

Synthesis, Characterization and Crystal Structures of 1,2-Disubstituted Ferrocenyl Stibines

Diego Pérez^a, Pankaj Sharma^a, Ana M. Ortiz^a, Armando Cabrera^a, Simon Hernández^a, Alfredo Toscano^a, and René Gutiérrez^b

^a Instituto de Química, Universidad Nacional Autónoma de México, 04510, México D. F.

^b Facultad de Ciencias Químicas, Universidad Autónoma de Puebla, Puebla 72001, México

Reprint requests to Dr. Pankaj Sharma. Fax: 52-55-56162217. E-mail: pankajsh@servidor.unam.mx

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New 1,2-disubstituted ferrocenyl stibines containing a $-\text{CH}_2\text{OR}$ pendant arm were synthesized and characterized by various spectral and analytical methods. Nucleophilic substitution of *rac*-diphenyl[(2-trimethylammoniomethylferrocen-1-yl)]stibine iodide by methanol produces compound $\text{Fc}(\text{CH}_2\text{OMe})\text{SbPh}_2$ (**1**). The acetylation of diphenyl(2-dimethylaminomethylferrocen-1-yl)stibine by acetic anhydride affords compound $\text{Fc}(\text{CH}_2\text{OCOCH}_3)\text{SbPh}_2$ (**2**), which on further reaction with sodium hydroxide affords the alcohol $\text{Fc}(\text{CH}_2\text{OH})\text{SbPh}_2$ (**3**). The molecular structures of the stibines **1**, **2** and **3** were determined by X-ray crystallography. None of the heterobimetallic compounds containing a $-\text{CH}_2\text{OR}$ arm shows hypervalent interactions in the solid state. By contrast, hypervalent interactions were found in ferrocenyl stibines with a $-\text{CH}_2\text{NR}_2$ pendant arm.

Key words: 1,2-Disubstituted Ferrocene, Organoantimony, Stibine, X-Ray Structures

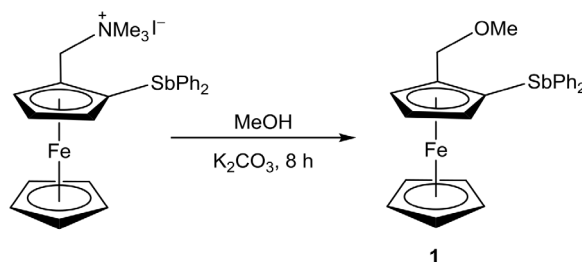
Introduction

Ferrocenyl ligands with one or more heteroatom donor centers are of interest because of their applications in enantioselective catalysis, rigid conformational behavior and planar chirality combination [1–7]. In this regard, 1,2-disubstituted ferrocenyl phosphines are well known compounds which are synthesized from *N,N*-dimethylaminomethylferrocene (Ugi amine) and have a number of industrial applications [8]. However, the number of reports decreases as we go from lighter to higher pnictogens, and there exist only a few examples of ferrocenyl stibines in the literature [9, 10]. Very recently our group has reported the synthesis of some 1,2-disubstituted ferrocenyl stibines, by nucleophilic substitution on quaternary ferrocenyl stibine ammonium salts with different primary amines and heterocyclic secondary amines [11], and some of these ferrocenyl stibines present Sb–N hypervalent interactions. Our group has also reported the synthesis of ether and thioether derivatives from quaternary ferrocenyl stibine ammonium salts by nucleophilic substitution with different phenols and thiols [12]. In these stibines, intramolecular Sb–O coordination was not observed. Considering the vast number of ferrocene ligands, the unique stereoelectronic properties of the ferrocene framework, the existence of very few reports on

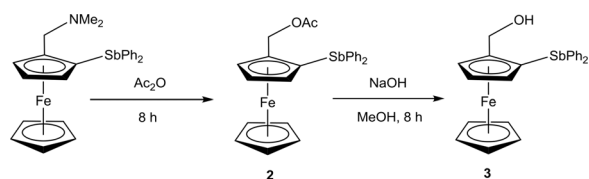
ferrocenes bonded to antimony atoms in the literature, and our interest in stibine ligands, this work was undertaken.

Results and Discussion

rac-diphenyl[(2-trimethylammoniomethylferrocen-1-yl)]stibine iodide and *rac*-diphenyl(2-dimethylaminomethylferrocen-1-yl)stibine were obtained as reported in the literature [11, 12]. Compound **1** was prepared by a nucleophilic attack of MeOH on the ammonium salt (Scheme 1), and compound **2** was synthesized by an acetylation of the amine. A subsequent saponification reaction of the acetate with 2 M NaOH in a methanol/THF mixture finally afforded compound **3** (Scheme 2).



Scheme 1. Synthetic route to compound **1**.

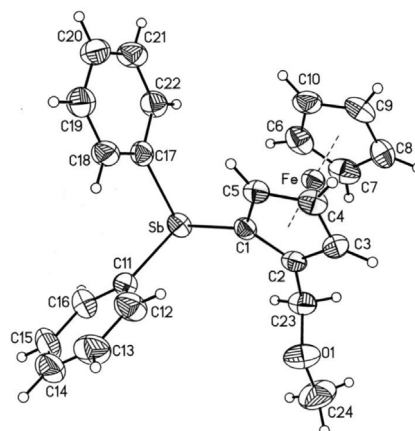
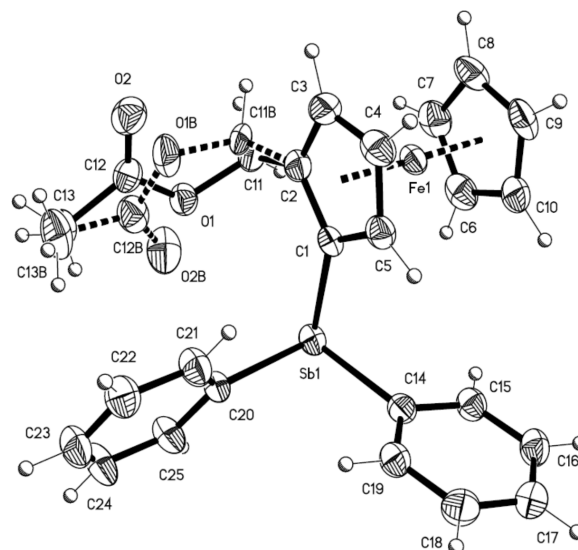
Scheme 2. Synthetic procedure for compounds **2** and **3**.

All three stibines **1–3** are air stable, melt without decomposition and are soluble in polar organic solvents, *e. g.* chloroform or dichloromethane, and are insoluble in water and show little solubility in non polar solvents, *e. g.* hexane or pentane.

For all three new compounds, in the (+)-FAB spectra molecular ion peaks were observed along with fragments corresponding to the successive loss of organic entities attached to the antimony atoms. The assignment of individual proton signals in the ^1H NMR spectra was based on signal integral values and confirmed by COSY and HETCOR experiments.

In the ^1H spectra a similar chemical shift pattern was observed for the ferrocene fraction and the phenyl rings. The methylene protons of the FcCH_2O moieties are not magnetically equivalent. This phenomenon has been observed in the ^1H NMR spectra of complexes containing both monodentate and bidentate 1,2-disubstituted ferrocenyl ligands as well [9–11, 13, 14]. The stereoheterotopic methylene protons give rise to two AB doublets. A singlet observed at *ca.* 4.1 ppm in the ^1H spectra of the stibines can be assigned to the unsubstituted Cp ring protons. Higher chemical shifts were observed for both aromatic and ferrocenyl protons adjacent to the Sb–C bond in all compounds in comparison to those of similar ferrocenyl phosphines [15]. Such higher chemical shifts are also observed in the ^{13}C NMR spectra with respect to phosphines.

Single crystals of compounds **1–3** were obtained by slow diffusion of hexane in chloroform solutions. The molecular structures of **1**, **2** and **3** have been confirmed by X-ray crystallography and are shown in Figs. 1–3. Crystal data for all structural analyses are given in Table 1. Selected bond lengths and angles for all compounds are listed in Table 2. Compounds **1** and **2** are monomeric in nature, and no significant inter- or intramolecular interactions were observed, while compound **3** presents hydrogen bonding interactions. It is worth noting that all compounds possess planar chirality as a consequence of the 1,2-disubstitution on the ferrocenyl Cp ring. Few other ferrocenyl stibines have previously been characterized by

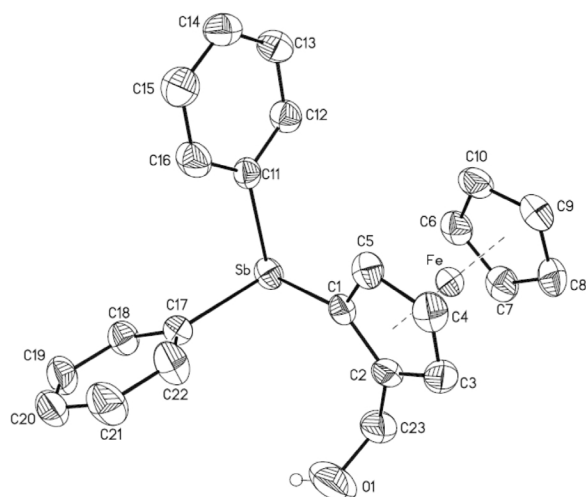
Fig. 1. ORTEP view of diphenyl(2-methoxymethylferrocenyl)stibine (**1**).Fig. 2. ORTEP view of diphenyl[(2-acetoxymethylferrocenyl)]stibine (**2**).

X-ray diffraction. The antimony atoms adopt distorted trigonal pyramidal structures without considering the lone pairs of electrons with bond angles at Sb smaller than 100° . compound **1** presents an average Sb–C bond length of 2.148(3) Å. The crystal structure of compound **2** presents disorder in the acetate fragment and was modeled in two major contributions. The average Sb–C bond length is 2.144(3) Å. Compound **3** also presents an Sb–C average bond length of 2.144(3) Å and shows hydrogen bonding with an $\text{H}(1\text{A})\cdots\text{O}(1)$ distance of 2.49 Å and an $\text{O}(1)\text{--H}(1\text{A})\cdots\text{O}(1)\#1$ angle of 126.9° . The average Sb–C_{ferrocenyl} bond length found in the ferrocenyl stibines is 2.126(3) Å, which

Compounds	1	2	3
Empirical formula	C ₂₄ H ₂₃ FeOSb	C ₂₅ H ₂₃ FeO ₂ Sb	C ₂₃ H ₂₁ FeOSb
Formula weight	505.02	533.03	491.00
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Crystal size, mm ³	0.34 × 0.22 × 0.18	0.244 × 0.158 × 0.152	0.22 × 0.10 × 0.04
<i>a</i> , Å	7.6488(13)	7.919(1)	7.4987(10)
<i>b</i> , Å	10.3899(17)	10.311(1)	10.4577(13)
<i>c</i> , Å	13.429(2)	13.440(1)	13.1717(17)
α , deg	76.262(2)	92.351(2)	70.984(2)
β , deg	88.746(2)	92.507(2)	82.760(2)
γ , deg	83.095(2)	95.767(2)	84.154(2)
<i>V</i> , Å ³	1029.1(3)	1089.7(2)	966.7(18)
<i>Z</i>	2	2	2
<i>D</i> _{calcd} , g cm ⁻³	1.63	1.62	1.69
μ (MoK α), cm ⁻¹	2.0	1.9	2.1
<i>F</i> (000), e	504	532	488
<i>hkl</i> range	±9, ±12, ±16	±9, ±12, ±16	-8 → 9, ±12, ±15
2 θ , deg	2.03–25.37	1.99–25.36	1.64–25.38
Refl.measured / unique / <i>R</i> _{int}	8536 / 5759 / 0.038	12117 / 3994 / 0.024	8025 / 3527 / 0.054
Param. refined	245	310	245
<i>R</i> (<i>F</i>) / <i>wR</i> (<i>F</i> ²) ^{a,b} (all refl.)	0.0347 / 0.0598	0.0308 / 0.0645	0.0319 / 0.0621
GoF(<i>F</i> ²) ^c	0.954	1.039	1.000
$\Delta\rho_{\text{fin}}$ (max / min), e Å ⁻³	0.47 / -0.36	0.52 / -0.24	0.78 / -0.48

Table 1. Crystallographic data for compounds **1–3**.

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$;
^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$,
 $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where
 $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$; ^c GoF =
 $[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

Fig. 3. ORTEP view of diphenyl[(2-hydroxymethylferrocenyl)]stibine (**3**).

is shorter than the average Sb–C_{phenyl} bond length of these compounds (2.156(3) Å) and is also slightly shorter than Sb–C_{phenyl} bond lengths in other tertiary stibines. A similar observation was reported earlier [11, 12]. This shortening of the Sb–C_{ferrocenyl} bond lengths is ascribed to the electron-donating ability of the ferrocenyl group [11].

In summary, three new 1,2-disubstituted ferrocenyl stibines containing a -CH₂OR pendant arm have been synthesized and characterized. Molecular structures of

Table 2. Selected bond lengths (Å) and angles (deg) for **1**, **2**, and **3** with estimated standard deviations in parentheses.

	1	2	3		
Sb–C1	2.130(3)	Sb–C1	2.123(3)	Sb–C1	2.125(3)
Sb–C11	2.157(3)	Sb–C14	2.157(3)	Sb–C11	2.153(3)
Sb–C17	2.159(3)	Sb–C20	2.153(3)	Sb–C17	2.154(3)
C2–C23	1.491(3)	C2–C11	1.500(5)	C2–C23	1.494(5)
C23–O1	1.391(4)	C2–C11B	1.498(6)	C23–O1	1.408(4)
O1–C24	1.429(4)	O1–C11	1.457(8)	C23–O1A	1.401(6)
C11–Sb–C17	96.3(1)	C1–Sb–C20	95.7(1)	C1–Sb–C11	94.2(1)
C1–Sb–C11	98.0(1)	C1–Sb–C14	94.4(1)	C1–Sb–C17	95.8(1)
C11–Sb–C17	96.3(1)	C20–Sb–C14	98.0(1)	C11–Sb–C17	97.2(1)

these ferrocenyl stibines **1**, **2** and **3** have been determined by X-ray crystallography. None of these heterobimetallic compounds possesses hypervalent interaction in the solid state. This type of interaction was found previously in similar compounds with -CH₂NR₂ pendant arms.

Experimental Section

General

All solvents were distilled immediately prior to use, and the reactions were performed under an atmosphere of oxygen-free dry nitrogen. Melting points were obtained on a MEL-TEMP II Fisher instrument and are uncorrected. (+)-FAB mass spectra were recorded on a Jeol SX102 double-focusing mass spectrometer with reverse geometry using a 6 kV xenon beam and nitrobenzyl alcohol as matrix. ¹H and ¹³C NMR spectra were recorded in CDCl₃

on a Jeol Eclipse 300 spectrometer (^1H : 300.5311 MHz; ^{13}C : 75.5757 MHz).

Diphenyl[(2-methoxymethylferrocen-1-yl)]stibine (1)

In a Schlenk tube, under N_2 , 10 mL of methanol was added to a mixture of 0.645 g (1 mmol) of *rac*-diphenyl[(2-trimethylammoniomethylferrocen-1-yl)]stibine iodide and 1.38 g (10 mmol) of K_2CO_3 in 5 mL of acetonitrile. After stirring for 8 h at 80 °C the solvent was evaporated, and the mixture was extracted with chloroform and dried with anhydrous Na_2SO_4 . Compound **1** was obtained as orange-yellow crystals after recrystallization from a chloroform/hexane mixture. Yield: 38%. – IR (film): $\nu = 3048$ (C–H aromatic), 1261 (C–O), 1093–1020 (C–O–C), 455 cm^{-1} (Sb–C). – ^1H NMR (300 MHz, CDCl_3 , ppm): $\delta = 4.55$ (s, 1 H, CH, C_3H_5), 4.16, 4.37 (AB, 2 H, $J = 10.6$ Hz, CH_2), 7.25–7.56 (m, 10 H, Ph), 4.04 (s, 5 H, C_5H_5); 3.14 (s, 3 H, OCH_3). – ^{13}C NMR (75 MHz, CDCl_3): $\delta = 57.7$ (OCH_3), 69.1 (C_5H_5), 70.7 (CH_2), 71 ($\text{C}_{\text{Fc-Sb}}$), 71.3 (C_{Fc}), 72.0 (C_{Fc}), 74.6 (C_{Fc}), 89.5 ($\text{C}_{\text{Fc-O}}$), 128.1 (C_{Ph}), 128.6 (C_{Ph}), 136.9 (C_{Ph}), 139.8 ($\text{C}_{\text{Ph-Sb}}$). – MS ((+)-FAB): m/z (%) = 504 (100) $[\text{M}]^+$, 473 (100) $[\text{M}-\text{CH}_3\text{O}]^+$, 427 (10) $[\text{M}-\text{C}_6\text{H}_5]^+$, 275 (10) $[\text{SbPh}_2]^+$. – Elemental analysis (%): calcd. C 57.06, H 4.59; found C 56.87, H 4.48.

Diphenyl[(2-acetoxymethylferrocen-1-yl)]stibine (2)

In a Schlenk tube, under N_2 , 7 mL of acetic anhydride was added to a mixture of 0.516 g (1 mmol) of *rac*-diphenyl-(*N,N*-dimethylaminomethylferrocenyl)stibine and 15 mL of CHCl_3 . After stirring for 8 h at 80 °C the solvent was evaporated, and the mixture was extracted with chloroform and dried with anhydrous Na_2SO_4 . compound **2** was obtained as yellow crystals after recrystallization from a chloroform/hexane mixture. Yield: 89%. – IR film: $\nu = 3043$ (C–H aromatic), 1730 (C=O), 1220–1060 (C–O), 454 (Sb–C) cm^{-1} . – ^1H NMR (300 MHz, CDCl_3): $\delta = 3.15$ (s, 3 H, COCH_3), 3.78 (1 H, d, CH, C_3H_5), 4.10 (s, 5 H, C_5H_5), 4.31 (1 H, t, CH, C_3H_5), 4.49 (1 H, d (broad), CH, C_3H_5), 4.93, 5.05 (AB, 2 H, $J = 10.4$ Hz, CH_2), 7.26–7.39 (m, 10 H, Ph). – ^{13}C NMR (75 MHz, CDCl_3): $\delta = 87.21$ ($\text{C}_{\text{Fc-Sb}}$), 75.34 ($\text{C}_{\text{Fc-CH}_2\text{OAc}}$), 73.28 (C_{Fc}), 71.31 (C_{Fc}), 63.52 (C_{Fc}), 69.17 (C_5H_5), 136.76 ($\text{C}_{\text{Ph-Sb}}$), 135.91 (C_{Ph}), 128.69 (C_{Ph}), 128.31 (C_{Ph}), 63.52 (CH_2), 166.50 (OC). – MS ((+)-FAB):

m/z (%) = 533 (100%) $[\text{M}]^+$, 473 (24) $[\text{M}-\text{C}_2\text{H}_3\text{O}_2]^+$, 275 (10) $[\text{SbPh}_2]^+$. – Elemental analyses (%): calcd. C 56.31, H 4.35; found C 56.03, H 4.22.

Diphenyl[(2-hydroxymethylferrocen-1-yl)]stibine (3)

In a Schlenk tube, under N_2 , 10 mL of an aqueous NaOH solution (2 M) was added to a solution of 0.533 g (1 mmol) of compound **2** in 2 mL of methanol and 15 mL of THF. After stirring for 6 h at 80 °C the solvents were evaporated, and the mixture was extracted with chloroform and dried with anhydrous Na_2SO_4 . Compound **3** was obtained as yellow crystals after recrystallization from a chloroform/hexane mixture. Yield: 78%. – IR film: $\nu = 3049$ (C–H aromatic), 3464 (C–O), 1214 (C–O), 451 (Sb–C) cm^{-1} . – ^1H NMR (300 MHz, CDCl_3): $\delta = 1.44$ (s, 1 H, OH), 4.02 (t, 1 H, CH, C_3H_5), 4.10 (s, 5 H, C_5H_5), 4.29 (d, 1 H, CH, C_3H_5), 4.39 (broad, 1 H, CH, C_3H_5), 4.34, 4.45 (AB, 2 H, $J = 10.7$ Hz, CH_2), 7.29–7.36 (m, 10 H, Ph). – ^{13}C NMR (75 MHz, CDCl_3): $\delta = 63.52$ (CH_2), 74.7 ($\text{C}_{\text{Fc-CH}_2\text{OH}}$), 61.57 (C_{Fc}), 68.37 (C_5H_5), 70.92 (C_{Fc}), 71.38 (C_{Fc}), 93.19 ($\text{C}_{\text{Fc-Sb}}$), 137.17 ($\text{C}_{\text{Ph-Sb}}$), 136.71 (C_{Ph}), 135.92 (C_{Ph}), 128.74 (C_{Ph}), 166.50 (OC). – MS (EI, 70 eV): m/z (%) = 490 (100) $[\text{M}]^+$, 472 (2) $[\text{M}-\text{H}_2\text{O}]^+$, 413 (6) $[\text{M}-\text{C}_6\text{H}_5]^+$, 394 (26) $[\text{M}-\text{H}_2\text{O}-\text{C}_6\text{H}_5]^+$, 275 (10) $[\text{SbPh}_2]^+$. – Elemental analyses (%): calcd. C 56.24, H 4.31; found C 57.03, H 4.18.

Crystal structure determinations

The X-ray intensity data were measured at 293 K on a Bruker SMART APEX CCD-based X-ray diffractometer by using monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). The detector was placed at a distance of 4.837 cm from the crystals in all cases. Empirical absorption corrections were applied. The program SHELXTL (version 6.12) was used for all calculations.

CCDC 806069–806071 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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