stibines Ph<sub>2</sub>SbFc (**1**) or Fc<sub>2</sub>SbCl (**3**) containing dimethylaminoethyl-pendant arm on a ferrocenyl ring on reaction with MeI gives vinyl substituted ferrocenylstibines. All the new stibines were characterized by IR, mass, <sup>1</sup>H, <sup>13</sup>C, COSY, HETCOR NMR spectroscopy. The structures of all of these 1,2-disubstituted ferrocenylstibines were determined by X-ray diffraction analyses. The compounds **3** and **4** show hypervalent bonding between the antimony and nitrogen atoms giving **6** and **5** coordinated antimony, respectively. This is the first report on ferrocenylstibines containing a vinyl group in their framework.

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**Keywords:** Ferrocenyl; Stibines; Hypervalent antimony

## 1. Introduction

Recently, the chemistry of hypervalent compounds bearing heavier pnictogens (in particular Sb, Bi) has attracted interest [1–6]. Intramolecular interactions between antimony and nitrogen atoms have been widely reported [7–13], and 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>- and 8-(Me<sub>2</sub>N)C<sub>10</sub>H<sub>6</sub>-moieties have often been applied to stabilize organoantimony molecular complexes, cations, or compounds containing metal–metal bonds [9–13]. Our group has reported the first ferrocenylstibines containing a 2-dimethylaminomethyl and a 2-dimethylamino ethyl side chain. These stibines also present Sb–N hypervalent interactions [14].

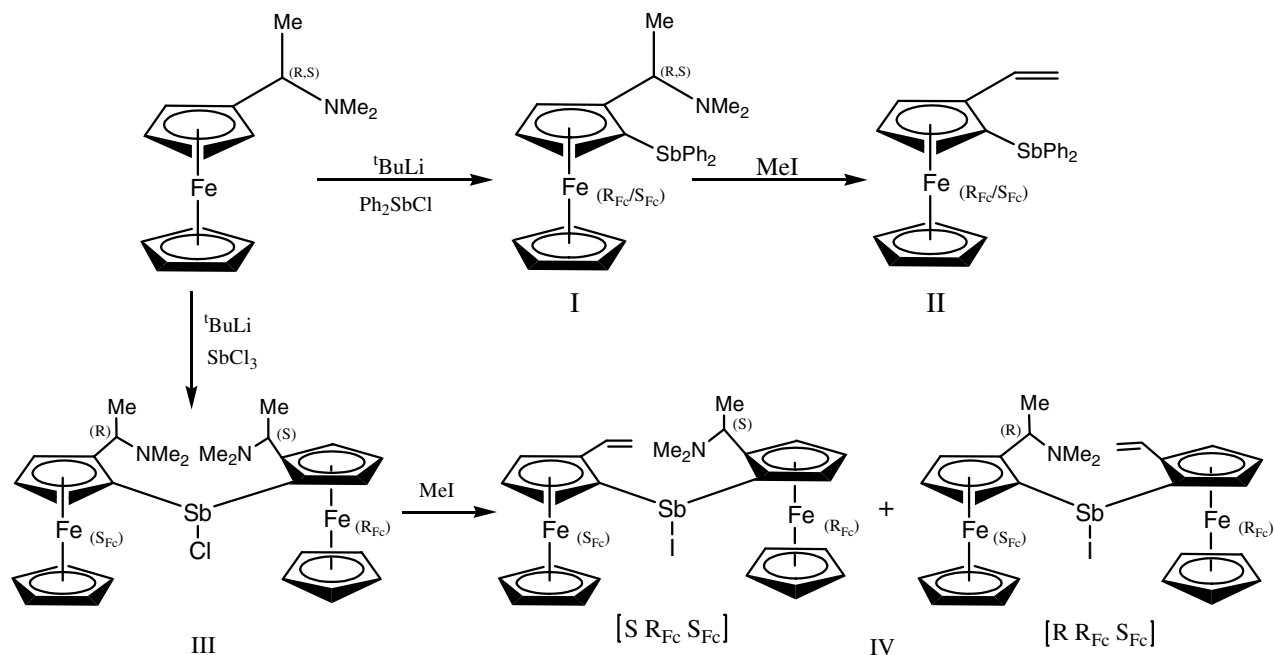
On the other hand, 1,2-disubstituted bidentate ferrocenylphosphines are important catalytic precursors for many different types of reactions, e.g., hydrogenation, carbonyl-

ation, hydrosilylation [15–17], however, most of the reports on these phosphines contain other donor atoms such as P, O, and N apart from one phosphorus atom. Ferrocene ligands that combine the usual donor groups with potentially  $\pi$ -donating functionalities such as alkenyl groups still present an area remaining largely a virgin field, which markedly contrasts with the number of functionalized vinylferrocenes already known. For instance, racemic vinylferrocenes bearing an additional functional group (Cl, C(O)Ph, C(OH)Ph<sub>2</sub>, C(O)NHPh) in position 2 of the ferrocene unit were prepared by base-induced elimination from the respective (2-ferrocenylethyl)ammonium salts [18,19].

Similarly, phosphorus substituted vinylferrocenes were also synthesized either unintentionally or served just as reaction intermediates [20]. Here, we wish to report the unusual formation of (vinyl-ferrocenyl)stibines by a salt formation reaction of dimethylaminoethylferrocenyl stibines with MeI (Scheme 1).

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## 2. Results and discussion

The ferrocenyl stibines (**1**) and (**3**) were synthesized by treatment of *Rac.* (*N,N*-dimethylamino)ethylferrocene with *t*-BuLi, followed by electrophilic attack with Ph<sub>2</sub>SbCl or SbCl<sub>3</sub>, respectively. It is to be noted that when (*N,N*-dimethylamino)ethylferrocenyl stibines (**1**) and (**3**) react with one or more equivalent of MeI, the corresponding (vinylferrocenyl)stibine were obtained. A similar formation of the corresponding phosphorus analogue of (**2**) was reported [20]. It is worth mentioning that when the side arm is Me<sub>2</sub>NCH<sub>2</sub>, a trimethylammonium salt was obtained and its crystal structure was reported by our group.

All the compounds are soluble in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>. These stibines are stable on melting without decomposition. These compounds were analyzed by FAB<sup>+</sup> mass spectrometry. For all the three compounds molecular ion peaks were observed along with fragments corresponding to the successive loss of organic entities attached to the antimony atom. In the far IR spectra of these compounds, Sb–C vibrations have been observed. In all the compounds, the assignment of individual proton signals in the <sup>1</sup>H NMR spectra was based on *J*<sub>HH</sub> coupling constant values and was confirmed by COSY

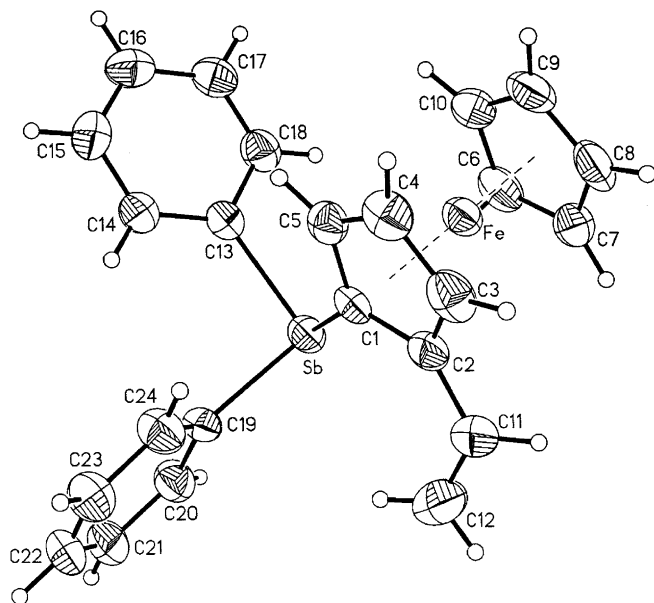


Fig. 1. Molecular structure of diphenyl (2-vinylferrocenyl)stibine (**2**).

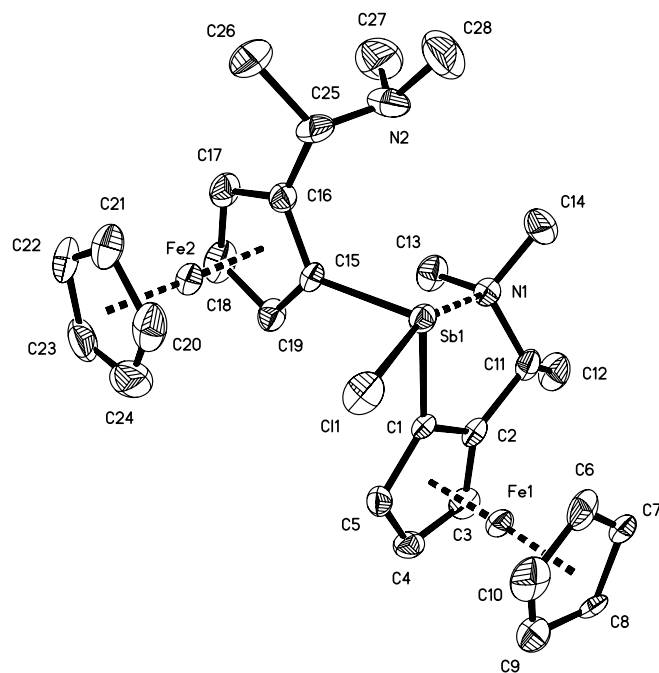


Fig. 2. Molecular structure of chloro-bis(*N,N*-dimethylaminoethylferrocenyl)stibine (**3**).

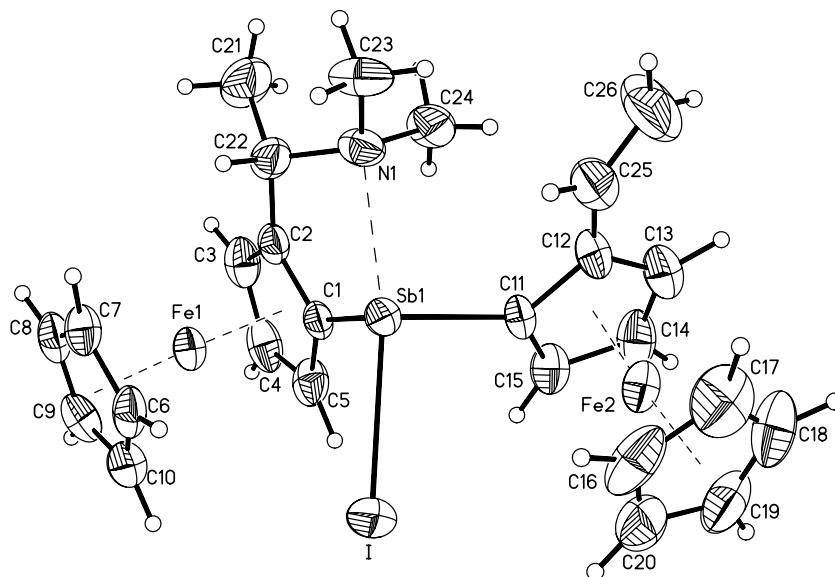


Fig. 3. Molecular structure of iodo-(*N,N*-dimethylaminoethylferrocenyl)(2-vinylferrocenyl)stibine (**4**).

and HETCOR. The molecular structures of **2**, **3**, and **4** have been confirmed by X-ray crystallography as shown in Figs. 1–3. All these compounds are monomeric in nature and no significant intermolecular interactions were observed. All the three compounds possess planar chirality but compounds **3** and **4** also possess central chirality. Compound **3** is enantiomerically pure and corresponds to the diastereoisomer [R(C11),S(C25),S(Fc1),R(Fc2)] which was confirmed by the Flack parameter, while compound **4** corresponds to Sc,RFc (and Rc,SFc) diastereoisomers Scheme 1. Crystal data for all structural analyses are given in Table 1. Selected bond lengths and angles for all compounds are listed in Table 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 the other known tertiary stibines. The shortest Sb–C<sub>(ferrocenyl)</sub> bond length is ascribed 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.

The Sb–C<sub>(ferrocenyl)</sub> bond distance found in compound **2** is 2.135(4) Å, which is slightly larger than Sb–C<sub>(ferrocenyl)</sub> distance found in previously reported stibine (**1**) [2.124(2) Å], which may be due to the extended conjugation and hence decreasing the donor ability of ferrocenyl group. The Sb–C

Table 1  
Crystallographic data for compounds **2–4**

Compounds	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>24</sub> H <sub>21</sub> FeSb	C <sub>28</sub> H <sub>36</sub> ClFe <sub>2</sub> N <sub>2</sub> Sb	C <sub>26</sub> H <sub>29</sub> Fe <sub>2</sub> INSb
Formula weight	487.01	669.49	715.85
Crystal color and shape	Yellow prism	Orange prism	Orange prism
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> $\bar{1}$
Crystal size (mm)	0.34 × 0.10 × 0.06	0.326 × 0.162 × 0.072	0.46 × 0.10 × 0.05
<i>a</i> (Å)	7.5690(7)	12.4021(8)	9.8530(7)
<i>b</i> (Å)	10.3697(10)	13.1049(9)	11.9888(8)
<i>c</i> (Å)	13.3918(13)	17.055(1)	12.1523(8)
$\alpha$ (°)	70.275(2)	90	83.044(1)
$\beta$ (°)	84.266(2)	90	72.712(1)
$\gamma$ (°)	84.068(2)	90	66.278(1)
<i>V</i> (Å <sup>3</sup> )	981.75(16)	2771.9(3)	1254.84(15)
<i>Z</i>	2	4	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.647	1.604	1.895
$\mu$ (mm <sup>-1</sup> )	2.118	2.116	3.453
2 $\theta$ (°)	2.09–25.03	1.96–25.01	1.76–25.00
Reflections collected	8052	22661	10361
Independent reflections	3448	4886	4424
<i>R</i> <sub>int</sub>	0.0426	0.0536	0.0459
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0368	0.0383	0.0441
Flack's parameter		0.00(3)	
Goodness-of-fit	0.943	1.007	0.949
Maximum/minimum $\Delta\rho$ (e Å <sup>-3</sup> )	0.8810/–0.6350	0.8539/–0.6042	0.8519/–0.4180

Table 2  
Selected bond length (Å) and selected bond angles (°) for compounds 2–4

Compound 2		Compound 3		Compound 4	
Sb–C(1)	2.135(4)	Sb(1)–C(1)	2.093(5)	Sb(1)–C(1)	2.124(6)
Sb–C(19)	2.157(4)	Sb(1)–C(15)	2.144(5)	Sb(1)–C(11)	2.131(6)
Sb–C(13)	2.161(4)	Sb(1)–Cl(1)	2.515(2)	Sb(1)–N(1)	2.646(5)
		Sb(1)–N(1)	2.584(5)	Sb(1)–I	2.8537(6)
		Sb(1)···N(2)	3.614(6)		
C(1)–Sb–C(19)	96.36(15)	C(1)–Sb(1)–C(15)	95.3(2)	C(1)–Sb(1)–C(11)	97.3(2)
C(1)–Sb–C(13)	94.62(15)	C(1)–Sb(1)–Cl(1)	91.13(16)	C(1)–Sb(1)–N(1)	71.4(2)
C(19)–Sb–C(13)	97.09(15)	C(15)–Sb(1)–Cl(1)	98.85(15)	C(11)–Sb(1)–N(1)	90.0(2)
		C(1)–Sb(1)–N(1)	73.19(19)	C(1)–Sb(1)–I	90.52(16)
		C(15)–Sb(1)–N(1)	88.54(18)	C(11)–Sb(1)–I	94.25(16)
		Cl(1)–Sb(1)–N(1)	163.29(12)	N(1)–Sb(1)–I	161.85(12)
		C(1)–Sb(1)–N(2)	142.74(17)		
		C(15)–Sb(1)–N(2)	60.34(19)		
		Cl(1)–Sb(1)–N(2)	118.57(11)		
		N(1)–Sb(1)–N(2)	78.10(15)		

(ferrocenyl) bond distance is shorter than the average Sb–C (phenyl) bond lengths presented in the compound **2**. In the same manner the average Sb–C<sub>(ferrocenyl)</sub> bond distance found in compound **4** is 2.131(6) Å is slightly longer than the Sb–C<sub>(ferrocenyl)</sub> bond distance observed in stibine (**3**).

In compound **2**, geometry around antimony is pyramidal and the average C–Sb–C angle is 96.02(2), which is not very different from the bond angles found in other tertiary stibines [21–24]. The vinyl group is directed toward the diphenylstibino substituent while remaining parallel with the parent cyclopentadienyl ring, which allows an efficient conjugation that is demonstrated by the angles by C=C bond and the Cp1 planes [–11.51(6)°]. The structure is very similar to recently reported phosphorus analogues [25]. In compound **3** and **4** distance between nitrogen atom of NMe<sub>2</sub> group and the central antimony atom is 2.584(5) Å and 2.646(5) Å, which is much shorter (69%) and (71%), respectively, than the sum of their *Van der waals* radii (3.74 Å). These distances are slightly longer than the covalent bond length of 2.11 Å [26]. This result indicates hypervalent bond formation between antimony and nitrogen. There exists another very weak hypervalent Sb–N interaction [3.614(6) Å] in compound **3** which gives tetragonal bipyramidal geometry around the antimony atom in this compound where two carbons and two nitrogen form the tetragonal plane while lone pair and chlorine occupy the apical positions. In compound **4**, the geometry about antimony atom is distorted pseudo trigonal bipyramid where the two carbon atoms bound to the antimony atom (1Fc and 1Fc) occupy the equatorial plane. The apical positions are occupied by the nitrogen atom and the carbon atom of phenyl group with a C–Sb–N angle 158.7°. The lone pair of electrons can be considered to occupy the equatorial position.

### 3. Experimental

All the solvents were distilled immediately prior to use. All the reactions were performed under an atmosphere of oxygen-free dry nitrogen. Elemental analyses were deter-

mined on a Perkin–Elmer 240. Melting points were obtained on a MEL-TEMP II Fisher and are uncorrected. EI and FAB<sup>+</sup> 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. IR spectra were recorded on a Nicolet-Magna 750 FT-IR spectrometer as nujol mulls. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> or CD<sub>3</sub>OD on JEOL ECLIPSE 300 (<sup>1</sup>H: 300.5311 MHz; <sup>13</sup>C: 75.5757) spectrometer.

#### 3.1. X-ray crystallography

The X-ray intensity data were measured at 293 K on a Bruker SMART APEX CCD-based X-ray diffractometer by using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The detector was placed at a distance of 4.837 cm from the crystals in all cases. Analysis of the data showed in all cases negligible decays during data collections. An analytical face indexed absorption correction was applied. Crystal structures were refined by full-matrix least squares. SMART software (data collection and data reduction) and SHELXTL were used for solution and refinement of the structures.

#### 3.2. Syntheses

##### 3.2.1. Synthesis of diphenyl(*N,N*-dimethylaminoethylferrocenyl)stibine (**1**)

Compound **1** was synthesized according to our earlier report [14].

##### 3.2.2. Synthesis of diphenyl(2-vinylferrocenyl)stibine (**2**)

In a Schlenk tube, to a solution of stibine **1** (0.6 g, 1.1 mmol) in CHCl<sub>3</sub> (20 ml), was added CH<sub>3</sub>I (3.2 mmol) with continuous stirring. The reaction was stirred for 2 h and the solution was concentrated under vacuum to obtain an abundant yellow solid product, which was isolated by filtration on a glass filter. The compound was dried and

recrystallized from chloroform. Yield: 95%; m.p.: 115–117 °C; IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 472 (Sb–C), 1627 (C=C), 2960, 2923 (C–H stretch), 3063 (C–H aromatic). FAB<sup>+</sup>  $m/z$ : 486 (100%) [M]<sup>+</sup>, 409 (49%) [M–Ph]<sup>+</sup>, 331 (16%) [FcCH=CH<sub>2</sub>Sb]<sup>+</sup>, 212 (59%) [FcCH=CH<sub>2</sub>]<sup>+</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  in ppm): 3.75 (m, 1H, CH, C<sub>5</sub>H<sub>3</sub>), 4.03 (s, 5H, CH, C<sub>5</sub>H<sub>5</sub>), 4.34 (t, 1H,  $J_{\text{HH}} = 2.4$  Hz, CH, C<sub>5</sub>H<sub>3</sub>), 4.68 (m, 1H, CH, C<sub>5</sub>H<sub>3</sub>), 5.00 (dd, 1H,  $J_{\text{HH}} = 1.3$  Hz,  $J_{\text{HH}} = 1.1$  Hz, CH=CH<sub>2</sub>), 5.29 (dd, 1H,  $J_{\text{HH}} = 1.3$  Hz,  $J_{\text{HH}} = 1.4$  Hz, CH=CH<sub>2</sub>), 6.55 (2d, 1H,  $J_{\text{HH}} = 10.7$  Hz,  $J_{\text{HH}} = 10.7$  Hz, CH=CH<sub>2</sub>), 7.26–7.57 (m, 10H, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  in ppm): 68.3 (CH, C<sub>5</sub>H<sub>3</sub>), 69.8 (CH, C<sub>5</sub>H<sub>5</sub>), 71.4 (CH, C<sub>5</sub>H<sub>3</sub>), 72.0 (CH, C<sub>5</sub>H<sub>3</sub>), 75.0 (C–Sb, C<sub>5</sub>H<sub>3</sub>), 112.4 (C–CH=CH<sub>2</sub>), 128.3 (CH=CH<sub>2</sub>), 128.7 (CH=CH<sub>2</sub>), 133.7 (CH, Ph), 135.1 (CH, Ph), 135.8 (CH, Ph), 136.9 (C–Sb, Ph).

### 3.2.3. Synthesis of chloro-bis(*N,N*-dimethylaminoethylferrocenyl)stibine (**3**)

To a solution of antimony trichloride (1.36 g, 6 mmol) in ether (10 ml),  $\alpha$ -(*N,N*-dimethylamino)ethylferrocenyllithium (2.55 g, 10 mmol) {synthesized *in situ* according to reported method [14]}, was added drop-wise under a nitrogen atmosphere at –20 °C with continuous stirring. The mixture was further stirred for 24 h at room temperature and then reaction was quenched with ice. After extraction with dichloromethane (3 × 10 ml) and drying over sodium sulfate, solvent was removed under vacuum. The compound was dried and recrystallized from chloroform and after concentration gives the orange product. Yield: 59%; m.p. 128–130 °C; IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 492 (Sb–C), 3094 (C–H aromatic). FAB<sup>+</sup>  $m/z$ : 668 (20%) [M]<sup>+</sup>, 633 (6%) [M–Cl]<sup>+</sup>, 590 (62%) [M–Cl–NMe<sub>2</sub>]<sup>+</sup>, 545 (7%) [M–Cl–2NMe<sub>2</sub>]<sup>+</sup>, 411(26%) [M–FcCHMeNMe<sub>2</sub>]<sup>+</sup>, 378 (13%) [SbFcCHMeNMe<sub>2</sub>]<sup>+</sup>, 257(83%) [FcCHMeNMe<sub>2</sub>]<sup>+</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  in ppm): 1.16 (d,  $J_{\text{HH}} = 6.6$  Hz, 3H, H<sub>3</sub>C–CH), 1.76 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H, H<sub>3</sub>C–CH), 1.93 (s, 6H, NMe<sub>2</sub>), 2.42 (s, 6H, NMe<sub>2</sub>), 4.08 (m, 1H, CH–H<sub>3</sub>C), 4.13 (s, 5H, CH, C<sub>5</sub>H<sub>5</sub>), 4.17 (m, 1H, CH–H<sub>3</sub>C), 4.21 (m, 3H, CH, C<sub>5</sub>H<sub>3</sub>), 4.26 (s, 5H, CH, C<sub>5</sub>H<sub>5</sub>, and 2H, CH, C<sub>5</sub>H<sub>3</sub>), 4.36 (m, 1H, CH, C<sub>5</sub>H<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  in ppm): 8.4 (CH<sub>3</sub>), 15.7 (CH<sub>3</sub>), 38.9 (NMe<sub>2</sub>), 39.9 (NMe<sub>2</sub>), 60.0 (CH), 61.5 (CH), 67.5 (CH, C<sub>5</sub>H<sub>3</sub>), 67.8 (CH, C<sub>5</sub>H<sub>3</sub>), 68.4 (CH, C<sub>5</sub>H<sub>3</sub>), 69.3 (CH, C<sub>5</sub>H<sub>5</sub>), 69.4 (CH, C<sub>5</sub>H<sub>3</sub>), 69.8 (CH, C<sub>5</sub>H<sub>3</sub>), 70.5 (CH, C<sub>5</sub>H<sub>3</sub>), 74.1 (CH, C<sub>5</sub>H<sub>3</sub>), 79.8 (C–Sb), 84.8 (C–Sb), 96.0 (C, C<sub>5</sub>H<sub>3</sub>).

### 3.2.4. Synthesis of iodo-(*N,N*-dimethylaminoethylferrocenyl)(2-vinylferrocenyl)stibine (**4**)

In a Schlenk tube, to a solution of stibine **3** (0.73 g, 1.1 mmol) in CHCl<sub>3</sub> (20 ml), CH<sub>3</sub>I (64 mmol) was added with continuous stirring. The reaction was stirred for 2 h at room temperature and the solution was concentrated under vacuum to obtain an orange solid product, which was isolated by filtration on a glass filter. The compound was dried and recrystallized from chloroform. Yield: 75%; m.p.: 105–107 °C; IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 484 (Sb–C), 904 (alkene),

1622 (C=C), 2991, 2875 (C–H stretch). FAB<sup>+</sup>  $m/z$ : 716 (6%) [M]<sup>+</sup>, 588 (20%) [M–I]<sup>+</sup>, 543 (20%) [M–I–NMe<sub>2</sub>]<sup>+</sup>, 333(12%) [FcCH=CH<sub>2</sub>Sb]<sup>+</sup>, 212 (25%) [FcCH=CH<sub>2</sub>]<sup>+</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  in ppm): 1.04 (d, 3H,  $J_{\text{HH}} = 6.7$  Hz, CH<sub>3</sub>), 1.76 (br s, 6H, Me<sub>2</sub>N), 4.09 (m, 1H, CH–H<sub>3</sub>C), 4.13 (m, 1H, CH, C<sub>5</sub>H<sub>3</sub>), 4.36 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.19 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.26 (t, 1H,  $J_{\text{HH}} = 2.1$  Hz,  $J_{\text{HH}} = 2.3$  Hz, CH, C<sub>5</sub>H<sub>3</sub>), 4.29 (s, 5H, CH, C<sub>5</sub>H<sub>5</sub>), 4.33 (m, 2H, CH, C<sub>5</sub>H<sub>3</sub>), 4.48 (m, 1H, CH, C<sub>5</sub>H<sub>3</sub>), 4.69 (m, 1H, CH, C<sub>5</sub>H<sub>3</sub>), 5.07 and 5.10 (dd, 1H,  $J_{\text{HH}} = 1.1$  Hz,  $J_{\text{HH}} = 1.1$  Hz, CH=CH<sub>2</sub>), 5.32 and 5.38 (dd, 1H,  $J_{\text{HH}} = 1.1$  Hz,  $J_{\text{HH}} = 1.0$  Hz, CH=CH<sub>2</sub>), 6.68 (2d, 1H,  $J_{\text{HH}} = 10.7$  Hz,  $J_{\text{HH}} = 10.6$  Hz, CH=CH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  in ppm): 7.5 (CH<sub>3</sub>–CH), 31.50 (NMe<sub>2</sub>), 61.2 (CH–CH<sub>3</sub>), 64.7 (CH, C<sub>5</sub>H<sub>3</sub>), 67.4 (CH, C<sub>5</sub>H<sub>3</sub>), 69.2(CH, C<sub>5</sub>H<sub>3</sub>), 69.4 (CH, C<sub>5</sub>H<sub>3</sub>), 70.1 (CH, C<sub>5</sub>H<sub>3</sub>), 70.2 (CH, C<sub>5</sub>H<sub>5</sub>), 71.0(CH, C<sub>5</sub>H<sub>5</sub>), 71.3 (CH, C<sub>5</sub>H<sub>3</sub>), 87.6(C–Sb, C<sub>5</sub>H<sub>3</sub>), 95.1 (C–Sb, C<sub>5</sub>H<sub>3</sub>), 111.2 (CH=CH<sub>2</sub>), 136.0 (CH=CH<sub>2</sub>).

## 4. Supplementary materials

CCDC 628777, 628778, and 628779 contain the supplementary crystallographic data for **1**, **2**, and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

## Acknowledgements

The authors are thankful to DGAPA (IN210905) for financing projects and one of the authors J.V. is thankful to DGAPA for PD fellowship.

## References

- [1] T. Murafuji, T. Mutoh, K. Satoh, K. Tsunenari, N. Azuma, H. Suzuki, *Organometallics* 14 (1995) 3848.
- [2] M. Weinman, A. Gehrig, B. Schiemenz, G. Huttner, B. Nuber, G. Reiwald, H. Lang, *J. Organomet. Chem.* 563 (1998) 3147.
- [3] Y. Takaguchi, A. Hosowaka, S. Yamada, J. Motoyoshishya, H. Aoyama, *J. Chem. Soc., Perkin Trans. I* (1998) 5299.
- [4] D.A. Atwood, A.H. Cowley, J. Ruiz, *Inorg. Chim. Acta* 198–200 (1992) 271.
- [5] H. Suzuki, T. Murafuji, Y. Matano, N. Azuma, *J. Chem. Soc., Perkin Trans. I* (1993) 2969.
- [6] P. Sharma, D. Pérez, N. Rosas, A. Cabrera, A. Toscano, *J. Organomet. Chem.* 691 (2006) 579.
- [7] P. Sharma, D.A. Castillo, N. Rosas, A. Cabrera, E. Gomez, A. Toscano, F. Lara, S. Hernandez, G. Espinosa, *J. Organomet. Chem.* 689 (2004) 2583.
- [8] C.J. Carmalt, A.H. Cowley, R.D. Culp, R.A. Jones, S. Kamepalli, N.C. Norman, *Inorg. Chem.* 36 (1997) 2770.
- [9] T. Tokunaga, H. Seki, S. Yasuike, M. Ikoma, J. Kurita, K. Yamaguchi, *Tetrahedron* (2000) 8833.
- [10] T. Tokunaga, H. Seki, S. Yasuike, M. Ikoma, J. Kurita, K. Yamaguchi, *Tetrahedron Lett.* 41 (2000) 1031.
- [11] H.J. Breunig, I. Ghesner, M.E. Ghesner, E. Lork, *Inorg. Chem.* 42 (2003) 1751.

- [12] L.M. Opris, A. Silvestru, C. Silvestru, H.J. Breunig, E. Lork, J. Chem. Soc., Dalton Trans. (2003) 4367.
- [13] S. Kamepalli, C.J. Karmalt, R.D. Culp, A.H. Cowley, R.A. Jones, N.C. Norman, *Inorg. Chem.* 35 (1996) 6179.
- [14] P. Sharma, J.G. Lopez, C. Ortega, N. Rosas, A. Cabrera, C. Alvarez, A. Toscano, E. Reyes, *Inorg. Chem. Commun.* 9 (2006) 85.
- [15] T. Ireland, K. Tappe, G. Grossheimann, P. Knochel, *Chem. Eur. J.* 8 (2002) 843.
- [16] H.U. Blazer, *Adv. Synth. Catal.* 344 (2002) 17.
- [17] H.L. Pederson, M. Johannsen, *Chem. Commun.* (1999) 2517.
- [18] D.W. Slocum, C.A. Jennings, T.R. Engelmann, B.W. Rockett, C.R. Hauser, *J. Org. Chem.* 36 (1971) 377.
- [19] N.S. Khrushcheva, O.V. Shakhova, V.I. Sokolov, *Russ. Chem. Bull., Int. Ed.* 52 (2003) 2146.
- [20] T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, M. Kumada, *Bull. Chem. Soc. Jpn.* 53 (1980) 1138.
- [21] P. Sharma, N. Rosas, A. Cabrera, A. Toscano, M.J. Silva, D. Perez, L. Velasco, J. Perez, R. Guiterrez, *J. Organomet. Chem.* 690 (2005) 3286.
- [22] J. Vela, P. Sharma, A. Cabrera, C. Alvarez, N. Rosas, S. Hernandez, A. Toscano, *J. Organomet. Chem.* 634 (2001) 5.
- [23] P. Sharma, A. Cabrera, N. Rosas, S. Hernandez, R. Lelagadec, J. Valdes, J.L. Arias, *Main Group Met. Chem.* 21 (1998) 303.
- [24] A.N. Sobolev, I.P. Romm, V.K. Belsky, E.N. Guryanova, *J. Organomet. Chem.* 179 (1979) 153.
- [25] P. Stepnicka, I. Cisarova, *Inorg. Chem.* 45 (2006) 8785.
- [26] J. Emsley, *The Elements*, 3rd ed., Clarendon, Oxford, 1998.