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# New 1,2-disubstituted ferrocenyl stibines containing N-heterocyclic pendant arm: Sb–N hypervalent compounds

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ABSTRACT

New 1,2-disubstituted ferrocenyl stibines viz. containing -$CH_2NR$ or -$CH_2NHR$ pendant arm at the *ortho*-position have been synthesized and characterized by various physicochemical methods. These new ferrocenylstibines were prepared by the nucleophilic substitution reaction of diphenyl[(*N*,*N*,*N*-trimethylaminomethylferrocenyl)iodide]stibine by different primary amines and secondary heterocyclic amines viz. furan-2-ylmethylamine, *p*-aminoacetophenone, 3-(1-hydroxyethyl)-aniline, 4-hydroxypiperidine, 1-ethylpiperazine and 4-(4-bromophenyl)-4-hydroxypiperidine. Molecular structure of stibine (**2**), (**3**), (**5**) and (**7**) have been determined by X-ray crystallography. Stibine (**2**), (**5**) and (**7**) show a weak hypervalent Sb–N interaction while stibine (**3**) does not show this interaction in solid state.



## 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 $sp^3$-nitrogen atoms have been widely reported in the literature [7–13]. Very recently, ferrocenylstibines containing 2-dimethylaminomethyl and 2-dimethylaminoethyl side chains have been reported. In the molecular structures of these ferrocenylstibines, Sb–N hypervalent interactions were observed [14–16].

On the other side, for the introduction of ferrocenylmethyl group in nucleophilic substrates, most of the attention was paid to quaternary ammonium salts of *N*,*N*,*N*-trimethylaminomethylferrocene. In particular, new reactions of N-, C-, S- and P-ferrocenylmethylation of different compounds were performed with the use of *(*N*,*N*,*N*-trimethylaminomethylferrocenyl)iodide (**1a**) [17,18]. Also there appears only one report on the one-pot alkylation of [1-*N*,*N*-dimethylaminomethyl-2-diphenylphosphino]ferrocene (**1b**) with benzyl bromide and subsequent replacement of the ammonium group with a nucleophile [19] but on the other hand, reaction of ferrocenyl phosphine (**1b**) with 1 equiv. of methyl iodide gives preferably an unstable N-methylated product, which further reacts with O- and N-nucleophiles in a manner analogous to that for the nonphosphinylated salt [$FcCH_2NMe_3$]I,[20,21]. Reaction of **1b** with excess of MeI yields the respective P,N-dimethylated salt. It was noted that either protection of phosphorus group or use of benzyl bromide as an alkylating agent is advantageous to get the N-methylated product. But in the reaction of diphenyl[(*N*,*N*-dimethylaminomethyl ferrocenyl)] stibine with excess of MeI, a very stable N-methylated product was isolated. Considering the vast number of ferrocene ligands, the unique stereoelectronic properties of the ferrocene framework, existence of a very few reports on ferrocene bonded antimony in the literature and our interest in stibine ligands, this work was undertaken.

## 2. Results and discussion

All the compounds were synthesized by the nucleophilic substitution reaction of diphenyl[(*N*,*N*,*N*-trimethylaminomethylferrocenyl)iodide]stibine salt with different amines in acetonitrile (Scheme 1). All these stibines (**2**)–(**7**) are soluble in polar organic solvents e.g. chloroform, dichloromethane and are insoluble in water and show little solubility in non polar solvents e.g. hexane, pentane.

Primary amines used in this work, on reaction with trimethylammonium salt, in equimolar ratio give secondary ferrocenyl amines. These secondary ferrocenyl amines do not react further with trimethylammonium salt and no tertiary diferrocenyl amine was obtained. The formation of monoferrocenyl derivatives may be interpreted because of the bulkiness of ferrocenyl moiety. In the far IR spectra of these compounds, Sb–C and C–N vibrations were observed. For all these compounds, in the $FAB^+$ spectra molecular ion peaks were observed along with fragments corresponding to the successive loss of organic entities attached to antimony atom. Fragmentation pattern in all these compounds are similar. For compounds **4** and **6** high resolution mass spectra were also obtained, and molecular ion peaks at 609.0712 (Calc. *m*/*z* 609.0715) and 586.1031 (Calc. *m*/*z* 586.1031) respectively, were observed, confirming the molecular formulas for these compounds.

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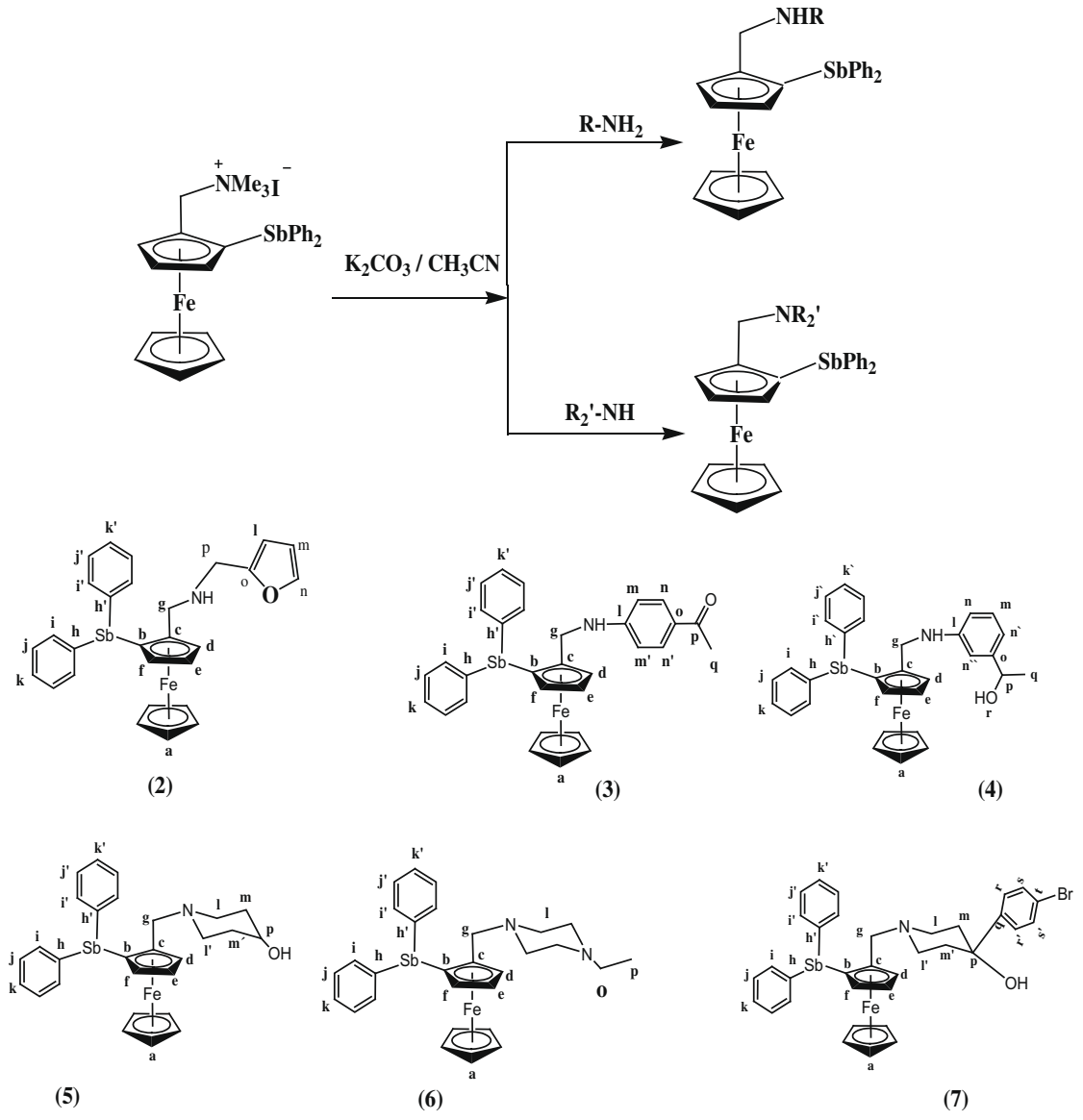


**Scheme 1.**

In all the compounds, the assignment of individual proton signals in the $^1$H NMR spectra was based on $J_{HH}$ coupling constant values and was confirmed by COSY and HETCOR experiments. Though Sb–N interactions were observed in the structural characterizations, evidence for such interactions could not be detected in $^1$H NMR spectra of these stibines. In the $^1$H spectra of all these compounds similar chemical shifts pattern was observed for ferrocene fraction and phenyl rings. A singlet observed at approximately 4.0 ppm in the $^1$H spectra of all these stibines, can be assigned to the un substituted Cp ring protons. The methylene protons of the FcN moiety are not magnetically equivalent. This phenomenon has been observed in the $^1$H NMR spectra of complexes containing both mono dentate and bi dentate 1,2-disubstituted ferrocenyl ligands [22,23]. This is also a consequence of the asymmetry of the bi substituted Cp ring. The stereoheterotopic methylene protons give rise to two AB doublets. The $^1$H NMR data of (**4**) show the presence of only one set of enantiomers out of two possible set of enantiomers. It was not possible to assign the signal to the appropriate diastereomer and the X-ray crystal structure would be of interest. Similarly in the $^{13}$C NMR spectra non existence of two sets of signals were observed confirming the presence of one

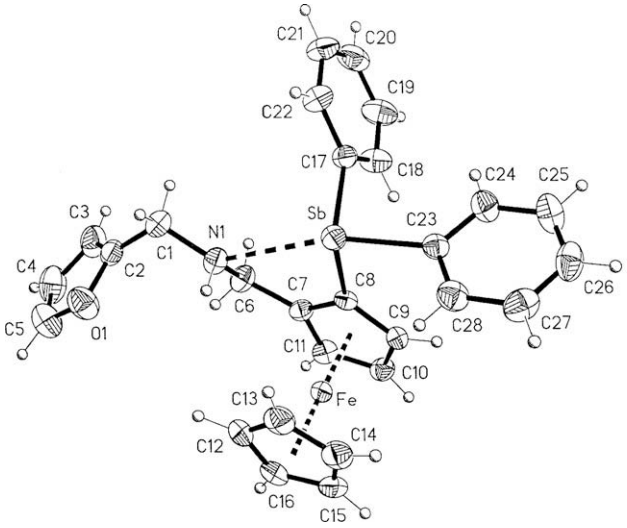


**Fig. 1.** ORTEP diagram of diphenyl[2-(furan-2-ylmethylamino)methylferrocen-1-yl]-stibine (**2**), showing 40% probability ellipsoids.

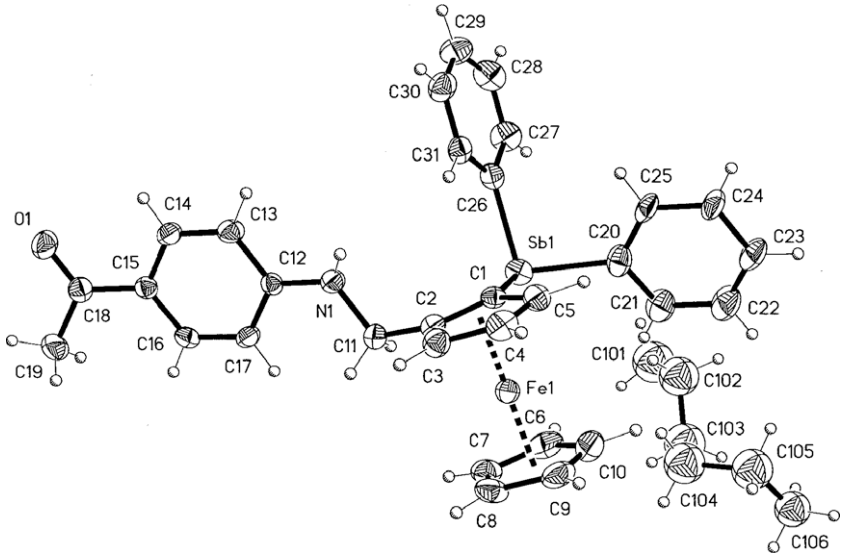


**Fig. 2.** ORTEP diagram of diphenyl[2-(4-acetylaniline)methylferrocen-1-yl] stibine (**3**) showing 40% probability ellipsoids.

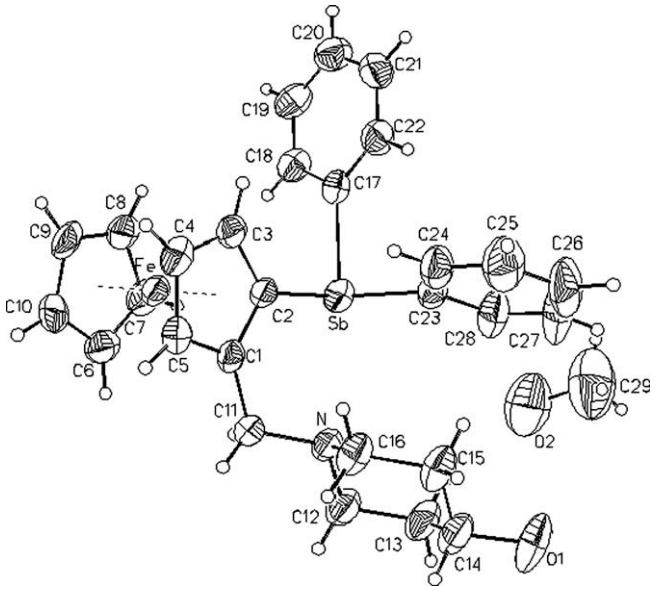


**Fig. 3.** ORTEP diagram of diphenyl[2-(4-hydroxypiperidin-1-yl)methylferrocen-1-yl] stibine (**5**) showing 40% probability ellipsoids.

diastereomer. The two phenyl groups of $SbPh_2$ fraction are magnetically non equivalent and appear at different chemical shifts.

The molecular structures of (**2**), (**3**), (**5**) and (**7**) have been confirmed by X-ray crystallography and are shown in Figs. 1–4. 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 $Sb–C_{(ferrocenyl)}$ bond length found in these ferrocenylstibines is 2.123 Å, which is slightly shorter than that $Sb–C_{(phenyl)}$ bond length, the same observation was reported earlier also [14,15]. All these compounds possess planar chirality. In the structure of compound (**3**), although the space group is non centrosymmetric, it contains symmetry elements of 2nd order and so the unit cell contains a pair of enantiomers (S,R) The compound (**3**) crystallizes with 0.25 mol of hexane as solvent of crystallization and the solvent was modeled in three major contributions in 0.10:0.10:0.05 molar ratio.

In the molecular structure of compound (**3**) the two phenyl groups attached to antimony atom are disordered. In both the compounds, the distance between nitrogen atom of $NMe_2$ group and the central antimony atom is 2.989(3) Å and 3.287 Å, respectively, which is shorter than the sum of their Van der Walls Radii (3.74 Å) and longer than a covalent bond (2.11 Å). Taking into consideration Sb–N interaction, the geometry around antimony in compound (**2**) is distorted pseudo trigonal bipyramid with a lone

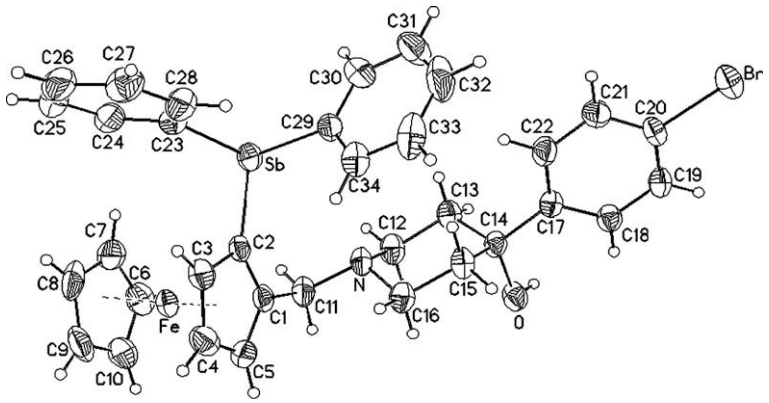


**Fig. 4.** ORTEP diagram of diphenyl[2-(4-(4-bromophenyl))-4-hydroxypiperidin-1-yl] methylferrocen-1-yl}stibine (**7**) showing 40% probability ellipsoids.

**Table 1**
Crystallographic data for compounds **2**, **3**, **5** and **7**.

| Compounds | **2** | **3** | **5** | **7** |
|---|---|---|---|---|
| Empirical formula | $C_{28}H_{26}FeNOSb$ | $C_{32.5}H_{31.5}FeNOSb$ | $C_{29}H_{34}FeNO_2Sb$ | $C_{34}H_{33}BrFeNOSb$ |
| Formula weight | 570.10 | 629.29 | 606.17 | 729.12 |
| Crystal color | Yellow prism | Yellow prism | Yellow prism | Yellow prism |
| Crystal system | Triclinic | Orthorhombic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | *Iba*2 | $P\bar{1}$ | $P\bar{1}$ |
| Crystal size (mm) | 0.144 × 0.088 × 0.082 | 0.472 × 0.128 × 0.052 | 0.33 × 0.16 × 0.07 | 0.38 × 0.20 × 0.18 |
| *a* (Å) | 11.644(1) | 15.457(1) | 7.9390(10) | 9.7572(8) |
| *b* (Å) | 11.713(1) | 42.469(1) | 11.946(2) | 11.168(1) |
| *c* (Å) | 11.732(1) | 8.6561(5) | 15.006(2) | 14.6486(13) |
| $\alpha$ (°) | 60.877(1) | 90 | 80.525(3) | 80.199(1) |
| $\beta$ (°) | 61.427(1) | 90 | 88.537(2) | 76.433(1) |
| $\gamma$ (°) | 84.462(1) | 90 | 77.301(2) | 78.197(1) |
| *V* (Å$^3$) | 1208.04(18) | 5682.3(6) | 1369.3 (3) | 1506.3(2) |
| *Z* | 2 | 8 | 2 | 2 |
| $D_{calc}$ (g/cm$^3$) | 1.567 | 1.472 | 1.470 | 1.608 |
| $\mu$ (mm$^{-1}$) | 1.738 | 1.486 | 1.541 | 2.732 |
| $2\theta$ (°) | 2.02–25.37 | 1.92–2534 | 25.36 | 25.33 |
| Flacks parameter | | 0.01 | | |
| Reflections collected | 13629 | 30588 | 11421 | 12516 |
| Independent reflections | 4403 | 5190 | 5010 | 5505 |
| $R_{int}$ | 0.0348 | 0.0528 | 0.0490 | 0.0397 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0335 | 0.0384 | 0.0403 | 0.0321 |
| $wR_2$ [all data] | 0.0759 | 0.0828 | 0.0609 | 0.0574 |
| Goodness-of-fit | 0.992 | 1.040 | 0.843 | 0.849 |
| Max./min. $\Delta\rho$ (e Å$^{-3}$) | 0.0623/–0.265 | 0.659/–0.276 | 0.825/–0.591 | 0.789/–0.429 |

**Table 2**
Selected bond length (Å) and selected bond angles (°) for compounds **2**, **3**, **5** and **7**.

| Compound (**2**) | | Compound (**3**) | |
|---|---|---|---|
| Sb–C(8) | 2.135(3) | C(1)–Sb | 2.135(4) |
| Sb–C(17) | 2.154(4) | Sb–C(20) | 2.154(12) |
| Sb–C(23) | 2.176(3) | Sb–C(26) | 2.155(9) |
| Sb···N(1) | 2.989(3) | | |
| C(8)–Sb–C(17) | 93.42 (11) | C(1)–Sb–C(20) | 96(2) |
| C(8)–Sb–C(23) | 93.56(11) | C(1)–Sb–C(26) | 93.2(7) |
| C(17)–Sb–C(23) | 97.17(11) | C(20)–Sb–C(26) | 97.4(17) |
| Compound (**5**) | | Compound (**7**) | |
| Sb–C(2) | 2.118(4) | Sb–C(2) | 2.128(3) |
| Sb–C(23) | 2.124(4) | Sb–C(23) | 2.165(3) |
| Sb–C(17) | 2.160(4) | Sb–C(29) | 2.150(3) |
| Sb···N | 3.287(3) | Sb···N | 3.59(2) |
| C(2)–Sb–C(23) | 97.06(15) | C(2)–Sb–C(29) | 99.36(12) |
| C(2)–Sb–C(17) | 95.27(14) | C(2)–Sb–C(23) | 93.21(11) |
| C(23)–Sb–C(17) | 94.99(15) | C(29)–Sb–C(23) | 95.70(12) |

pair of electron along with two carbon atoms (1Ph and 1Fc) occupying the equatorial position. Nitrogen atom and one of the C (phenyl group) atom are on the axial position with a C–Sb–N angle 161.03(10)°. The $C_{23}$–Sb (Sb–Ph) bond [2.176(3) Å] *trans* to the nitrogen atom is slightly longer than the other Sb–C (Sb–Ph) bonds, 2.154(4) Å. A similar structure and lengthening of one of the Sb–C bond length were reported earlier in similar compounds [14]. In compound (**3**) the geometry around antimony atom is pyramidal. The average C–Sb–C bond angle is 95.53° which is similar to the average bond angles found in triphenylstibine or *tris*(2-thienyl)stibine [24,25]. There exists intermolecular hydrogen bonding N–H···O [2.29(5) Å] in the crystal structure.

Compound (**5**) crystallizes with one molecule of methanol as a solvent of crystallization piperidine ring exists in chair conformation with the hydroxyl group at the equatorial position. Puckering amplitudes of the piperidine ring describe a slightly distorted chair with $q3 \gg q2$. Indeed, the total puckering amplitude *Q* [0.571(3) Å] lies only slightly under the *Q* value of an ideal cyclohexane chair (0.63 Å) [26]. The molecule is monomeric and presents an intramolecular Sb···N [3.287(3)] interaction. Taking in account this interaction, the geometry around antimony is distorted trigonal bipyramidal.

The molecule is monomeric in compound (**7**), and piperidine ring exists in chair conformation with the hydroxyl group at the axial position. Similar to compound (**5**), the puckering amplitudes of the piperidine ring describe a slightly distorted chair conformation with $q3 \gg q2$ and the total puckering amplitude *Q* [0.573(5) Å] lies only slightly under the *Q* value of an ideal cyclohexane chair (0.63 Å) [25]. The molecule presents both inter and intramolecular interactions. There exists a weak Sb–N interaction and Sb–N hypervalent bond is long [3.59(2) Å]. Taking in account this interaction the geometry around antimony is distorted trigonal bipyramidal. An intermolecular hydrogen bonding O–H···O [2.922(4) Å] was observed in the crystal structure, forming a pseudo dimer in the solid state.

In conclusion, new 1,2-disubstituted ferrocenyl stibines viz. containing -$CH_2$NR or -$CH_2$NHR pendant arm at the *ortho*-position have been synthesized and characterized and crystal structures of some of these new stibines are reported.. 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.

## 3. General synthesis

In a Schlenk tube, to a solution of 0.3 mmol of *Rac*-diphenyl[(*N*,*N*,*N*-trimethylaminomethylferrocenyl)iodide]stibine and 3 mmol of $K_2CO_3$, in $CH_3CN$ (15 ml), 0.35 mmol of corresponding amine was added under nitrogen atmosphere. The mixture was refluxed at 85–90 °C with continuous stirring for about 72 h. After extraction with dichloromethane or chloroform (3 × 15 ml) and drying over sodium sulfate, solvent was removed under vacuum and crude product was obtained. The crude product was purified by column chromatography and the product was re-crystallized from a chloroform–hexane mixture.

### 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 using a monochromatized Mo Kα radiation (Kα 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.

#### 3.1.1. Diphenyl[2-(furan-2-ylmethylamino)methylferrocen-1-yl]stibine (**2**)

The compound was synthesized by a similar procedure to general synthesis and furfuryl amine was used for the reaction. The single crystals of the compound were grown in pentane. Yield; m.p.: 86–88 °C; IR ($\nu$ cm$^{-1}$): 454 (Sb–C), 2922, 2852 (C–H aliphatic), 3060 (C–H aromatic), 3386 (N–H hydrogen-bonded); FAB$^+$ *m/z*: 569 (75%) [M]$^+$, 473 (100%) [M–($C_4H_3O$)$CH_2$NH]$^+$, 397 (36%) [M−Ph]$^+$, 275 (23%) [$SbPh_2$]$^+$, 199 (59%) [$FcCH_2$]$^+$; $^1$H NMR ($CDCl_3$, $\delta$ in ppm): 2.17 (br, s, 1H, NH), 3.36 (d, 1H, $J_{HH}$ = 13.21 Hz, $CH_2$), 3.45 (d, 1H, $J_{HH}$ = 14.58 Hz, $CH_2$), 3.56 (d, 1H, $J_{HH}$ = 12.38 Hz, $CH_2$), 3.62 (d, 1H, $J_{HH}$ = 13.21 Hz, $CH_2$), 3.72 (m, 1H, C*H*, $C_5H_3$), 4.07 (s, 5H, C*H*, $C_5H_5$), 4.23 (t, 1H, $J_{HH}$ = 2.20 Hz, C*H*, $C_5H_3$), 4.42 (m, 1H, C*H*, $C_5H_3$), 6.03 (d, 1H, $J_{In}$ = 0.83 Hz, C*H*, Furan), 6.27 (m, 1H, $J_{Im}$ = 1.93 Hz, C*H*, Furan), 7.25–7.57 (m, 11H, Ph and Furan); $^{13}$C NMR ($CDCl_3$, $\delta$ in ppm): 43.45 ($C_g$), 47.48 ($C_p$), 69.13 ($C_a$), 69.39 ($C_e$), 71.56 ($C_f$), 70.40 ($C_b$), 74.72 ($C_d$), 107.29 ($C_c$), 110.22 ($C_l$), 109.70 ($C_m$), 110.61 ($C_n$) 128.29, 128.40 ($C_i$, $C_{j''}$) 128.55, 128.71 ($C_k$, $C_{k'}$) 135.91, 136.59 ($C_{i'}$, $C_j$) 139.55 141.86 ($C_h$, $C_{h'}$).

#### 3.1.2. Diphenyl[2-(4-Acetylaniline)methylferrocen-1-yl] stibine (**3**)

The compound was synthesized by a similar procedure to general synthesis p-amino acetaphenone was used for the reaction. The compound was crystallized in hexane. Yellow Solid (42%); Empirical formula: $C_{31}H_{28}$FeNOSb; m.p: 147–150 °C; IR($\nu$ cm$^{-1}$): 3404 (N–H), 3057 (C–H aromatic), 1595(C–O), 453 (Sb–C). FAB$^+$ *m/z* 607(8%) [M]$^+$, 592 (7%) [M–$CH_3$]$^+$, 473 (70%) [$FcCH_2SbPh_2$]$^+$, 397 (27%) [$FcCH_2SbPh$]$^+$, 275 (13%) [$SbPh_2$]$^+$; $^1$HNMR ($CDCl_3$, $\delta$ ppm) 2.47 (s, 3H, $CH_3$), 3.82 (m, 1H, $C_5H_3$), 3.94 (N–H), 4.01 (d$^2$, 1H, $J_{HH}$ = 4.95 Hz, $CH_2$), 4.09 (d$^2$, 1H, $J_{HH}$ = 4.95 Hz, $CH_2$), 4.15 (s, 5H, $C_5H_5$), 4.29 (t, 1H, $C_5H_3$), 4.45 (m, 1H, $C_5H_3$), 6.22 (d, 2H, H–Ar), 6.20–6.40 (m, 10H, Ph), 7.76 (d, 2H, H–Ar); $^{13}$C NMR ($CDCl_3$, ppm) 25.9 ($C_q$), 43.6 ($C_g$), 69.2 ($C_a$), 70.5 (C, $C_e$), 71.9 (C, $C_f$), 72.16 ($C_b$), 74.6 ($C_d$), 90.0 ($C_c$), 111.4 ($C_n$, $C_{n'}$), 126.9 ($C_o$), 128.5, 128.9 ($C_j$, $C_{j'}$, $C_k$, $C_{k'}$), 130.5 ($C_m$, $C_{m'}$), 135.9, 136.4 ($C_h$, $C_{h'}$), 136.6, 139.0 ($C_j$, $C_{j'}$), 151.2 ($C_l$), 196.2 ($C_p$).

#### 3.1.3. Diphenyl {2-[3-(1-hydroxyethyl)aniline]methylferrocen-1-yl}stibine (**4**)

3-(1-Hydroxyethyl)-aniline was used in place of p-aminoacetaphenone. Yellow Solid (35%); Empirical formula: $C_{31}H_{28}$FeNOSb; m.p: 86–88 °C; IR ($\nu$ cm$^{-1}$): 3384 (O–H) y (N–H), 3057 (C–H aromatic), 455 (Sb–C) FAB$^+$ *m/z* 609 (100%) [M]$^+$, 532 (5%) [M−Ph]$^+$, 473 (38%) [$FcCH_2SbPh_2$]$^+$, 397 (15%) [$FcCH_2SbPh$]$^+$, 275 (15%) [$SbPh_2$]$^+$; $^1$H NMR ($CDCl_3$, $\delta$ ppm) 1.44 (d, 3H, $CH_3$), 1.53 (s, 1H, NH), 3.77 (m, 1H, $C_5H_3$), 3.94 (d, 1H, $CH_2$), 3.86 (s, 5H, $C_5H_5$), 4.27 (m, 1H, $C_5H_3$), 4.46 (m, 1H, $C_5H_3$), 4.06 (m, 1H, $CH_2$), 4.74 (m, 1H, CH), 6.31 (m, 2H, H–Ar), 6.66 (m, 1H, H–Ar), 7.07 (m, 1H, H–Ar), 7.25–7.38 (m, 10H, Ph); $^{13}$C NMR ($CDCl_3$, ppm) 24.8 ($C_q$), 44.2 ($C_g$), 69.1 ($C_a$), 70.3 ($C_e$), 71.2 ($C_p$), 72.5 ($C_d$), 74.6 ($C_f$), 109.7 ($C_m$), 112.0 ($C_n$), 128.4, 129.8 ($C_{n'}$, $C_{n''}$, $C_k$, $C_{k'}$, $C_j$, $C_{j'}$), 135.7,136.7 ($C_i$, $C_{i'}$).

#### 3.1.4. Diphenyl[2-(4-hydroxypiperidin-1-yl)methylferrocen-1-yl] stibine (**5**)

4-Hydroxypiperidine was used for the reaction. Yellow Solid (20%); Empirical formula: $C_{28}H_{30}$FeNOSb; m.p: 126 °C (dec.); IR ($\nu$ cm$^{-1}$): 3476 (O–H), 3057 (C–H aromatic), 1428 (O–H), 1063 (C–O), 452 (Sb–C) FAB$^+$ *m/z* 573 (58%) [M]$^+$, 440 (50%) [M−56]$^+$, 397 (100%) [$FcCH_2SbPh$]$^+$, 275 (13%) [$SbPh_2$]$^+$; $^1$H NMR ($CDCl_3$, $\delta$ ppm) 1.20 (m, 4H, -$CH_2CH_2$), 1.40 (m, 1H, OH), 1.83–1.99 (m, 2H, $CH_2$), 2.43–2.63 (m, 2H, $CH_2$), 3.01 (d$^2$ $J_{HH}$, 12.9 Hz, 1H, $CH_2$N), 3.79 (d$^2$ 1H $J_{HH}$, 12.9 Hz,, $CH_2$N), 3.79 (m, 1H, $C_5H_3$), 3.39 (m, 1H, CH), 4.0 (s, 5H, $C_5H_5$), 4.20 (t, 1H, $C_5H_3$), 4.30 (m, 1H, $C_5H_3$), 7.25–7.31 (m, 5H, Ph), 7.45–7.56 (m, 5H, Ph); $^{13}$C NMR ($CDCl_3$, ppm) 33.2 ($C_m$), 34.0 ($C_{m'}$), 49.6 ($C_l$), 51.1 ($C_{l'}$), 58.7 ($C_g$), 67.8 ($C_p$), 69.1 ($C_a$), 69.5 ($C_f$), 72.3 ($C_d$), 72.3 ($C_b$), 74.1 ($C_e$), 90.5 ($C_c$), 128.0, 128.3 ($C_j$, $C_{j'}$,$C_k$, $C_{k'}$), 135.7, 136.6 ($C_i$, $C_{i'}$) 138.6, 140.4($C_h$, $C_{h'}$).

#### 3.1.5. Diphenyl[2-(4-ethylpiperazin-1-yl)methylferrocen-1-yl]stibine (**6**)

1-Ethylpiperazine was used for the reaction. Yellow Solid (44%); Empirical formula: $C_{28}H_{30}$FeNOSb; m.p: 140 °C (dec.); IR ($\nu$ cm$^{-1}$): 3058 (C–H aromatic), 455 (Sb–C); FAB$^+$ *m/z* 586 (98%) [M]$^+$, 473 (16%) [$FcCH_2SbPh_2$]$^+$, 397 (100%) [$FcCH_2SbPh$]$^+$, 275 (27%) [$SbPh_2$]$^+$; $^1$H NMR ($CDCl_3$, $\delta$ ppm) 0.91 (t, 3H, $CH_3$), 2.21 (q, 2H, $CH_2$), 2.26 (m, 8H, $C_4H_8N_2$), 3.01 (d$^2$ $J_{HH}$, 12.9 Hz, 1H, $CH_2$), 3.82 (d$^2$ $J_{HH}$, 12.6 Hz, 1H, C$H_2$), 3.78 (m, 1H, $C_5H_3$), 4.0 (s, 5H, $C_5H_5$), 4.20 (t, 1H, $C_5H_3$), 4.31 (m, 1H, $C_5H_3$), 7.25–7.32 (m, 5H, Ph), 7.44–7.56 (m, 5H, Ph) $^{13}$C NMR ($CDCl_3$, ppm) 11.6 ($C_{p)}$, 51.7 ($C_o$), 52.0 ($C_l$), 58.8 ($C_g$), 69.1 ($C_a$), 69.4 ($C_f$), 72.2 ($C_d$), 72.3 ($C_b$), 74.1 ($C_e$), 90.2 ($C_c$), 127.9, 128.2 ($C_j$, $C_{j'}$,$C_k$, $C_{k'}$), 135.8, 136.5 ($C_i$, $C_{i'}$), 139.2, 140.4 ($C_h$, $C_{h'}$).

#### 3.1.6. Diphenyl {2-[4-(4-bromophenyl)-4-hydroxypiperidin-1-yl] methylferrocen-1-yl}stibine (**7**)

4-(4-Bromophenyl)-4-hydroxypiperidine was used for the reaction. Yellow solid (31%); Empirical formula: $C_{34}H_{33}$BrFeNSb; m.p: 145 °C (dec.); IR ($\nu$ cm$^{-1}$): a 3455 cm$^{-1}$ (O–H), 3043 (C–H aromatic), 454 (Sb–C) FAB$^+$ *m/z* 728 (100%) [M]$^+$, 650 (16%) [M−Br], 473 (19%) [$FcCH_2SbPh_2$]$^+$, 397 (100%) [$FcCH_2SbPh$]$^+$, 275 (34%) [$SbPh_2$]$^+$; $^1$H NMR ($CDCl_3$, $\delta$ ppm) 1.2– 2.8 (m, 8H, $C_5H_8N$), 3.01 (m, 1H, $CH_2$), 3.80 (m, 1H, $C_5H_3$), 3.91 (d$^2$, 1H, $J_{HH}$ = 12.9 Hz, $CH_2$), 4.03 (s, 5H, $C_5H_5$), 4.21 (m, 1H, $C_5H_3$), 4.34 (m, 1H, $C_5H_3$), 6.92 (d, 2H, H–Ar), 7.56–7.31 (m, 12H); $^{13}$C NMR ($CDCl_3$, ppm) 36.8, 38.8 ($C_m$, $C_{m'}$), 46.8,50.3 ($C_l$, $C_{l'}$), 58.9 ($C_g$), 69.1 ($C_a$), 70.9 ($C_e$), 71.0 ($C_b$), 72.3 ($C_f$), 74.2 ($C_d$), 120.9 ($C_t$), 126.4 ($C_r$, $C_{r'}$), 130.9 ($C_s$, $C_{s'}$), 128.0, 128.5 ($C_j$, $C_{j'}$,$C_k$, $C_{k'}$), 135.5, 136.5 ($C_i$, $C_{i'}$).

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## Appendix A. Supplementary material

CCDC 698470, 698471, 698472 and 698473 contain the supplementary crystallographic data for compound (**2**), (**3**), (**5**) and (**7**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.07.019.

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