4-Butyl-2-pentyl-1,5-hexadiene (13). Spectral data: ^{1}H NMR ($CDCl_3$) δ 0.88 (6 H, CH_3R), 1.26 (12 H, CH_2), 2.01 (5 H, CH_2—C=C, CH—C=C), 4.62 (4 H, CH_2=C), 5.1-5.8 (1 H, CH=C).

(*Z*,*Z*)-6-Methyl-6,8-tetradecadiene (14) and (*E*,*Z*)-6-Methyl-6,8-tetradecadiene (15). These isomeric dienes were partially resolved by GC but had retention times that precluded isolation by GC. Spectral data: ^{1}H NMR ($CDCl_3$) δ 0.97 (6 H, CH_3R), 1.27 (12 H, CH_2), 1.77 (3 H, CH_3C=C), 2.07 (4 H, CH_2C=C), 5.08-5.98 (3 H, C=CH—CH=CH).

(*Z*)-3-Butyl-2-pentyl-1,4-hexadiene (16). Spectral data: ^{1}H NMR ($CDCl_3$) δ 0.91 (6 H, CH_3R), 1.33 (12 H, CH_2), 1.64 (3 H, CH_3C=C), 2.01 (2 H, CH_2C=C), 2.95 (1 H, C=C—CH—C=C), 4.81 (2 H, CH_2=C), 5.05-5.85 (2 H, HC=CH).

5-Pentyl-2,4-decadiene (17). Spectral data: ^{1}H NMR ($CDCl_3$) δ 0.89 (6 H, CH_3R), 1.28 (12 H, CH_2), 1.74 (3 H, CH_3C=C), 2.09 (4 H, CH_2C=C), 5.16-5.97 (3 H, C=CHCH=CH).

(*E*)-5-Methyl-2-pentyl-1,3-nonadiene (18). Spectral data: ^{1}H NMR ($CDCl_3$) δ 0.94 (6 H, CH_3R), 1.22 (12 H, CH_2), 2.09 (3 H, CH_2C=C, CHC=C), 4.73 (2 H, CH_2=C), 5.31-6.04 (2 H, C=CCH=CH).

Acknowledgment. Grateful acknowledgement is made to the Robert A. Welch Foundation (Grant W-794) for support of this work.

Registry No. 3, 4049-81-4; **3** dianion, 82865-66-5; **9**, 82865-74-5; **10**, 82865-75-6; **11**, 82865-67-6; **12**, 82865-68-7; **13**, 82865-69-8; **14**, 82865-70-1; **16**, 82865-71-2; **17**, 82865-72-3; **18**, 82865-73-4; **19**, 82865-76-7; **21**, 82865-77-8.

Stabilization of Stibabenzene and Bismabenzene by 4-Alkyl Substituents[1]

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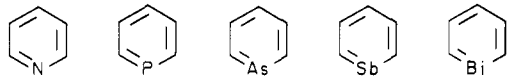
Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109. *Received February 26, 1982*

Abstract: Stibabenzenes and bismabenzenes are readily prepared by dehydrohalogenation of 1-chlorostibacyclohexa-2,5-dienes and 1-chlorobismacyclohexa-2,5-dienes, respectively. 4-Alkyl-substituted derivatives **16** and **19** are markedly more stable toward polymerization than the parent compounds. Stibabenzene, bismabenzene, and 4-methylbismabenzene are in mobile equilibrium with their head-to-head Diels-Alder dimers. The ^{1}H NMR spectra of stibabenzenes and bismabenzenes show very low field signals for the α-protons due to very large diamagnetic anisotropies of the Sb and Bi atoms.

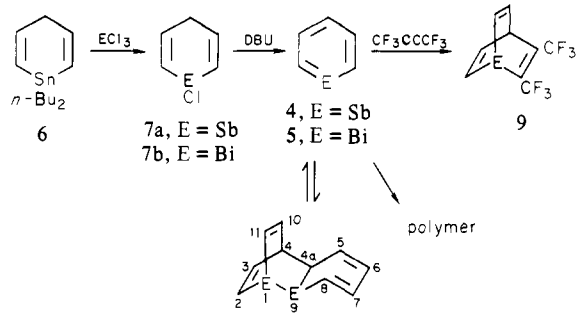
Pyridine (**1**) and its heavier homologues **2-5** comprise a unique



1 **2** **3** **4** **5**

series in which elements of an entire column of the periodic table have been incorporated into aromatic rings. This series is of considerable interest for the study of aromaticity and heavier element-carbon π bonding. Detailed investigations of phosphabenzene (**2**)[2-7] and arsabenzene (**3**)[4-8] have shown that they display a high degree of aromatic character. On the other hand, stibabenzene (antimonin, **4**) and bismabenzene (bismin, **5**) have been subjected to much less work. We have made only preliminary reports of their synthesis[9-11] and spectra.[12-14] We now wish to record in detail our observations on stibabenzene and bismabenzene.

Stibabenzene. The ease with which vinyltin compounds undergo exchange reactions with main group element halides[15] makes stannacyclohexadienes excellent precursors for antimony and bismuth heterocycles. Thus the reaction of 1,1-dibutylstannacyclohexa-2,5-diene (**6**) with a tetrahydrofuran solution of an-



6 7a, E = Sb; 7b, E = Bi 4, E = Sb; 5, E = Bi **9**

10

timony trichloride gave a mixture of dibutyltin dichloride and 1-chlorostibacyclohexa-2,5-diene (**7a**). Pure **7a** may be obtained by recrystallization from pentane. The reaction of a tetrahydrofuran solution of **7a** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) affords stibabenzene (**4**), which may be codistilled with tetrahydrofuran from the hydrochloride of the base. It is particularly convenient to treat a tetraglyme solution of the crude

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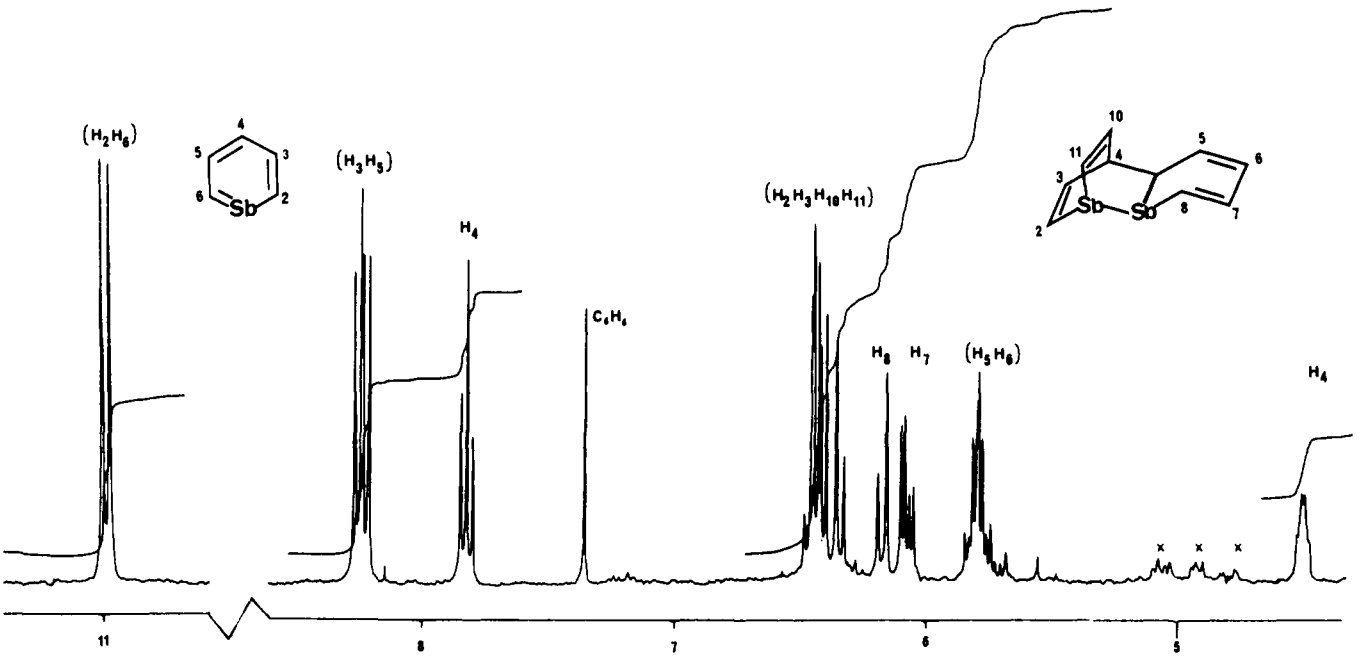


Figure 1. Low-field portion of the 360-MHz proton NMR spectrum of stibabenzene and its dimer. The spectrum was recorded in tetrahydrofuran-d_8 at −70 °C. Peak assignments are indicated while peaks for unidentified impurities are noted by ×.

mixture of dibutyltin dichloride and **7a** directly with DBU. Vacuum distillation affords pure stibabenzene as a pale yellow-green oil.

While stibabenzene may be readily characterized spectroscopically, it is a very labile material. On standing at 25 °C for a few minutes, it polymerizes to a resinous yellow solid that is insoluble in organic solvents. On exposure to oxygen, it immediately forms an intractable yellow tar. Stibabenzene readily reacts with hexafluorobutyne at 0 °C to give 1,4 Diels–Alder adduct **9a**.

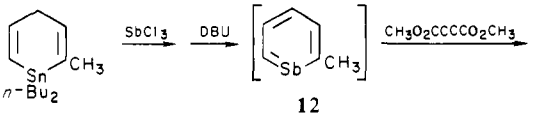
When stibabenzene is cooled to −40 °C in a tetrahydrofuran-d_8 solution, it reversibly forms Diels–Alder dimer **10a**. By CA and IUPAC rules, compound **10a** is named 4,4a-dihydro-1,4-etheno-1*H*-antimonino[1,2-*b*][1,2]diantimonin, with numbering as shown. This dimer shows a closely spaced ^{1}H NMR spectrum with absorption of the eight nonequivalent vinyl protons between δ 5.8 and 6.5 (see Figure 1). This spectrum could be assigned by analysis of the partially decoupled 360-MHz spectra and by comparison with the ^{1}H NMR spectrum of the dimer obtained for stibabenzene-*3,5-d*$_2$. Proton assignments were made as follows. The doublet (J = 12 Hz) at δ 6.15 assigned to H_8 was coupled to the doublet of doublets (J = 12, 5 Hz) at δ 6.06 assigned to H_7. Irradiation at δ 6.06 collapsed the multiplet at δ 5.80 to a doublet (J = 11 Hz) at δ 5.95 assigned to H_6 and a doublet of doublets (J = 11, 5 Hz) at δ 5.82 assigned to H_5. The high-field triplet (J = 5 Hz) at δ 2.82 was assigned to H_{4a}, while the multiplet at δ 4.57 was assigned to the diallylic bridgehead proton H_4. Irradiation at δ 4.57 caused the δ 2.82 signal to collapse to a doublet (J = 5 Hz) and the complex four-proton multiplet centered at δ 6.35 to collapse to two overlapping AB patterns (J = 11.5 Hz). Thus the δ 6.35 signal was assigned to H_2, H_3, H_{11}, and H_{10}.

Bismabenzene. The reaction of 1,1-dibutylstannacyclohexa-2,5-diene with bismuth trichloride in tetrahydrofuran gave a precipitate of 1-chlorobismacyclohexa-2,5-diene (**7b**), which could be recrystallized from tetrahydrofuran. The addition of 1 equiv of DBU to a solution of **7b** in tetrahydrofuran at 25 °C caused an immediate exothermic reaction with the formation of DBU–HCl and an intractable black precipitate. On the other hand, addition of DBU to a dilute solution of **7b** at −78 °C followed by warming to 0 °C afforded a golden red solution. Addition of excess hexafluorobutyne gave 1,4 Diels–Alder adduct **9b**.

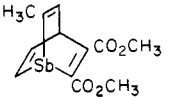
Examination of the ^{1}H NMR spectrum of the reaction mixture from **7b** and DBU at −20 °C revealed a spectrum that has been assigned to bismabenzene dimer **10b** (4,4a-dihydro-1,4-etheno-1*H*-bismino[1,2-*b*][1,2]dibismin). This spectrum has been assigned in a manner similar to that used for **10a** and has previously been discussed in detail.[11] Careful examination of the ^{1}H NMR spectrum at −20 °C revealed very weak low-field signals that have been assigned to bismabenzene. A doublet (J = 10 Hz) at δ 13.25 was assigned to the protons α to bismuth, while a triplet ($J \sim$ 10 Hz) at δ 9.86 was assigned to the peaks β to bismuth. A multiplet at δ 7.70 may be due to the protons γ to bismuth, but this assignment must be regarded as very tentative due to weakness of this signal and its overlap with peaks for **10b** and unidentified impurities. Warming to temperatures ≥0 °C caused the peaks assigned to bismabenzene to increase in intensity and broaden. Eventually the spectrum was lost simultaneously with formation of black intractable tar.

Alkyl-Substituted Stibabenzenes and Bismabenzenes. Investigation of stibabenzene and particularly bismabenzene has been hampered by the lability of the parent compounds. It has been found that alkyl derivatives of some very labile unsaturated systems such as cyclobutadiene[16] and cyclopentadienone[17] are markedly more stable than their parents. Since it was our hope that alkyl substitution might similarly stabilize stibabenzene and bismabenzene, we have explored syntheses of alkylheterobenzenes.

2-Alkylstannacyclohexa-2,5-dienes are readily available from stannohydration of 1,4-diynes.[18] Thus 1,1-dibutyl-2-methylstannacyclohexa-2,5-diene (**11**) reacts with antimony trichloride



11 12



13

to give a mixture of 1-chloro-2-methylstibacyclohexa-2,5-diene

(16) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem., Ed. Engl.* **1978**, *17*, 520.
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(18) Ashe, A. J., III; Chan, W.-T. *J. Org. Chem.* **1979**, *44*, 1409.

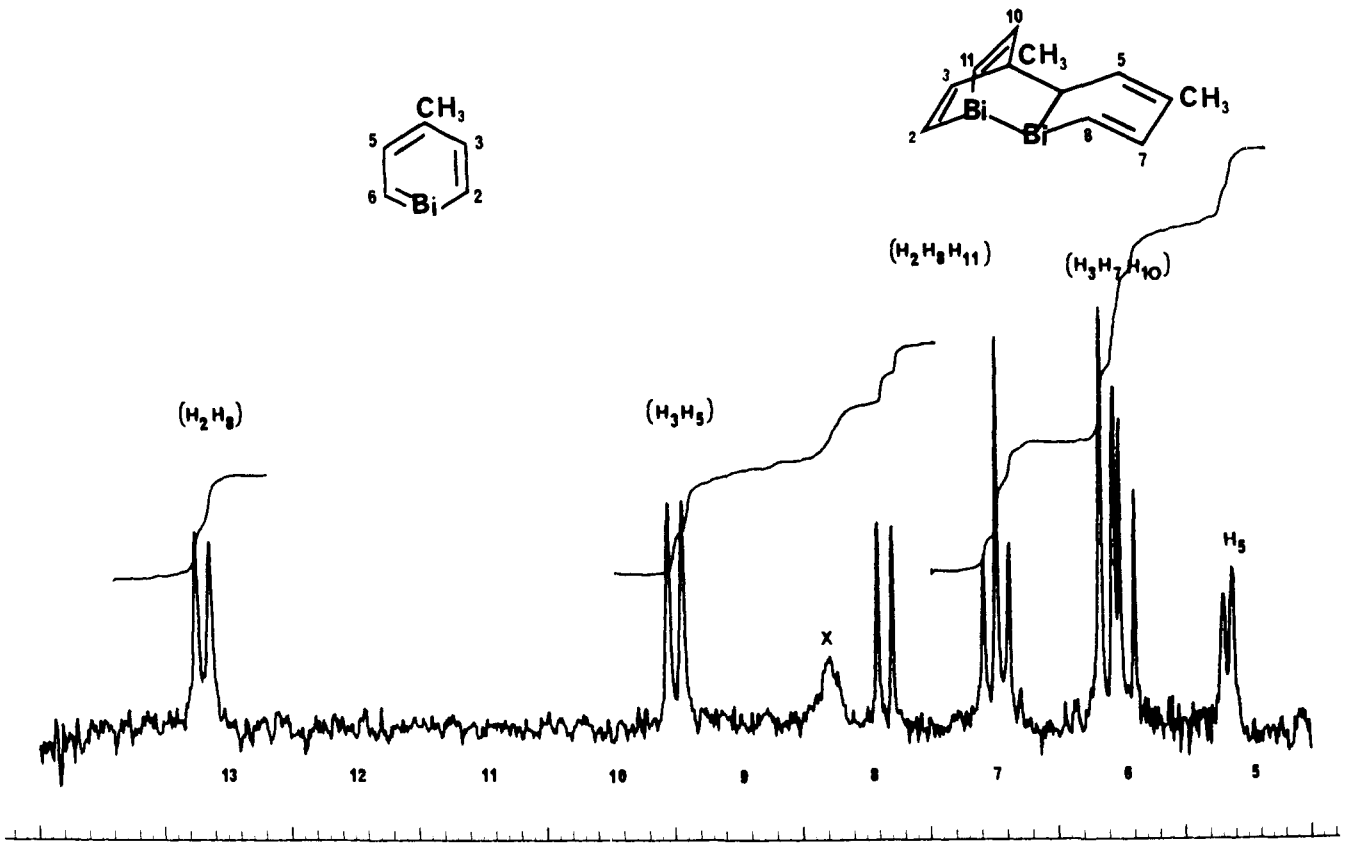
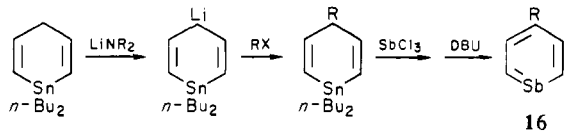


Figure 2. Low-field portion of the 100-MHz proton NMR spectrum of 4-methylbismabenzene and its dimer. The spectrum was recorded in tetrahydrofuran-d_8 at −10 °C. Peak assignments are indicated while a peak for an unidentified impurity is noted by ×.

and dibutyltin dichloride. In situ addition of DBU followed by codistillation with tetrahydrofuran gave a yellow solution that showed a ^{1}H NMR spectrum with only very broad ill-defined peaks in the aromatic region (δ 11–7). Addition of excess dimethyl acetylenedicarboxylate afforded the expected Diels–Alder adduct **13**. Thus 2-methylstibabenzene (**12**) appears even more labile than stibabenzene. We have not further explored this route to 2-substituted stibabenzenes.

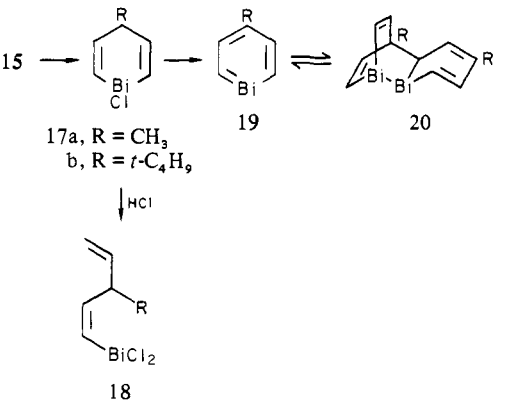
4-Alkylstannacyclohexadienes needed to prepare 4-alkylheterobenzenes may be obtained by direct functionalization of **6**.[19,20] Treating **6** with lithium diisopropylamide in tetrahydrofuran gives the lithium stannacyclohexadienide **14** which on quenching with methyl iodide afforded **15a** in 65% yield. Similarly, the reaction of *tert*-butyl bromide gave 20% of **15b**.[21]



6 14 15a, R = CH_3; b, R = t-C_4H_9 16

Both **15a** and **15b** could be converted in the usual manner to the corresponding stibabenzenes **16a** and **16b**. 4-Methylstibabenzene and 4-*tert*-butylstibabenzene are easily distillable liquids. Qualitatively, 4-methylstibabenzene was more stable than the unsubstituted compound. Pure stibabenzene polymerized almost immediately at 25 °C while pure **16a** showed no change after 1 h at 25 °C. After standing for 24 h at 25 °C, it also underwent polymerization. Neither **16a** nor **16b** forms detectable quantities of Diels–Alder dimer, although **16a** may be easily converted to the expected Diels–Alder adduct with dimethyl acetylenedicarboxylate.

The reaction of **15a** with bismuth trichloride gave 1-chloro-4-methylbismacyclohexa-2,5-diene (**17a**) (of unknown stereochemistry). Compound **17a** may be obtained pure but is very acid sensitive. On standing in tetrahydrofuran, it was partially converted to uninvestigated product(s), which show a ^{1}H NMR spectrum with characteristic vinyl absorption (δ 4.49–5.77). This spectrum is consistent with an assignment as **18a**,[1] although we have been unable to obtain a pure sample. Formation of **18a** is enhanced by the addition of external HCl while it may be totally inhibited by the addition of a trace of triethylamine.



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1-Chloro-4-methylbismacyclohexa-2,5-diene reacts with DBU in tetrahydrofuran to afford a solution of 4-methylbismabenzene (**19a**) and its Diels–Alder dimer (**20a**) (see Figure 2 for the ^{1}H NMR spectrum). The monomer and dimer are in rapid thermal equilibrium since the relative intensity of the dimer signals increase on cooling and decrease on warming. On warming of the solution above 10 °C, the signals for both **19a** and **20a** broaden simultaneously with the formation of an intractable black tar.

(19) Smith, T. W. Ph.D. Thesis, The University of Michigan, 1977.
(20) Jutzi, P.; Baumgärtner, J. *J. Organomet. Chem.* **1978**, *148*, 247.
(21) While the alkylation of **14** by *tert*-butyl bromide appears surprising, it might be noted that sodium cyclopentadienide undergoes the same reaction. See: Alder, K.; Ache, H.-J. *Chem. Ber.* **1962**, *95*, 503.

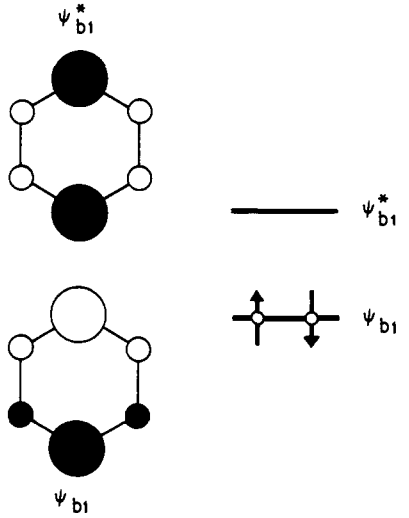


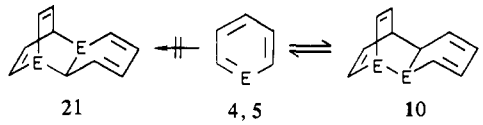
Figure 3. Schematic representation of the HOMO and LUMO of stibabenzene and bismabenzene. The shaded and nonshaded circles indicate different signs of the HMO coefficients, while the areas are proportional to the squares of the coefficients of the corresponding benzene-like orbitals. The heteroatom is located lowermost.

4-*tert*-Butyl-1-chlorobismacyclohexa-2,5-diene (**19b**) is readily prepared from **17b**. Like **17a**, it is very acid sensitive. Direct reaction of **17b** with DBU in tetrahydrofuran at −20 °C gave a solution of 4-*tert*-butylbismabenzene (**19b**). On cooling no dimer could be detected. Solutions of 4-*tert*-butylbismabenzene were stable for several hours at 0 °C. On warming of the solutions to 45 °C, the ^{1}H NMR signals of **19b** diminished and were lost after 30 min.

Qualitatively, the 4-alkyl substituents markedly increase the kinetic stability of the stibabenzene and bismabenzene systems while a 2-alkyl group had no stabilizing effect. It seems very unlikely that a single alkyl substituent will exert a large electronic perturbation on the ring. It appears most likely that the 4-alkyl substituents are sterically retarding the polymerization that destroys the heterobenzene.[22] Thus the 4-position seems implicated as the most reactive position toward (presumed radical-like) attack.

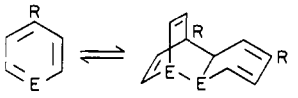
Why is the 4-position—most remote from the heteroatom—likely to be the primary site of reaction? An explanation can be offered by using a frontier molecular orbital approach.[23] Analysis of the photoelectron spectrum of stibabenzene and bismabenzene has shown that the HOMO has b_1 symmetry as illustrated in Figure 3.[12] Similarly, it has been argued from analysis of the electron transmission spectrum of stibabenzene that the LUMO also has b_1 symmetry.[24] Both HOMO and LUMO have large orbital coefficients at C_4. It seems plausible that the half-filled orbital of an attacking radical might interact with both heterobenzenes LUMO and HOMO. Most efficient overlap at C_4 seems indicated; thus C_4 is most reactive.[25]

It appears somewhat surprising that bismabenzene and stibabenzene form head-to-head Diels–Alder dimers **10** rather than head-to-tail dimers **21**. It can be argued that dimers **10** are



21 4, 5 10

Table I. Thermodynamic Parameters for the Dimerization of Stibabenzene and Bismabenzenes



E	R	$\Delta H°$, kcal/mol	$\Delta S°$, cal/(mol deg)	K_{eq} at 253 K, L/mol
Sb	H	−7.3 ± 0.3	−23	19
Bi	H	−12[a]	−23	2.9×10^5
Bi	CH_3	−9.9 ± 0.2	−24	2.5×10^3

[a] Calculated from the $\Delta F°_{253}$ by assuming $\Delta S° = -23$ cal/(mol deg).

thermodynamically favored over dimers **21**. In terms of group equivalents, the enthalpy difference between **10** and **21** can be expressed as the difference between an E–E bond and a C–C bond for **10** and two E–C bonds for **21**. Unfortunately, little thermodynamic data are available for organobismuth or -antimony compounds. However, we propose that data on bond dissociation energies may be used to estimate the value of $\Delta(\Delta H_f)$. For the bismuth dimers $\Delta(\Delta H_f) \sim D_{CC} + D_{BiBi} - 2D_{BiC}$. $D_{CC} \sim 83$ kcal/mol (for ethane),[26] $D_{BiC} \sim 34.1$ kcal/mol (for trimethylbismuth),[27] and D_{BiBi} is unknown since the only characterized organodibismuthines are **10b** and **20a**.[28,42] As a guess, we will take $D_{BiBi} \sim 20$ kcal/mol. On this basis, the $\Delta(\Delta H_f)$ is estimated to be 35 kcal/mol. For the antimony dimers: $\Delta(\Delta H_f) \sim 83$ (D_{CC}) + 35 (D_{SbSb})[29] − 2 (51.5) (D_{CSb} for trimethylstibine)[27] = 15 kcal/mol. Although there are large uncertainties in these numbers, it seems likely that the head-to-head dimers are considerably more stable.

The equilibrium constants for the conversion of stibabenzene, bismabenzene, and 4-methylbismabenzene to their respective dimers have been measured at −20 °C (Table I). For stibabenzene and 4-methylbismabenzene, plots of ln K_{eq} vs. $1/T$ have been used to determine the $\Delta H°$ and $\Delta S°$ for dimerization. The observed $\Delta S°$ values are appropriate for Diels–Alder dimerization. They are very close to $\Delta S°_{298} = -25.8$ cal deg^{-1} mol^{-1} found for the dimerization of cyclopentadiene.[30] If we assume that the entropy change for the dimerization of bismabenzene is similar, a $\Delta H°_{253}$ value of −12 kcal/mol can be calculated.

The $\Delta H°$ for dimerization of bismabenzene is 5 kcal/mol more favorable than for stibabenzene. With the assumption of a similar trend for the lighter heterobenzenes arsabenzene and phosphabenzene, their $\Delta H°$ values must be $\gtrsim 0$. Experimentally, we have been unable to detect dimerization for **2** and **3**, but we have found the rates of Diels–Alder reactions of **2** and **3** are lower than for **4** and **5**.[10]

It is tempting to associate the lower $\Delta H°$ dimerization of **4** and **5** with a lower delocalization energy of these heterocycles. The relative $\Delta H°$ values will depend upon the difference between twice the loss of delocalized bonding of C_5H_5E and the gain of bond strength for the formed E–E single bond of **10**. For the group 5 elements (P, As, Sb, and Bi), E–E bond strength decreases with increasing atomic number.[31] Thus the energy of the delocalized bonding of the heavier heterobenzenes must decrease.[32]

^{1}H NMR Spectra. The ^{1}H NMR and ^{13}C NMR spectra of stibabenzene along with phosphabenzene and arsabenzene have

(22) For a similar stabilization of 10-substituted phosphaanthracenes and arsaanthracenes, see: Vermeer, H.; Bickelhaupt, F. *Tetrahedron Lett.* **1970**, 3255. Jongsma, C.; Vermeer, H.; Bickelhaupt, F.; Schäfer, W.; Schweig, A. *Tetrahedron* **1975**, *31*, 2931.

(23) See: Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley-Interscience: New York, 1976.

(24) Burrow, P. D.; Ashe, A. J., III; Bellville, D. J.; Jordan, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 425.

(25) While the frontier molecular orbitals clearly indicate that C_4 is the most reactive carbon, they also suggest that the metal atom E will be equally reactive. We suggest that reactivity at carbon is higher since a stronger bond (R–C vs. R–E) will be formed.

(26) Cottrell, T. L. "Strength of Chemical Bonds", 2nd ed.; Butterworths: London, 1958.

(27) Skinner, H. A. *Adv. Organomet. Chem.* **1964**, *2*, 49.

(28) However, see: Panneth, F. A.; Loleit, H. *J. Chem. Soc.* **1935**, 366. Dessy, R. E.; Chivers, T.; Kitching, W. *J. Am. Chem. Soc.* **1966**, *88*, 467.

(29) There are no data for bond dissociation energies of distibines. However, it is reported that tetramethyldistibine is thermally stable at 100 °C, but at 200 °C for 20 h it decomposes quantitatively to trimethylstibine and antimony metal. This suggests a bond dissociation energy of 30–40 kcal/mol. Burg, A. B.; Grant, L. R. *J. Am. Chem. Soc.* **1959**, *81*, 1.

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(31) Dessy, R. E.; Weissman, P. M.; Pohl, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5117.

(32) A similar argument has previously been made from the rates of Diels–Alder reaction with hexafluorobutyne. See ref 10.

Table II. Proton Chemical Shifts of Heterobenzenes[a]

position	benzene	pyridine[b]	phospha-benzene[c]	arsa-benzene[c]	stiba-benzene[c]	bisma-benzene
H_α (H_2,H_6)	7.37	8.29	8.61	9.68	10.94	13.25
H_β (H_3,H_5)		7.39	7.72	7.83	8.24	9.8
H_γ (H_4)		7.75	7.38	7.52	7.78	7.8[d]

[a] Chemical shift values are in ppm downfield from Me_4Si. [b] Schneider, W. G.; Bernstein, H. J.; Pople, J. A. *Can. J. Chem.* 1957, *35*, 1489. [c] Reference 33. [d] Assignment is only tentative due to relatively poor quality of the spectrum.

Table III. ^{13}C Chemical Shifts (with $^1J_{CH}$ Values) for Selected Heterobenzenes

position	benzene	phosphabenzene[a]	arsabenzene[a]	stiba-benzene[a]	4-methyl-stibabenzene[b]	4-methyl-bisma-benzene[b,e]	4-*tert*-butyl-bismabenzene[b]
C_2	128.7 (159)	154.1 (157)	167.7 (159)	178.3	179.2 (158)	213.2	211.7[d]
C_3		133.6 (156)	133.2 (157)	134.4	138.1 (153)	137.9	132.9 (150)
C_4		128.8 (161)	128.2 (161)	127.4	138.1	*c*	*c*

[a] Reference 33. [b] This work. [c] The C_4 resonance was not observed. [d] The breadth of the signal precluded measurement of $^1J_{CH}$. [e] Assuming identical substituent shifts for 4-methylstibabenzene and 4-methylbismabenzene, the unsubstituted bismabenzene would show δ_{C_2} 212.3 and δ_{C_3} 134.2. The trend in the series 2, 3, 4 suggest that δ_{C_4} of bismabenzene would be close to 127.0.

previously been discussed in detail.[32] The preparation of more stable derivatives of bismabenzene has allowed us to obtain their ^1H NMR and ^{13}C NMR spectral parameters. We have also obtained the $^1J_{CH}$ values for **16a** and **19b**. These values extend trends already noted for **2** and **3**.

The ^1H NMR spectra of bismabenzene and indeed all of the group 5 heterobenzenes are remarkable largely for the very low field chemical shift values of the α-protons (H_2, H_6). The α-proton signals range from δ 8.6 for **2** to δ 13.25 for **5**, while the β- and γ-proton signals follow the downfield trend at a reduced magnitude (see Table II).

These progressive large downfield shifts are most readily explained in terms of the magnetic anisotropy of the group 5 atom. Magnetic anisotropy is expected to increase with atomic number,[34] in agreement with the observed trend. Furthermore, magnetic anisotropic effects on C_5H_5E protons should be strongly distance dependent (R_{EH}^{-3} in the McConnell equation),[35] in agreement with the trend of $\alpha > \beta > \gamma$ shifts. If the main component of the anisotropy of E is assumed to be coaxial with the E p_z orbital, all protons lie in the plane of maximum deshielding with a shift given[36] by

$$\Delta\sigma = (\Delta\chi)/3N_0R_{EH}^3$$

These plots of the proton chemical shifts of the H_α, H_β, and H_γ of each C_5H_5E (corrected for electronegativity effects)[37] should be a linear function of the inverse cube of the distance between E and H (R_{EH}^{-3}) with a slope equal to $\Delta\chi/3N_0$ (see Figure 4). Extrapolation of R_{EH}^{-3} to 0 allows correction for the local anisotropic effect. After this correction, the chemical shift values of **2–5** are upfield from benzene. These nonlocal chemical shift values are consistent with smaller ring currents from **2–5** and hence a lower aromaticity than for benzene.

The magnetic anisotropies have been computed from the slopes of the plots in Figure 4. These are found to be as follows: $\Delta\chi_P = 62 \times 10^{-6}$, $\Delta\chi_{As} = 103 \times 10^{-6}$, $\Delta\chi_{Sb} = 202 \times 10^{-6}$, $\Delta\chi_{Bi} = 276 \times 10^{-6}$. The values of $\Delta\chi$ for Sb and Bi are large in comparison to Pascal constants of single-bonded atoms (e.g., Bi = 37×10^{-6}) and are even large when compared to the $\Delta\chi$ values associated with the aromatic hydrocarbons (e.g., benzene = 54.9×10^{-6}).[34]

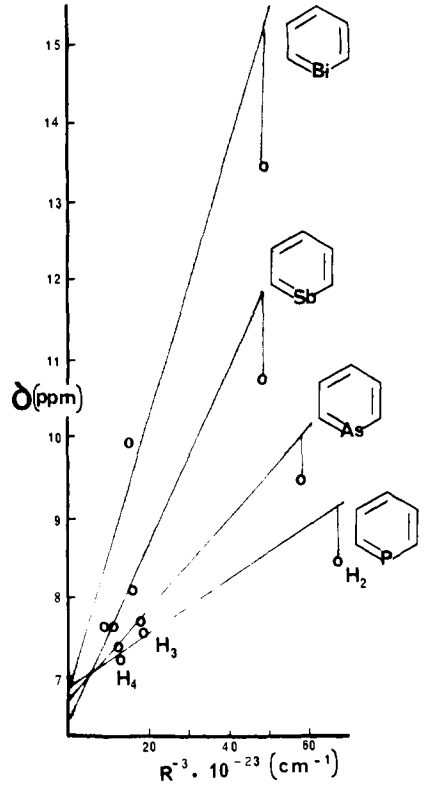

Figure 4. Plots of the proton chemical shifts of the heterobenzenes vs. R_{EH}^{-3}, where R is the interatomic distance between the group 5 atom and H_α, H_β, and H_γ. The vertical lines indicate the estimated magnitude of the ortho inductive effects after ref 37. The slopes of the lines are equal to $\Delta\chi_E/3N_0$ while the intercepts indicate the chemical shift value expected in the absence of group 5 atom anisotropic effect.

The ^{13}C chemical shifts for selected stibabenzenes and bismabenzenes are given in Table III. The signals assigned to the α-carbon atoms of the bismabenzenes **19** were quite broad, presumably due to rapid scalar relaxation by the adjacent ^{209}Bi. The relative assignment of the α and β signals was also made in analogy to those of **2** and **3** in which the α-carbon showed considerably lower field signals. This trend continues for **4** and **5**. For bismabenzenes, the α signals are more than 80 ppm downfield from that of benzene. On the other hand, there is very little variation of the β- and γ-carbon signals for any of the compounds in the series.

The α-carbon chemical shifts of **2–5** show a good linear correlation with the α-proton shifts ($\delta_C = 12.44\ \delta_H + 46.05 \pm 2.18$ ppm). The β and γ shifts do not correlate. While the major

(33) Ashe, A. J., III; Sharp, R. R.; Tolan, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 5451.
(34) Dorfman, Ya. G. "Diamagnetism and the Chemical Bond"; Arnold: London, 1965.
(35) McConnell, H. M. *J. Chem. Phys.* **1957**, *27*, 226.
(36) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: Oxford, 1965; p 131.
(37) Electronegativity effects on the ortho CH groups were corrected by using the equation $\Delta(\delta) = 1.61(N_E - N_C)$ where N is the Allred–Rochow electronegativity. See: Narasimhan, P. T.; Rogers, M. T. *J. Am. Chem. Soc.* **1960**, *82*, 5983.

contribution to the proton chemical shifts have been ascribed to diamagnetic effects, the magnitude of the α-carbon shifts seems too large to be due to an anisotropic effect.[38] We only note here that very large downfield ^{13}C shifts have been found for other compounds containing multiple bonds to heavy elements.[39]

Finally, the one-bond $^{13}C-H$ coupling constants for bismabenzenes and stibabenzenes are very similar to those of the other heterobenzenes. $^1J_{CH}$ values are closely related to the percent s character of the CH bonds.[40] The near identity of all the $^1J_{CH}$ values implies a hybridization close to sp^2 for all the carbon atoms of these aromatics.

Experimental Section

The NMR spectra were recorded with either a Varian T60A, JEOL JNMPS 100 PFT, or Brüker WH-360 spectrometer. Chemical shifts are reported to the nearest 0.1 ppm for routine T60A spectra and to 0.01 ppm for higher field spectra. Coupling constants are reported to the nearest 0.5 Hz. Mass spectra data were obtained by using a Finnigan 4021 GC–MS instrument operating at an ionizing voltage of 70 eV. C and H combustion analyses were obtained on new compounds by Spang Microanalytical Laboratory or Galbraith Laboratories. In all cases, analyses agreed with calculated values (±0.4%). It was not possible to obtain analyses on the sensitive stibabenzene and bismabenzene derivatives. VPC analyses and separations were performed by using an Antek 300 chromatograph. All operations were performed under argon or nitrogen.

1,1-Dibutylstannacyclohexa-2,5-diene-*3,5-d*$_2$. This material was prepared from 1,4-pentadiyne and dibutyltin dideuteride by the usual procedure:[18] MS (70 eV), *m/e* 302 (2, M^+ for $C_{13}H_{22}D_2{}^{120}Sn$), 245 (100, $M^+ - 57$); ^1H NMR (neat) δ 6.1 (br s, 2 H), 3.1 (br s, 2 H), 1.6–0.7 (m, 18 H).

4-Methyl-1,1-dibutylstannacyclohexa-2,5-diene. A solution of lithium diisopropylamide was prepared by treating 12 g (119 mmol) of diisopropylamine with 30 mL (66 mmol) of 2.2 N butyllithium in hexane in 200 mL of tetrahydrofuran. This was added to 20 g (66 mmol) of 1,1-dibutylstannacyclohexa-2,5-diene in 100 mL of tetrahydrofuran at −78 °C. The color changed to dark red-brown on addition. After 15 min, addition of an excess (12 mL) of methyl iodide discharged the color. The reaction mixture was added to 400 mL of water. After separation of the layers, the aqueous layer was extracted with 100 mL of pentane. The combined organic fractions were washed with water and then dried over anhydrous sodium sulfate. Distillation gave 13.7 g (65%) of product, bp 87–95 °C (0.1 torr). The product was identical with material prepared by an independent synthesis.[41]

4-*tert*-Butyl-1,1-dibutylstannacyclohexa-2,5-diene. A solution of lithium 1,1-dibutylstannacyclohexadienide was prepared as above from 10 g (33 mmol) of 1,1-dibutylstannacyclohexa-2,5-diene in 50 mL of tetrahydrofuran, 15 mL (33 mmol) of 2.2 N butyllithium in hexane, and 6 g of diisopropylamine in 35 mL of tetrahydrofuran. To this solution was added an excess (6 mL) of *tert*-butyl bromide. The mixture was allowed to reflux for 7 h, during which time it turned light red. After addition of 500 mL of water, the mixture was extracted with 2 × 100 mL of pentane. The extracts were dried over anhydrous magnesium sulfate. Distillation afforded 2.2 g (19%) of product: bp 120 °C (0.05 torr); ^1H NMR (CCl_4) δ 1.0 (s, 9 H), 0.9–1.4 (m, 18 H), 2.9 (t, J = 6 Hz, 1 H), 6.1 (d, J = 14 Hz, 2 H), 6.7 (d of d, J = 14, 6 Hz). Anal. Calcd for $C_{17}H_{32}Sn$: C, 57.51; H, 9.09. Found: C, 57.50; H, 9.10.

1-Chlorostibacyclohex-2,5-diene. A solution of 4.5 g (19.7 mmol) of antimony trichloride in 10 mL of tetrahydrofuran was added dropwise with stirring to 6.0 g (20 mmol) of 1,1-dibutylstannacyclohexa-2,5-diene in 10 mL of tetrahydrofuran. The reaction mixture warmed spontaneously and became gray-black. After the mixture stirred for 2 h at 25 °C, the solvent was removed, leaving an oily semicrystalline mass, which was washed twice with 50 mL of pentane to remove the dibutyltin dichloride. On drying, 4.0 g of crude product was obtained as gray crystals. On Soxhlet extraction with pentane, 2.8 g (61% yield) of yellow crystals, mp 115–117 °C dec, was obtained: ^1H NMR ($CDCl_3$) δ 3.4 (m, 2 H), 6.5 (d of t, J = 13, 3.5 Hz, 2 H), 6.9 (d of t, J = 13, 2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 140.1, 128.2, 36.4; MS, *m/e* 222 (17%, M^+ for $C_5H_6{}^{35}Cl{}^{121}Sb$), 186 (100%, $C_5H_5{}^{121}Sb$), 66 (95%, C_5H_6). Anal. Calcd for C_5H_6SbCl: C, 26.90; H, 2.70. Found: C, 27.07; H, 2.86.

1-Chlorostibacyclohexa-2,5-diene-*3,5-d*$_2$. In the same manner, 1,1-dibutylstannacyclohexa-2,5-diene-*3,5-d*$_2$ and antimony trichloride gave 1-chlorostibacyclohexa-2,5-diene-*3,5-d*$_2$: MS (70 eV), *m/e* 224 (9, M^+ from $C_5H_4D_2{}^{121}Sb{}^{35}Cl$), 68 (100%, $C_5H_4D_2{}^+$); ^1H NMR ($CDCl_3$) δ 3.4 (br s, 2 H), 6.7 (br s, 2 H).

Stibabenzene. Method A. A solution of 1-chlorostibacyclohexa-2,5-diene (0.8 g, 3.6 mmol) in 5 mL of tetrahydrofuran was placed in a small distillation apparatus. After the mixture cooled to −78 °C, 0.5 g of 1,8-diazabicyclo[5.4.0]undec-7-ene was added with stirring. A precipitate formed, and on warming to 25 °C, the mixture turned red-brown. Distillation at 25 °C under reduced pressure gave a pale yellow solution of stibabenzene in tetrahydrofuran.

Addition of excess 1,1,1,4,4,4-hexafluoro-2-butyne gave a brown solution. After standing at 0 °C for 2 h solvent was removed and the residue subjected to pot-to-pot distillation (0.1 torr). The 2,3-bis(trifluoromethyl)-1-stibabicyclo[2.2.2]octa-2,5,7-triene was purified by GLC. (5 ft × 0.25 in. column packed with 20% SE 30 on Chromosorb W at 100 °C, 30 lb He elution, retention time 2.5 min); ^1H NMR (CCl_4) δ 6.66 (t of t, J = 7, 2 Hz, 1 H), 7.20 (d of d, J = 8.5, 7 Hz, 2 H), 7.42 (d of d, J = 8.5, 2 Hz, 2 H). Anal. Calcd for $C_9H_5SbF_6$: C, 30.98; H, 1.44. Found: C, 31.00; H, 1.70.

Method B. In a 50-mL round-bottom flask, equipped with magnetic stirrer, 10-mL dropping funnel, and nitrogen inlet, was placed 20 mL of tetraglyme and 3 g (10 mmol) of 1,1-dibutylstannacyclohexa-2,5-diene. To this solution was added 2.5 g (11 mmol) of antimony trichloride in 10 mL of tetraglyme. The mixture was allowed to stir at 25 °C for 1 h. To the mixture 4 mL (26 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene was added at −78 °C. The mixture was warmed to 25 °C and the product distilled under reduced pressure at 25 °C as a light green oil. On standing at 25 °C stibabenzene changed to resinous yellow solid. On exposure to oxygen, it became cloudy yellow: ^1H NMR ($CDCl_3$) δ 7.8 (t, J = 9 Hz, 1 H), 8.2 (d of d, J = 12.5, 9 Hz, 2 H), 10.9 (d, J = 12.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 127.4, 134.4, 178.3; MS, *m/e* 186 (100%, M^+ for $C_5H_5{}^{121}Sb$); UV (C_6H_{12}) λ_{max} 312 ($\epsilon \sim 10^4$), 236 ($\sim 10^4$) nm.

Stibabenzene Dimer. When a tetrahydrofuran solution of stibabenzene was cooled, a new ^1H NMR spectrum was observed that has been assigned to dimer **10a**. Assignment has been made by examining the ^1H NMR spectrum of the dimer of stibabenzene-*3,5-d*$_2$ and by partial decoupling of the spectrum at 360 MHz: ^1H NMR (C_4D_8O) δ 2.82 (t, $J \sim 5$ Hz, H_{4a}), 4.57 (t of d, J = 6, 4 Hz, H_4), 5.80 (m, H_5, H_6), 6.06 (d of d, J = 12, 5 Hz, H_7), 6.15 (d, J = 12 Hz, H_8), 6.32 (d, J = 11.5 Hz, H_2 or H_{11}), 6.40 (m, H_3, H_{10}, and H_2 or H_{11}). The vicinal coupling constants are as follows: $J_{2,3} \sim J_{10,11}$ = 11.5 Hz, $J_{3,4} \sim J_{4,10}$ = 6 Hz, $J_{4,4a} \sim 4$ Hz, $J_{4a,5}$ = 5 Hz, $J_{5,6}$ = 11 Hz, $J_{6,7}$ = 5 Hz, $J_{7,8}$ = 12 Hz.

4-Methylstibabenzene. 4-Methyl-1,1-dibutylstannacyclohexa-2,5-diene (5.0 g, 17 mmol) in 5 mL of tetrahydrofuran was added dropwise with stirring at 25 °C to 3.7 g (16 mmol) of antimony trichloride in 15 mL of tetrahydrofuran. After stirring for 30 min, the mixture was placed in a small distilling apparatus. After cooling to −78 °C, 2.1 g (16.9 mmol) of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in 83 mL of tetrahydrofuran was added. On warming to 25 °C, the mixture turned red-brown. The tetrahydrofuran and 4-methylstibabenzene were codistilled under reduced pressure into a receiver at −78 °C. Careful vacuum distillation of the tetrahydrofuran left a green-yellow oil that solidified to nicely formed green crystals on cooling to −78 °C. On standing for 24 h at 25 °C, 4-methylstibabenzene formed a yellow-brown resinous solid: Anal. Calcd for $(C_6H_7Sb)_x$: C, 35.89; H, 3.51. Found: C, 36.11; H, 3.66. 4-Methylstibabenzene shows: ^1H NMR ($CDCl_3$) δ 2.2 (s, 3 H), 7.9 (d, J = 12 Hz, 2 H), 10.8 (d, J = 12 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 27.1 (CH_3, $^1J_{CH} \sim 132$ Hz), 138.1 (C_4), 138.1 (C_3, $^1J_{CH}$ = 153 Hz), 179.2 (C_2, $^1J_{CH}$ = 158 Hz); UV (THF) λ_{max} 320 ($\epsilon \sim 10^4$), 239 ($\sim 10^4$); IR ($CHCl_3$) 3010 s, 2980 s, 2920 m, 2870 m, 1550 s, 1465 m, 1375 m, 1355 s, 1325 m, 1275 s, 1180 s, 555 s cm^{-1}.

Reaction of 4-Methylstibabenzene with Dimethyl Acetylenedicarboxylate. To 4-methylstibabenzene prepared from 2.17 g of **15a** as above was added 1 mL of dimethyl acetylenedicarboxylate in 10 mL of tetrahydrofuran. After the solution was permitted to stand for 30 h at 25 °C, pot-to-pot distillation afforded 280 mg of 4-methyl-2,3-dicarbomethoxy-1-stibabicyclo[2.2.2]octa-2,5,7-triene as yellow crystals, which were recrystallized from hexane to mp 77–78 °C; ^1H NMR ($CDCl_3$) δ 1.78 (s, 3 H), 3.50 (s, 3 H), 3.63 (s, 3 H), 6.67 (d, J = 9 Hz, 2 H), 6.88 (d, J = 9 Hz, 2 H). Anal. Calcd for $C_{12}H_{13}O_4Sb$: C, 42.02; H, 3.82. Found: C, 42.11; H, 3.88.

4-*tert*-Butylstibabenzene. In the same manner 4-*tert*-butyl-1,1-dibutylstannacyclohexa-2,5-diene (2.6 g, 7 mmol) in 15 mL of tetrahydrofuran, antimony trichloride (1.67 g, 7.3 mmol), and excess (2 mL)

(38) With the assumption that the relative carbon shifts vary as R_{EC}^{-3} and use of the $\Delta\chi$ values derived from the proton spectra, the δ_{C_α} values for **2**, **3**, **4**, and **5** are calculated to be 135.3, 138.8, 143.0, and 145.0, respectively. R_{BiC} was taken as 2.16 Å.

(39) For carbene–transition metal complexes, see: McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 3519.

(40) Shoolery, J. N. *J. Chem. Phys.* **1959**, *31*, 1427.

(41) Ashe, A. J., III; Chan, W.-T. *Tetrahedron Lett.* **1975**, 2749.

(42) **Note Added in Proof**: Three dibismuthines have been reported recently: Becker, G.; Rössler, M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *B37*, 91. Breunig, H. J.; Müller, D. *Angew. Chem.* **1982**, *94*, 448. Ashe, A. J., III; Ludwig, E. G., Jr. *Organometallics*, in press.

1,5-diazabicyclo[4.3.0]non-5-ene gave 4-*tert*-butylstibabenzene as a green-yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.4 (s, 9 H), 8.3 (d, J = 12 Hz, 2 H), 10.8 (d, J = 12 Hz, 2 H).

2-Methylstibabenzene and Its Reaction with Dimethyl Acetylenedicarboxylate. In the same manner, 2-methyl-1,1-dibutylstannacyclohexa-2,5-diene (3.1 g, 10 mmol) in 10 mL of tetrahydrofuran, antimony trichloride (2.25 g, 10 mmol), and 1.5 g of DBU gave a yellow-brown oil of 2-methylstibabenzene. ^{1}H NMR (THF) showed only broad peaks, δ 11–7. Addition of 1 mL of dimethyl acetylenedicarboxylate in 10 mL of tetrahydrofuran followed by standing at 25 °C for 30 h gave 240 mg of 6-methyl-2,3-dicarbomethoxy-1-stibabicyclo[2.2.2]octa-2,5,7-triene as a yellow oil which was purified by GLC (5 ft × 0.25 in. column packed with 20% SE-30 Chromosorb W, 30 lb He elution, 200 °C, retention time 6.3 min): ^{1}H NMR ($CDCl_3$) δ 2.22 (d, J = 3 Hz, 3 H), 3.77 (s, 3 H), 3.75 (s, 3 H), 5.72 (t of d, J = 7.3, 1.3 Hz, 1 H), 6.64 (d of q, J = 7.3, 1.8 Hz, 1 H), 7.27 (d of d, J = 8.6, 7.3 Hz, 1 H), 7.44 (d of d, J = 8.6, 7.3 Hz, 1 H). Anal. Calcd for $C_{12}H_{13}O_4Sb$: C, 42.02; H, 3.82. Found: C, 42.01; H, 3.77.

1-Chlorobismacyclohexa-2,5-diene. A solution of 6.0 g (20 mmol) of 1,1-dibutylstannacyclohexa-2,5-diene in 30 mL of tetrahydrofuran was added dropwise with stirring to 6.0 g (20 mmol) of bismuth trichloride in 30 mL of tetrahydrofuran. On addition the solution warmed and turned yellow while a gray precipitate formed. After the mixture stirred at 25 °C for 30 min, the solvent was removed, leaving a yellow-gray crystalline mass. Washing with 2 × 50 mL of pentane removed the dibutyltin dichloride. The residue was extracted with 200 mL of tetrahydrofuran. After filtration and solvent removal, 4.2 g (72% yield) of light yellow crystals was obtained: mp 144–145 °C dec; ^{1}H NMR (C_4D_8O) δ 3.5 (m, 2 H), 6.7 (d of t, J = 12, 4 Hz, 2 H), 7.5 (d of t, J = 12, 2 Hz, 2 H); MS, m/e 310 (4%, M^+ for $C_5H_6{}^{35}ClBi$), 274 (14%), 66 (100%, $C_5H_6^+$). Anal. Calcd for C_5H_6BiCl: C, 19.34; H, 1.95. Found: C, 19.36; H, 2.05.

1-Chlorobismacyclohexa-2,5-diene-*3,5-d*$_2$. In the same manner 1,1-dibutylstannacyclohexa-2,5-diene-*3,5-d*$_2$ and bismuth trichloride gave 1-chlorobismacyclohexa-2,5-diene-*3,5-d*$_2$: ^{1}H NMR (C_4D_8O) δ 3.5 (br s, 2 H), 7.4 (br s, 2 H).

1-Chloro-4-methylbismacyclohexa-2,5-diene. In a similar manner, 3.1 g (10 mmol) of 4-methyl-1,1-dibutylstannacyclohexa-2,5-diene and 3.0 g (10 mmol) of bismuth trichloride in 15 mL of tetrahydrofuran gave 1.3 g (43% yield) of 1-chloro-4-bismacyclohexa-2,5-diene as white crystals that decomposed on heating to ca. 100 °C: ^{1}H NMR (C_4D_8O) δ 1.2 (d, J = 7 Hz, 3 H), 3.3 (m, 1 H), 6.4 (d of d, J = 12, 4 Hz, 2 H), 7.5 (d, J = 12 Hz, 2 H). On standing in tetrahydrofuran 1-chloro-4-methylbismacyclohexa-2,5-diene partially reacted to a product assigned the structure of (4-methyl-*cis*-hexa-1,4-dienyl)bismuth dichloride. Addition of a trace of hydrochloric acid enhanced this reaction, while it could be inhibited by addition of traces of trimethylamine. This product could not be obtained pure. ^{1}H NMR (C_4D_8O) δ 1.18 (d, J = 8 Hz, 3 H), 3.18 (m, 1 H), 4.49–4.91 (m, 2 H), 5.18–5.77 (m, 1 H), 9.94 (d, J = 11 Hz, 1 H), 10.74 (d of d, J = 11, 9 Hz, 1 H).

Reaction of 1-Chlorobismacyclohexa-2,5-diene with DBU or DBN. Method A. Addition of 1 equiv of DBU to 1-chlorobismacyclohexa-2,5-diene in tetrahydrofuran at 25 °C resulted in the immediate formation of a large black intractable precipitate.

Method B. To a solution of 800 mg (2.6 mmol) of 1-chlorobismacyclohexa-2,5-diene in 100 mL of tetrahydrofuran at −78 °C was added 288 mg (2.3 mmol) of DBU in 50 mL of tetrahydrofuran. As the solution was allowed to warm to 0 °C, the color became golden-yellow and a precipitate of DBU·HCl formed. Excess (3 mL) 1,1,1,4,4,4-hexafluoro-2-butyne was added and the mixture was allowed to stand at 0 °C for 30 min. Removal of solvent left a tar which was extracted with chloroform. The extracts were washed with water, dried, and subjected to pot-to-pot vacuum distillation (0.1 torr). The 2,3-bis(trifluoromethyl)-1-bismabicyclo[2.2.2]octa-2,5,7-triene was purified by GLC (5 ft × 0.25 in. column packed with 20% SE-30 on Chromosorb W at 100 °C, 30 lb He elution, retention time 5 min); ^{1}H NMR (CCl_4) δ 5.95 (t, J = 8 Hz, 1 H), 7.76 (t, J = 8 Hz, 2 H), 8.45 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_9H_5BiF_6$: C, 24.79; H, 1.15. Found: C, 24.81; H, 1.25.

Method C. 1-Chlorobismacyclohexa-2,5-diene (107 mg, 0.35 mmol) was dissolved in 10 mL of tetraglyme. The solution was completely degassed and then cooled to −78 °C. DBN (39 mg, 0.31 mmol) in 200 μL of tetraglyme was added. The mixture was allowed to warm to ca. 45 °C directly on the gas inlet of a mass spectrometer; MS, m/e 274 (30%, M^+ for C_5H_5Bi), 209 (100%), low m/e peaks obscured by impurities.

Method D. A saturated solution of 1-chlorobismabenzene-2,5-diene in 1 mL of tetrahydrofuran-d_8 was prepared at 25 °C. After the mixture cooled to −78 °C, an excess (250 mg) of DBN was added. On warming to −20 °C, the color darkened to a red-yellow and a precipitate of DBN·HCl formed. The solution was decanted from the solid, and the ^{1}H NMR spectra were recorded. The ^{1}H NMR spectrum of the dimer of bismabenzene (**10b**) has been assigned on the basis of the partial proton-decoupled spectrum and the spectrum derived from 1-chlorobismacyclohexa-2,5-diene-*3,5-d*$_2$. A weak ^{1}H NMR signal assigned to bismabenzene was also recorded. Warming to >0 °C caused broadening of all signals and eventual loss of the spectrum simultaneous with the formation of an intractable black tar. Bismabenzene: ^{1}H NMR (C_4D_8O) δ 13.25 (d, J = 10 Hz, H_2, H_6), 9.86 (t, $J \sim$ 10 Hz, H_3, H_5), 7.70? (m, H_4). Bismabenzene dimer: ^{1}H NMR (C_4D_8O) δ 7.51 (d, J = 11 Hz), 6.95 (d, J = 11 Hz), 6.84 (d, J = 11 Hz) (H_2, H_8, H_{11}), 6.22 (m, H_3, H_7, H_{10}), 5.58 (m, H_5, H_6), 4.37 (t of d, J = 7, 4 Hz, H_4); H_{4a} obscured by peaks from DBN and THF.

4-Methylbismabenzene. To a solution of 4-methyl-1-chlorobismacyclohexa-2,5-diene (1.0 g, 3.1 mmol) in 3 mL of tetrahydrofuran-d_8 at −78 °C was added 2 mL (13 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene via syringe. As the solution warmed to −20 °C, it darkened and a precipitate formed after 15 min. Filtration gave a red-gold solution of 4-methylbismabenzene and its dimer. 4-Methylbismabenzene: ^{1}H NMR (C_4D_8O) δ 13.25 (d, J = 11 Hz, H_2, H_6), 9.52 (d, J = 11 Hz, H_3, H_5); CH_3 not observed due to interfering peaks. ^{13}C NMR 213.2 (C_2), 137.9 (C_3). 4-Methylbismabenzene dimer: ^{1}H NMR (C_4D_8O) 7.90 (d, J = 12 Hz), 7.05 (d, J = 12 Hz), 6.95 (d, J = 12 Hz) (H_2, H_8, H_{11}), 6.11 (d, J = 11 Hz), 6.00 (d, J = 11 Hz) (H_3, H_7, H_{10}), 5.20 (d, J = 6 Hz, H_5); H_{4a}, C_4CH_3, C_6CH_3 not observed due to interfering peaks.

4-*tert*-Butylbismabenzene. To 0.5 g (1.6 mmol) of bismuth trichloride in 10 mL of tetrahydrofuran was added a solution of 0.5 g (1.5 mmol) of 4-*tert*-butyl-1,1-dibutylstannacyclohexa-2,5-diene in 10 mL of tetrahydrofuran containing one drop of triethylamine. The mixture was stirred for 1 h at 25 °C. The solvent was removed under reduced pressure. The residue was washed 3 times with 50 mL of pentane and after washing dissolved in 20 mL of tetrahydrofuran containing one drop of triethylamine. The solution was filtered and solvent removed under reduced pressure, leaving 0.5 g (90%, crude) of a golden oil. The very acid sensitive 4-*tert*-butyl-1-chlorobismacyclohexa-2,5-diene was used immediately without purification; ^{1}H NMR (C_4D_8O) δ 1.0 (s, 9 H), 3.2 (t, J = 5 Hz, 1 H), 6.7 (d of d, J = 11, 5 Hz, 2 H), 7.4 (d, J = 11 Hz, 2 H). To a solution of the 4-*tert*-butyl-1-chlorobismacyclohexa-2,5-diene in 3.0 mL of tetrahydrofuran-d_8 at −78 °C was added 1 mL (6.5 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene via a syringe. After warming to −10 °C for 10 min, the light yellow solution turned golden-red and a large precipitate formed. Filtration gave a clear golden-red solution of 4-*tert*-butylbismabenzene from which NMR spectra were recorded. Warming to >45 °C destroyed the sample with formation of intractable black tar. Removal of solvent at 0 °C in vacuo gave a black tar from which a mass spectrum was recorded: ^{1}H NMR (C_4D_8O) δ 1.42 (s, 9 H), 9.92 (d, J = 11 Hz, 2 H), 13.47 (d, J = 11 Hz, 2 H); ^{13}C NMR (C_4D_8O) δ 132.9 (C_3, $^1J_{CH}$ = 150 Hz), 211.7 (br peak, C_2); MS, m/e 330 (41%, M^+ for $C_9H_{13}Bi$), 315 (8%), 209 (100%); peaks below m/e 153 obscured by residual DBU.

Monomer–Dimer Equilibria. A stock solution of tetrahydrofuran-d_8 containing 0.005 M benzene as an internal standard was prepared. This solution was used to prepare solutions of stibabenzene, bismabenzene, and 4-methylbismabenzene as above. Aliquots were placed in each of several NMR tubes. The ^{1}H NMR spectra of stibabenzene were recorded at 15 °C intervals over the range −15 to −60 °C. All spectra showed monomer and dimer. The concentrations of monomer and dimer relative to benzene were obtained from integration of the signals at δ 8.24 (2 H) for monomer and δ 6.18 (1 H) for dimer. The ^{1}H NMR spectra of 4-methylbismabenzene were recorded at 10 °C intervals over the range 0 to −30 °C. The concentrations of monomer and dimer were obtained from integration of the signals at δ 9.6 (2 H) for monomer and δ 7.0 (2 H) for dimer. Thd $\Delta H°$ values were obtained in the usual manner from least-squares plots of ln K_{eq} vs. $1/T$, where $K_{eq} = [D]/[M]^2$. For bismabenzene monomer/dimer concentrations were obtained only at −20 °C from integration of the signals at δ 13.25 (2 H) for monomer and δ 7.5 (1 H) for dimer.

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Registry No. 4, 289-75-8; **5**, 289-52-1; 6, 31732-31-7; **6-*3,5-d*$_2$**, 82995-52-6; **7a**, 34688-66-9; **7b**, 39553-69-0; **7b-*3,5-d*$_2$**, 82995-54-8; **9a**, 39553-73-6; **9b**, 39553-70-3; **10a**, 82995-65-1; **10a-*3,5,7,10-d*$_4$**, 82995-57-1; **10b**, 59348-16-2; **11**, 56578-02-0; **12**, 82995-66-2; **13**, 82995-60-6; **15a**, 57242-05-4; **15b**, 82995-53-7; **16a**, 70735-88-5; **16b**, 82995-59-3; **17a**, 82995-55-9; **17b**, 82995-56-0; **18a**, 82995-61-7; **19a**, 82995-62-8; **19b**, 82995-64-0; **20a**, 82995-63-9; 1,1,1,4,4,4-hexafluoro-2-butyne, 692-50-2; 4-methyl-2,3-dicarbomethoxy-1-stibabicyclo[2.2.2]octa-2,5,7-triene, 82995-58-2; $CH_3O_2CCCCO_2CH_3$, 762-42-5.