with the results summarized in Table III.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the Ministry of Colleges and Universities of Ontario, and Nova/Polysar Ltd. for financial support of this work.

Supplementary Material Available: Complete lists of bond lengths and angles and tables of H atom coordinates and isotropic thermal parameters and heavy-atom anisotropic thermal parameters for compound 4 (5 pages); a table of structure factors for compound 4 (12 pages). Ordering information is given on any current masthead page.

Notes

Molecular and Crystal Structure of 2,2′,5,5′-Tetramethyl-1,1′-distibaferrocene: A Short Sb···Sb Inter-Ring Contact

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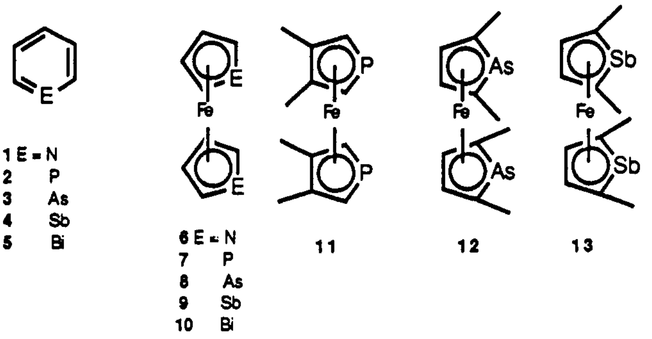
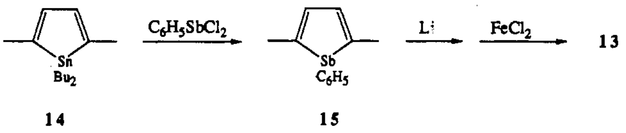
Summary: 2,2′,5,5′-Tetramethyl-1,1′-distibaferrocene (**13**) was obtained from the reaction of 1-phenyl-2,5-dimethylstibole with lithium followed by $FeCl_2$. Red crystals of **13** form in Pc space group with $Z = 2$, $a = 6.811$ (1) Å, $b = 11.336$ (3) Å, $c = 8.918$ (3) Å, and $\beta = 102.80$ (2)°. The full structure has been determined and shows a ferrocene-like arrangement with a close (3.68 Å) inter-ring Sb···Sb contact.

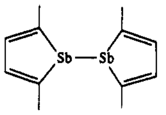
The group 15 heterobenzenes 1–5 are an important series in which elements of an entire column of the periodic table have been incorporated into aromatic rings.[1-3] The comparison of properties, particularly structural properties,[4-6] of 1–5 has provided insight into the concepts of aromaticity and π-bonding between carbon and the heavier main-group elements.[1-3] The group 15 diheteroferrocenes 6–10 form a similar series that can be compared with the heterobenzenes. Derivatives of 6,[7] 7,[8-10] 8,[8,11-13] and 9[8,14] have been reported. Prior structural data are available for 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (11)[9] and 2,2′,5,5′-tetramethyl-1,1′-diarsaferrocene (12).[12] We report here on the crystal and molecular structure of 2,2′,5,5′-tetramethyl-1,1′-distibaferrocene (13).



Results and Discussion

Compound 13 was prepared by a route modified compared to that previously reported.[14] The exchange reaction of phenylantimony dichloride with 1,1-dibutyl-2,5-dimethylstannole (14) gave a 63% yield of 1-phenyl-2,5-di-





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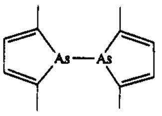

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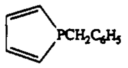

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[†] University of Michigan.

[‡] Mu'tah University.

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Table I. Summary of Crystallographic Data for 13

Crystal Data	
empirical formula	$C_{12}H_{16}FeSb_2$
fw	459.60_8
cryst color and habit	deep red irregular fragment
cryst dimens	0.20 × 0.42 × 0.30 mm
cryst system	monoclinic
space group	*Pc* (No. 7)[a]
Z	2
unit cell dimens from 25 reflcns ($22.8° \le 2\theta \le 38.5°$)	
a	6.811 (1) Å
b	11.336 (3) Å
c	8.918 (3) Å
β	102.80 (2)°
V	671.4 (3) $Å^3$
d (calcd)	2.27_3 g cm^{-3}
F(000)	432 electrons
linear abs coeff (*μ*)	50.56 cm^{-1}
Data Collection	
diffractometer	Syntex $P2_1$
radiation type	Mo Kα, λ = 0.710 73 Å, *Lp* corrected, graphite monochromator
temp	ambient
scan type	$\theta/2\theta$ scan
2θ scan range	5–52°
octants used	$+h,+k,\pm l$ (h, 0/9; k, 0/14; l, $\overline{12}$/12) plus Friedel pairs
scan rate	1.5–5° min^{-1}, variable
scan width	1.0° below Kα_1 to 1.0° above Kα_2
bkgd/scan ratio	0.5
std reflcns	3 measd every 100 reflcns, linear decay ~3%
no. of data collcd	3153
no. of unique reflcns	2651, R_{int} = 0.0741
abs cor	empirical, ψ scans
R merge before/after cor	0.0515/0.0300
max/min transm	0.236/0.199
Solution and Refinement	
syst used	Siemens SHELXTL PLUS, VAXStation 3500
solution	Patterson
refinement method	full-matrix least-squares
function minimized	$\sum w(F_o - F_c)^2$
H atoms	riding model, d_{C-H} = 0.96 Å, common isotropic *U*(H) refined to 0.12 (2) $Å^2$
no. of refined reflcns with $F_o \ge 0.6\sigma(F)$	2645
no. of params refined	136
data/param ratio	19.4
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.0399
$R_w = [\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum w\lvert F_o\rvert^2]^{1/2}$ ($w^{-1} = \sigma^2(F_o) + 0.003431(F_o)^2$)	0.0530
GOF	0.90
mean shift/error	<0.001
max shift/error	0.001
secondary extinction	3.1 (4) × 10^{-7}
resid electron dens	+3.90/−2.03 e/$Å^3$ near Sb1 and Sb2

[a] Choice of space group was based on the strongly acentric intensity distribution as well as the failure to find a chemically reasonable solution in the centric alternative *P*2/*c*.

Table II. Positional Parameters and Isotopic Equivalent Thermal Parameters for 13[a]

atom	*x*	*y*	*z*	*U*(eq), Å
Sb1	0.00000	0.05462 (4)	0.00000	0.0511 (2)
C1	0.034 (1)	0.2012 (7)	−0.1437 (8)	0.054 (2)
C2	0.236 (2)	0.2374 (8)	−0.1192 (9)	0.059 (3)
C3	0.378 (1)	0.1831 (6)	0.0028 (9)	0.047 (2)
C4	0.305 (1)	0.0976 (5)	0.0865 (8)	0.041 (2)
C5	−0.133 (2)	0.246 (1)	−0.267 (1)	0.085 (4)
C6	0.443 (1)	0.0331 (8)	0.214 (1)	0.063 (3)
Sb2	−0.07426 (9)	0.27938 (4)	0.28027 (7)	0.0444 (2)
C7	0.238 (1)	0.3097 (6)	0.3215 (7)	0.039 (2)
C8	0.291 (1)	0.3964 (7)	0.2220 (8)	0.047 (2)
C9	0.133 (1)	0.4418 (5)	0.102 (1)	0.054 (3)
C10	−0.062 (1)	0.3957 (5)	0.0990 (9)	0.043 (2)
C11	0.388 (1)	0.256 (1)	0.453 (1)	0.061 (3)
C12	−0.242 (2)	0.4391 (7)	−0.019 (1)	0.067 (3)
Fe1	0.1477 (2)	0.25925 (7)	0.0850 (1)	0.0329 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, *U*(eq), defined as one-third of the trace of the orthogonalized U_{ij} tensor: $U(eq) = {}^1/_3 \sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

Table III. Bond and Selected Non-Bonded Distances (Å) for 13

Bond Distances			
Sb1–C1	2.141 (7)	Sb2–C7	2.106 (7)
Sb1–C4	2.108 (7)	Sb2–C10	2.102 (6)
Sb1–Fe1	2.5748 (9)	Sb2–Fe1	2.557 (1)
C1–C2	1.41 (1)	C7–C8	1.423 (9)
C1–C5	1.48 (2)	C7–C11	1.50 (1)
C1–Fe1	2.120 (6)	C7–Fe1	2.140 (5)
C2–C3	1.43 (1)	C8–C9	1.43 (1)
C2–Fe1	2.054 (7)	C8–Fe1	2.082 (7)
C3–C4	1.379 (9)	C9–C10	1.43 (1)
C3–Fe1	2.059 (7)	C9–Fe1	2.080 (6)
C4–C6	1.49 (1)	C10–C12	1.51 (1)
C4–Fe1	2.122 (6)	C10–Fe1	2.129 (6)
Inter-Ring Distances			
Sb1–Sb2	3.682 (1)	C6–C11	3.379 (11)
C5–C12	3.314 (11)		

Table IV. Selected Bond Angles (deg) for 13

Sb1–C1–C2	111.4 (6)	Sb2–C7–C8	112.9 (4)
Sb1–C1–C5	123.0 (8)	Sb2–C7–C11	123.8 (5)
Sb1–C4–C3	114.0 (5)	Sb2–C10–C9	114.2 (5)
Sb1–C4–C6	124.5 (5)	Sb2–C10–C12	125.1 (6)
C1–Sb1–C4	79.2 (3)	C7–Sb2–C10	79.7 (2)
C1–C2–C3	117.9 (7)	C7–C8–C9	117.4 (6)
C2–C3–C4	116.9 (7)	C8–C7–C11	122.9 (6)
C2–C1–C5	125.2 (8)	C8–C9–C10	115.3 (6)
C3–C4–C6	121.1 (7)	C9–C10–C12	120.5 (6)

methylstibole (15). Phenyl cleavage of 15 with lithium in THF at 25 °C gave a deep red solution of (2,5-dimethylstibolyl)lithium, which on reaction with $FeCl_2$ at −78 °C afforded a 50% yield of 13. The low-temperature reaction gives 13 uncontaminated with the coupling product 2,2′,5,5′-tetramethylbistibole (16),[15] which is a major product if the reaction is performed at 25 °C.[14]

Crystals of 13 suitable for X-ray diffraction were obtained by recrystallization from acetonitrile. Crystal data and data collection and refinement parameters are summarized in Table I. An ORTEP plot of the molecular structure of 13 that shows the numbering used in the refinement is illustrated in Figure 1. Table II gives the positional values, while Table III and IV give the more important distances and the bond angles for the non-hydrogen atoms. Table VI, a list of observed and calculated structure factors, is available in the supplementary material.

The molecular structure illustrated in Figure 1 show that 13 has a ferrocene-like arrangement. The iron atom is sandwiched between the two η^5-dimethylstibolyl rings, which are completely eclipsed. The structure closely resembles that of its arsenic analogue 12,[12] although the diphosphaferrocene 11 crystalizes in a different eclipsed conformation.[9] Structures 11 and 12 serve as useful comparison for 13. Relevant structural parameters of 11–13 and related compounds are collected in Table V.

The iron atom of 13 is π-bonded to all five atoms of each ring, although it is slightly closer to the β-carbons

Table V. Comparison of Selected Structural Parameters of Antimony, Arsenic, and Phosphorus Heterobenzenes, 1,1′-Diheteroferrocenes, and 1-Heteroles

compd	E	$d(EC_\alpha)$, Å	$d(C_\alpha C_\beta)$, Å	$d(C_\beta C_\gamma)$,^{a} Å	d(E out of ring plane), Å	$\angle C_\alpha EC_\alpha$, deg	ref
			Heterobenzenes, C_5H_5E				
4	Sb	2.05	1.40	1.39	0	93	6
3	As	1.85	1.39	1.40	0	97	5
2	P	1.73	1.41	1.38	0	101	4
			Tetramethyl-1,1′-diheteroferrocenes, $(C_4H_2Me_2E)_2Fe$				
13	Sb	2.11	1.41	1.43	0.21	79.5	this work
12	As	1.90	1.40	1.42	0.07	85.8	12
11	P	1.76	1.42	1.42	0.02	88.2	9
			1-Heteroles, (C_4R_4EX)				
16	Sb	2.14	1.32	1.46	0.08	81.5	15
17	As	1.94	1.34	1.44	0.17	87.1	16
18	P	1.78	1.34	1.44	0.21	90.7	17

^{a} $C_\beta C_\gamma = C_3C_4$ of **11–13** and **16–18**.

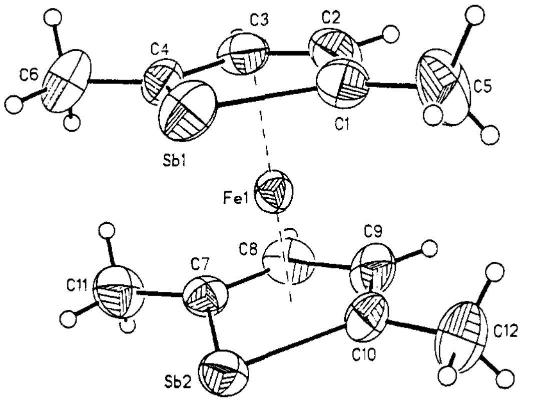
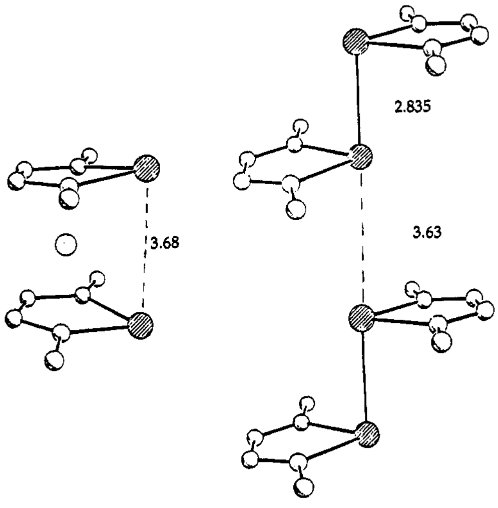


Figure 1. ORTEP drawing of the solid-state structure of 2,2′,5,5′-tetramethyl-1,1′-distibaferrocene (**13**), with thermal ellipsoids at the 50% probability level.

(2.05–2.08 Å) than to the α-carbons (2.08–2.14 Å), while the Sb–Fe distances are greater yet (2.56, 2.57 Å). The four carbon atoms of each stibolyl ring lie in parallel planes, while the antimony atoms are displaced away from the iron outside these planes by 0.21 Å each. The displacement of the pnictogen atom away from iron is similar but larger than that found for **12**, which in turn is greater than that for **11**. The increasing distortion in the ring series of Sb > As > P appears to be a consequence of accommodating the Fe π-bonding to the increasing size of the pnictogen atoms. It might be noted that, in the uncomplexed heterole rings **16**,[15] **17**,[16] and **18**,[17] the corresponding distortions from planarity decrease in the ring series Sb < As < P.

The intra-ring C–C bond distances of **13** (1.41–1.43 Å) are not significantly different. In contrast, the uncomplexed dimethylstibolyl rings of the nonaromatic **16** show a marked variation of single (1.46 Å) and double bonds (1.32 Å).[15] The SbC bonds (2.11 Å) of **13** are slightly shorter than those (2.14 Å) of **16**, although not as short as those of the uncomplexed aromatic stibabenzene **4** (2.05 Å).[6] Thus the intra-ring bond distances of **13** show that stibolyl groups are π-complexed heteroaromatic rings. This conforms to the pattern previously found for **11**[8] and **12**.[12]

The eclipsed conformation adopted by **13** is rather surprising, since there are very short separations between equivalent groups. The nonbonded Me⋯Me distance of 3.3 Å is likely to be repulsive.[18] The Sb⋯Sb separation of 3.68 Å is significantly shorter than van der Waals radius separation of 4.4 Å. Therefore, it seems likely that there is a direct inter-ring Sb⋯Sb bond.



13 16

Figure 2. Comparison of the inter-ring distance (Å) in **13** with the intermolecular Sb⋯Sb interaction in **16**.[15]

The π-bonding of the stibolyl rings and small value of the CSbC bond angle (79.5°) imply that antimony uses primarily p orbitals in bonding and the lone pair is essentially s hybridized. The Sb$_{p_z}$ orbitals should be directly aligned. The inter-ring Sb(5p_z)Sb(5p_z) overlap intergal of **13** is 0.168, which compares with the overlap intergal of 0.37 for a normal Sb–Sb σ bond at 2.83 Å.[19] Thus, appreciable bonding is possible.

It is particularly interesting to compare the juxtaposition of the two antimony atoms of **13** with the intermolecular Sb⋯Sb arrangement found in crystalline **16** (see Figure 2). The close intermolecular contacts found in **16**[15,20] and other distibines[21] indicate secondary intermolecular bonding. It is probably significant that the inter-ring Sb⋯Sb distance

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[18] Polymethylferrocenes have adopted staggered conformations: Schmitz, D.; Fleischhauer, J.; Meier, U.; Schleker, W.; Schmitt, G. *J. Organomet. Chem.* **1981**, *205*, 381.

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of **13** is virtually identical with the intermolecular Sb···Sb distance in **16**. A similar secondary bonding is likely.[22] We feel that a more detailed investigation of this phenomenon is desirable.

Experimental Section

General Data. All operations were performed under an atmosphere of nitrogen or argon. The NMR spectra were recorded on a Bruker AM 300 spectrometer. The mass spectra were determined by using a Finnigan 4023 GC/MS. The combustion analyses were determined by the Spang Miroanalytical Laboratory, Eagle Harbor, MI.

1-Phenyl-2,5-dimethylstibole (15). A solution of 3.5 g (13.0 mmol) of phenylantimony dichloride in 15 mL of tetrahydrofuran was added dropwise with stirring to 2.5 g (8.3 mmol) of 1,1-dibutyl-2,5-dimethylstannole in 20 mL of tetrahydrofuran. After being stirred at 25 °C for 1 h, the reaction mixture was added to 50 mL of 10% KF in 50% aqueous ethanol. After extraction with 20 mL of pentane, the extracts were washed with 3 × 50 mL of KF solution, separated, and dried over anhydrous magnesium sulfate. Distillation gave 1.45 g (63%) of product as light yellow oil, bp 68 °C (0.05 Torr). ^{1}H NMR ($CDCl_3$): δ 2.13 (s, 6 H), 6.79 (s, 2 H), 7.3–7.5 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 21.9 (CH_3), 128.3, 128.7, 135.5 (C_6H_5), 141.6 (*CH*), 154.5 (*SbC*). MS: *m/e* 280 (M^+ for $C_{12}H_{13}{}^{123}Sb$). Anal. Calcd for $C_{12}H_{13}Sb$: C, 51.66; H, 4.70. Found: C, 51.64; H, 4.75.

2,2′,5,5′-Tetramethyl-1,1′-distibaferrocene (13). Lithium wire (0.25 g, 36 mmol) was cut into pieces approximately 2 mm in diameter and placed in 25 mL of tetrahydrofuran. 1-Phenyl-2,5-dimethylstibole (0.5 g, 1.79 mmol) was added. After the mixture was stirred at 25 °C for 3 h, the color had changed to deep red. The solution was decanted from the excess lithium, cooled to −78 °C, and added to $FeCl_2$ (0.45 g, 3.6 mmol) in 10 mL of tetrahydrofuran at −78 °C. After the mixture was stirred for 2 h at −78 °C, followed by 12 h at 25 °C, the solvent was evaporated. The black-red residue was extracted with toluene to give a red solution. Evaporation of the solvent left a dark red oil, which was recrystallized from acetonitrile to give 400 mg (50%) of red crystals, mp 85–87 °C. ^{1}H NMR (C_6D_6): δ 1.72 (s, 12 H); 5.40 (s, 4 H). ^{13}C NMR (C_6D_6): δ 23.0 (CH_3), 93.5 (CH), 113.6 (CSb). MS: *m/e* 462 (M^+ for $C_{12}H_{16}{}^{123}Sb_2Fe$). UV ($C_6H_{12}$) [$\lambda$, nm ($\epsilon$)]: 490 (300), 388 sh (2000), 324 (7200), 260 (10800), 220 (19500). Anal. Calcd for $C_{12}H_{16}Sb_2Fe$: C, 31.36; H, 3.51. Found: C, 31.33; H, 3.52.

Acknowledgment. We are grateful to the Research Corp. for the partial support of this work.

Supplementary Material Available: Table VII, listing hydrogen atomic parameters for **13**, and Figure 3, showing a crystal packing diagram for **13** (2 pages); Table VI, listing observed and calculated structure factors for **13** (10 pages). Ordering information is given on any current masthead page.

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[22] Prior theoretical work suggests that secondary bonding can take place with π-bonded antimony. See: Canadell, E.; Shaik, S. S. *Inorg. Chem.* **1987**, *26*, 3797.