

The Group 5 Heterobenzenes

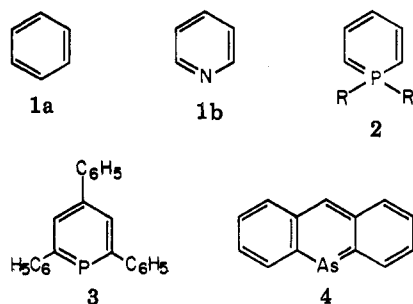
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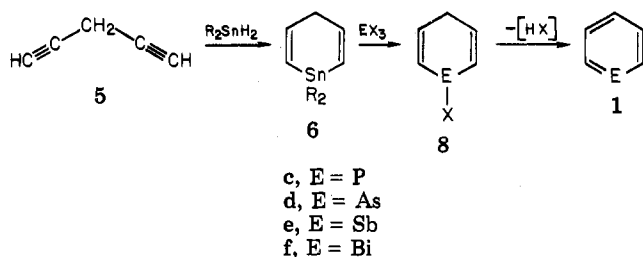
The close resemblance between benzene (1a) and pyridine (1b) is familiar to all chemists. This resemblance in terms of structure, spectra, and overall chemical stability demonstrates that a methine group of benzene can be replaced by an isoelectronic nitrogen without disrupting its aromaticity. Indeed, the properties of these two compounds have been the prime empirical guide in the formulation of the concept of aromaticity.¹ Thus, it is surprising that compounds similar to pyridine containing heavier heteroatoms were unknown until quite recently.

A fundamental breakthrough came in 1966 when Maerkl succeeded in preparing 2,4,6-triphenyl- λ^3 -phosphabenzene (3).² This compound is a rather stable



yellow crystalline material, which is presumably aromatic. Subsequently, Maerkl,³ Dimroth,⁴ and Bickelhaupt⁵ prepared a variety of heavily substituted λ^3 -phosphabenzene and began an elucidation of their chemistry. A number of related λ^5 -phosphabenzene 2 (involving pentavalent phosphorus) have also been investigated.^{3,4} Finally, several extremely labile highly fused derivatives of λ^3 -arsabenzene such as 4 were reported by Jutzi⁶ and Bickelhaupt.⁷

It can be argued that the heavy substitution of 3 and 4 may mask the properties of the phosphabenzene and arsenabenzene rings. Thus, a synthesis of the parent heterobenzenes seemed desirable. In 1971, we reported a simple synthesis of these materials based on the well-known exchange reactions of vinyltin compounds.⁸ Thus, 1,4-pentadiyne (5) may be converted in 50% yield



to 1,4-dihydro-1,1-dibutylstannabenzene (6).⁹ Com-

pound 6 exchanges with phosphorus tribromide to give dibutyltin dibromide and phosphabenzene (1c).¹⁰ Although intermediate 8c can be detected, it spontaneously loses HBr on gentle heating. Similarly, 6 and arsenic trichloride give arsabenzene 1d.¹⁰ Like most phosphines and arsines, 1c and 1d are somewhat air-sensitive but they are distillable liquids, stable to hydrolysis and to mild acids and bases.

Encouraged by these results, we attempted to extend the synthesis to the heavier group 5 heterobenzenes. The exchange reaction of 6 with antimony trichloride gave 1,4-dihydro-1-chlorostibabenzene (8e), which on treatment with base eliminated HCl to generate stibabenzene (13).¹¹ While stibabenzene can be isolated, it is a rather labile substance and rapidly polymerizes at room temperature. Bismuth trichloride reacts with 6 in the same manner, generating 8f. Treating 8f with base at ambient temperature causes loss of HCl but affords only intractable material. However, the intermediate bismabenzene has been detected spectroscopically¹² and via chemical trapping.¹³

Our facile synthesis has provided us with a unique family of heterobenzenes. Taken together with the parent pyridine, this series contains aromatic compounds in which carbon is multiply bonded to an entire column of elements. We hope that a detailed comparative study of their spectra and chemistry will provide key insight into the concepts of aromaticity and π bonding between carbon and other elements. The present Account summarizes results obtained to date.

The Spectra of the Group 5 Heterobenzenes

Considerable progress has been made in the investigation of the spectral properties of phosphabenzene, arsabenzene, and stibabenzene, while less data are available from the highly labile bismabenzene. Those spectra which bear most closely on the question of the aromaticity of heterobenzenes are now discussed.¹

(1) The empirical concept of aromaticity defies precise definition. A nonrigorous but operationally satisfactory approach is to discuss aromaticity in terms of "aromatic character". The particular properties of benzene and benzene-like molecules define aromatic character. For more detailed discussion of this problem see: (a) G. M. Badger, "Aromatic Character and Aromaticity", Cambridge University Press, New York, N.Y., 1969; (b) P. J. Garratt, "Aromaticity", McGraw-Hill, London, 1971; (c) G. Binsch, *Naturwissenschaften*, **60**, 369 (1973).

(2) G. Maerkl, *Angew. Chem., Int. Ed. Engl.*, **5**, 846 (1966).

(3) For reviews see: G. Maerkl, *Lect. Heterocycl. Chem.*, **1**, S-69 (1972); P. Jutzi, *Angew. Chem., Int. Ed. Engl.*, **14**, 232 (1975).

(4) K. Dimroth, *Fortschr. Chem. Forsch.*, **38**, 1 (1973).

(5) P. deKoe and F. Bickelhaupt, *Angew. Chem., Int. Ed. Engl.*, **6**, 567 (1967); **7**, 889 (1968); P. deKoe, R. van Veen, and F. Bickelhaupt, *ibid.*, **7**, 465 (1968).

(6) P. Jutzi and K. Deuchert, *Angew. Chem., Int. Ed. Engl.*, **8**, 991 (1969).

(7) H. Vermeer and F. Bickelhaupt, *Angew. Chem., Int. Ed. Engl.*, **8**, 992 (1969); *Tetrahedron Lett.*, 3255 (1970).

(8) L. Maier, D. Seyferth, F. G. A. Stone, and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 5884 (1957).

(9) A. J. Ashe, III, and P. Shu, *J. Am. Chem. Soc.*, **93**, 1804 (1971).

(10) A. J. Ashe, III, *J. Am. Chem. Soc.*, **93**, 3293 (1971).

(11) A. J. Ashe, III, *J. Am. Chem. Soc.*, **93**, 6690 (1971).

(12) A. J. Ashe, III, *Tetrahedron Lett.*, 415 (1976).

(13) A. J. Ashe, III, and M. D. Gordon, *J. Am. Chem. Soc.*, **94**, 7596 (1972).

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Table I
Proton Chemical Shifts of Heterobenzenes^a

Position	Benzene	Pyridine ^b	Phosphabenzene	Arsabenzene	Stibabenzene	Bismabenzene
H _α (H ₂ , H ₆)	7.37	8.29	8.61	9.68	10.94	13.25
H _β (H ₃ , H ₅)		7.38	7.72	7.83	8.24	9.8
H _γ (H ₄)		7.75	7.38	7.52	7.78	7.8 ^c

^a Chemical shift values are in ppm downfield from Me₄Si. ^b W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Can. J. Chem.*, **35**, 1489 (1957). ^c Assignment is only tentative due to relatively poor quality of the spectrum.

Table II
¹³C Chemical Shifts of Heterobenzenes and ¹J¹³CH Values

	Benzene ^a	Phosphabenzene	Arsabenzene	Stibabenzene
δ C ₂	128.7 (159) ^b	154.1 (157)	167.7 (159)	178.3 (158) ^c
δ C ₃		133.6 (156)	133.2 (157)	134.4 (153) ^c
δ C ₄		128.8 (161)	128.2 (161)	127.4 (---)

^a J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972. ^b J values in parentheses; hertz. ^c The ¹J_{13CH} values recorded are those for the more stable 4-methylstibabenzene.

NMR Characteristics. The currently most popular criterion of aromaticity relies on magnetic phenomena of conjugated molecules, which are conveniently measured by proton NMR spectroscopy. In particular, the peripheral protons of planar aromatic molecules show low-field chemical shift values which are attributed to the presence of a diamagnetic ring current.¹

The proton chemical shift values of all of the heterobenzenes are listed in Table I.^{12,14} Surely the most striking feature of these spectra is the large downfield shift of the α(H₂,H₆) protons that increases progressively with the atomic number of the group 5 atom. This shift relative to benzene increases from 1.2 ppm for phosphabenzene to 5.9 ppm for bismabenzene. The β(H₃,H₅) and γ(H₄) shifts also follow the same qualitative trend, but the shift magnitudes are considerably smaller. Interestingly, all of the chemical shift values of the heterobenzenes are downfield from benzene.

The major portion of the downfield shift must be accounted for by the effect of the magnetic anisotropy of the increasingly large heteroatom.¹⁴ Magnetic anisotropic effects are strongly dependent on internuclear separation (*R*⁻³ in the McConnell equation)¹⁵ and should decrease dramatically for the protons remote from the heteroatom.¹⁴ A plot of *R*_{EH}⁻³ vs. the observed shift allows extrapolation of the local magnetic anisotropic effects to zero. After this correction, the heavier heterobenzenes have residual chemical shift values at higher field than benzene (δ₀ 7.0 for phosphabenzene, δ₀ 6.8 for arsabenzene, and δ₀ 6.6 for stibabenzene). These residual upfield shifts are consistent with decreasing ring currents and hence decreasing aromaticity for the heavier heterobenzenes.

The ¹³C NMR data are collected in Table II.^{14,16} There is rather little variation of the chemical shift values of β- and γ-carbon atoms from that of benzene. However, the deshielding of the α-carbon atoms is progressive in the series phosphabenzene, arsabenzene, and stibabenzene. This reflects a similar trend in the α protons of the heterobenzenes. The source of this large downfield shift is not well explained by the current MO theory of magnetic shielding.¹⁷ However, it is

(14) A. J. Ashe, III, R. R. Sharp, and J. W. Tolman, *J. Am. Chem. Soc.*, **98**, 5451 (1976).

(15) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(16) Data for pyridine are omitted from Table II, although discussed in detail in ref 14. Unlike the heavier heterobenzenes, charge density effects appear to be very important for understanding the pyridine spectra.

(17) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

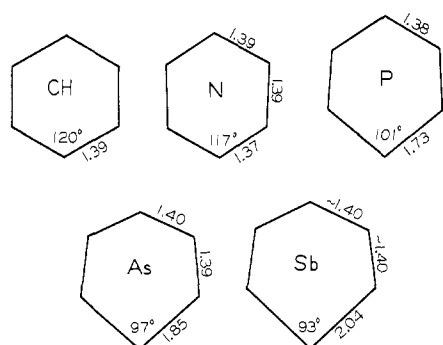


Figure 1. Structural parameters of the C₅H₅E molecules, benzene, pyridine, phosphabenzene, arsabenzene, and stibabenzene. (In each case the heteroatom occupies the lowest vertex of the hexagon.)

interesting to note that other compounds with carbon-metal atom multiple bonds also show low-field carbon signals.¹⁸

Finally, one might note that the one-bond ¹³CH coupling constants of the heavier heterobenzenes are remarkably similar to that of benzene.¹⁶ Since ¹J_{CH} values are usually assumed to be related to the percent s character of the CH bond, hybridization close to pure sp² is suggested.¹⁹

Structural Data. Structural data have played an important role in defining aromaticity.¹ The planarity, lack of bond alternation, and multiple bond character of the ring bonds of pyridine and benzene are associated with their aromaticity.

Gas-phase structural data have been obtained from electron diffraction^{20,21} and the microwave spectral studies^{22,23} of phosphabenzene and arsabenzene, while only microwave data²⁴ are available for stibabenzene. These data are illustrated in Figure 1.

Planar molecules have only two independent moments of inertia. Measurement of this inertial defect

(18) For carbene-transition metal complexes see: S. J. McLain, C. D. Wood, and R. R. Schrock, *J. Am. Chem. Soc.*, **99**, 3519 (1977), and references cited therein.

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

(20) T. C. Wong and L. S. Bartell, *J. Chem. Phys.*, **61**, 2840 (1974).

(21) T. C. Wong, A. J. Ashe, III, and L. S. Bartell, *J. Mol. Struct.*, **25**, 65 (1975).

(22) R. L. Kuczkowski and A. J. Ashe, III, *J. Mol. Spectrosc.*, **42**, 457 (1972).

(23) R. P. Lattimer, R. L. Kuczkowski, A. J. Ashe, III, and A. L. Meinzer, *J. Mol. Spectrosc.*, **57**, 428 (1975).

(24) R. L. Kuczkowski, G. Fong, and A. J. Ashe, III, *J. Mol. Spectrosc.*, in press.

is the most sensitive criterion of the planarity molecules.²⁵ The small experimental defect measured from the microwave spectra proves that all of the heterobenzenes are planar.^{22-24,26}

All the C-C bond lengths of pyridine, phosphabenzene, arsabenzene, and stibabenzene are extremely close to the "normal" aromatic bond length (1.395 Å) of benzene. Indeed, the variation of this series is smaller than that of the bonds of naphthalene and other fused benzocyclic systems.²⁷

The C-E bonds of the heterobenzenes are short in comparison to normal C-E single bonds.²⁸ For example, the CP bond of phosphabenzene is 7.5% shorter than the sum of the covalent radii of C and P.²⁹ The corresponding contractions are 6.6% for arsabenzene and 6.4% for stibabenzene.²⁹ Therefore, the C-E bonds possess appreciable multiple bond character.

The increased bond length in going from the C-C bonds of benzene to the CE bonds of the heterobenzenes combined with the progressive decrease in the CEC bond angle serves to minimize the structural change in the carbocyclic portion of the molecule. Thus, the ECC and CCC bond angles only slightly exceed the 120° benzene angles. However, it might be noted that the decreasing CEC bond angle is consistent with the trend of acyclic group 5 compounds.²⁸ Thus, the large heteroatoms are easily accommodated in the six-membered rings without added structural strain.

UV Photoelectron Spectra. Aromaticity is frequently defined in terms of a similarity of π bonding to that of benzene.¹ One of the more direct methods for probing the electronic structure of molecules is by the use of UV photoelectron spectroscopy.³⁰ PE spectroscopy allows the observation of all the ionization potentials of a molecule which correspond to energy differences between the ground state and various radical cation states. With due caution they are usually associated with the orbital energies of filled molecular orbitals of the ground state. Thus, the technique permits a "reading off" of the orbital energies and is an effective probe of electronic structure.

If the heterobenzenes are electronically similar to benzene, it would be valid to treat the replacement of the CH unit by E as a first-order perturbation.^{30,31} Thus, a carbon 2p atomic orbital should be replaced by an element np atomic orbital in the π system of benzene. The shift in energy, δe_j , of the benzene HMO

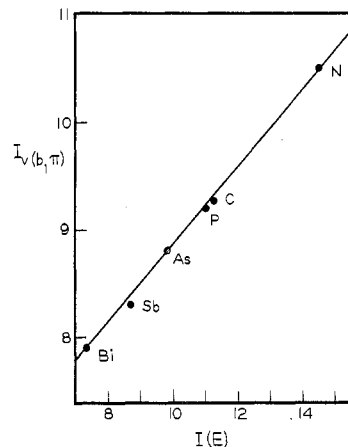
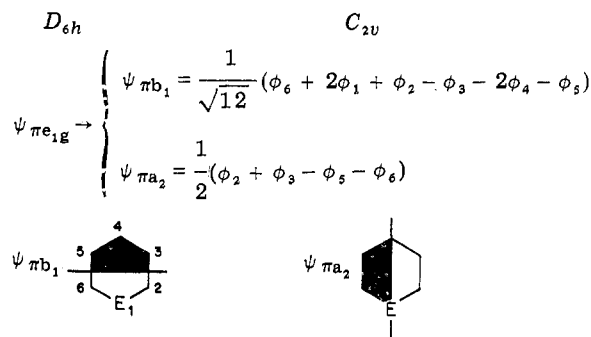


Figure 2. Regression of the ionization energies ($I_v(b_{1\pi})$) of the molecules C_5H_5E on the atomic ionization energies $I(E)$ of the free atoms $E = N, C, P, As, Sb,$ and Bi . (Energies are in electronvolts.)

orbital ψ_j by the perturbation $\delta\alpha_{jE}$ should be proportional to the square of the coefficient, c_{jE}^2 , of atom E.

For example, the highest occupied π -MO's of benzene are a degenerate pair of e_{2g} orbitals. In the C_{2v} symmetry of the heterobenzenes, these are split into orbitals of a_2 and b_1 symmetry.



Since the a_2 orbital has a node at atom E ($c_{a_2E} = 0$), its energy is expected and found to be roughly invariant with charges in E.³¹ On the other hand, for the b_1 orbital the shift in energy should be proportional to α_E (as measured by the ionization potential of the free atom E). A plot of the free atom ionization potentials of atoms E and the πb_1 ionization potentials should be linear. The experimental linear plot illustrated in Figure 2 shows a slope of 0.36, in almost perfect accord with the expected value ($c_{b_1E}^2 = 0.33$) from the first-order perturbation of the benzene HMO orbital. A similar correlation applies to the lower πa_{1u} orbital. The quality of this correlation as well as the overall similarity of the PE spectra of all the heterobenzenes conclusively demonstrate great similarity in the bonding of the heterobenzenes. This similarity is also supported by ab initio³² and other more sophisticated calculations.³³

Chemical Studies

Spectroscopic studies have shown that the λ^3 -heterobenzenes possess a high degree of aromatic character. Studies of chemistry of the heavier heter-

(25) T. Oka and Y. Morino, *J. Mol. Spectrosc.*, **6**, 472 (1961).

(26) For pyridine see: G. O. Sorensen, L. Mahler, and N. Rastrup-Andersen, *J. Mol. Struct.*, **20**, 119 (1974).

(27) D. W. J. Cruickshank and R. A. Sparks, *Proc. R. Soc. London, Ser. A*, **258**, 270 (1960); A. Almendinger, O. Bastiansen, and F. Dyvik, *Acta Crystallogr.*, **14**, 1056 (1961); G. S. Pawley and E. A. Yeats, *Acta Crystallogr., Sect. B*, **25**, 2009 (1969).

(28) For comparison the following structural parameters of "normal" tricoordinate group 5 compounds are listed: $(CH_3)_3P$: $r(PC) = 1.84$ Å, $\angle CPC = 98.9^\circ$, P. S. Bryan and R. L. Kuczkowski, *J. Chem. Phys.*, **55**, 3049 (1971); $(CH_3)_3As$: $r(AsC) = 1.96$ Å, $\angle CAsC = 96^\circ$, D. R. Lide, Jr., *Spectrochim. Acta*, **15**, 473 (1959); $Sb(CF_3)_3$: $r(SbC) = 2.20$ Å, $\angle CSbC = 100^\circ$, H. J. M. Bowen, *Trans. Faraday Soc.*, **50**, 463 (1954).

(29) The covalent radii are: 0.77, C; 1.10, P; 1.21, As; 1.41, Sb; and 1.52, Bi; from F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed., Wiley, New York, N.Y., 1966.

(30) For a general discussion of the application of PE spectra to these and similar compounds see: H. Bock, *Pure Appl. Chem.*, **44**, 343 (1975); E. Heilbronner, J. P. Maier, and E. Haselbach, *Phys. Meth. Heterocycl. Compd.*, **6**, 1 (1974).

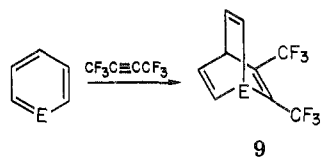
(31) C. Batich, E. Heilbronner, V. Hornung, A. J. Ashe, III, D. T. Clark, U. T. Cogley, D. Kilcast, and I. Scanlan, *J. Am. Chem. Soc.*, **95**, 928 (1973); J. Bastide, E. Heilbronner, J. P. Maier, and A. J. Ashe, III, *Tetrahedron Lett.*, **411** (1976).

(32) D. T. Clark and I. W. Scanlan, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1222 (1974).

(33) W. von Niessen, G. H. F. Diercksen, and L. S. Cederbaum, *Chem. Phys.*, **10**, 345 (1975); M. H. Palmer, R. H. Findlay, W. Moyes, and A. J. Gaskell, *J. Chem. Soc., Perkin Trans. 2*, 841 (1975).

obenzene have revealed further similarities to benzene, although their chemistry is rather divergent from that of pyridine.

Cycloaddition Reactions. Many aromatic hydrocarbons behave as dienes in the Diels–Alder reaction. Even benzene will react under forcing conditions (200 °C) with hexafluoro-2-butyne to give the indicated barrelene **9a**.³⁴ For comparison we have examined the

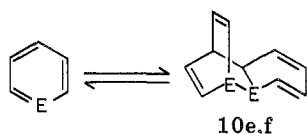


- 9
 a, E = CH
 c, E = P
 d, E = As
 e, E = Sb
 f, E = Bi

reaction of the group 5 heterobenzenes with dienophiles. The highly nucleophilic pyridine does not show Diels–Alder reactions but instead gives Michael addition to dienophiles.³⁵ In contrast, phosphabenzene reacts with hexafluoro-2-butyne at 100 °C to yield the corresponding 1-phosphabarrelene **9c**.^{13,36} Arsabenzene gives an analogous adduct **9d** at 25 °C while stibabenzene and bismabenzene react at even lower temperatures, yielding **9e** and **9f**.¹³

Qualitatively, the heavier heteroaromatics react more rapidly. The relative reactivity of many benzocyclic aromatic compounds correlates well with the loss of resonance energy from isolating the 1- and 4-positions from π conjugation.³⁷ Thus, it is tempting to associate the greater reactivity of the heavier heteroaromatics with a decrease in resonance energy of these rings.¹³

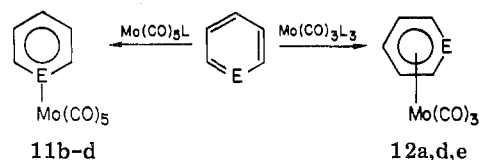
Bismabenzene is so reactive that it exists in the form of a Diels–Alder dimer (**10f**) at low temperature (<–10 °C).¹² Although the equilibrium is much less favorable, stibabenzene yields an analogous dimer **10e** at $T < -50$ °C.³⁸



Reactions with Lewis Acids. The chemistry of pyridine is dominated by the basicity of its heteroatom. As nitrogen is replaced by its more electropositive congeners one expects this basicity to be diminished. As had previously been observed for the highly substituted phosphabenzene,^{3,4} we have been unable to demonstrate that the heteroatoms of phosphabenzene and arsabenzene have any basic properties toward proton acids or alkylating agents. For example, they are not detectably protonated in trifluoroacetic or other strong acids.³⁹ In contrast to simple phosphines and arsines, they cannot be quaternized by methyl iodide or dimethyl sulfate.⁴⁰

Although the negligible basicity of phosphabenzene may be due to an electronic effect on the phosphorus lone pair,⁴¹ we suggest an alternative explanation. It is well-known that the usual phosphine and arsine bond angles (near 100°)²⁸ expand on quaternization.⁴² Expansion of the C_2PC_6 (or C_2AsC_6) bond angle of phosphabenzene or arsabenzene must push carbon atoms C_2 and C_6 apart. Appreciable separation of C_2 and C_6 can only be achieved by considerable bond-angle deformation in the carbocyclic portion of the molecule. Thus, the low basicity might be ascribed to the difficulty in achieving this structural change rather than any electronic peculiarity of the heteroatom lone pair.⁴³

In contrast to quaternization by “hard acids”, coordination of ordinary phosphines and arsines to transition metals does not markedly change the CPC (or CAsC) bond angles.⁴⁴ Thus, it is expected that phosphabenzene and arsabenzene should be able to form transition-metal σ complexes. Indeed, Noeth has demonstrated that 2,4,6-triphenylphosphabenzene forms a variety of σ complexes with $Cr(CO)_5$, $Mo(CO)_5$, and $W(CO)_5$.⁴⁵ We find that both phosphabenzene and arsabenzene give $Mo(CO)_5$ σ complexes by ligand displacement from $Mo(CO)_5$ complexes.⁴⁰ Spectroscopic measurements indicate that phosphabenzene is a weaker ligand than pyridine, although slightly stronger than arsabenzene. As yet, we have been unable to prepare presumably weaker stibabenzene σ complexes.



Electron-rich aromatic molecules are good π bases.⁴⁶ Since the π ionization potentials of all the heavier heterobenzenes are less than that of benzene,³¹ one expects them to be able to form π metal complexes. Noeth has prepared several π - $M(CO)_3$ -triphenylphosphabenzene complexes.⁴⁷ We have not yet succeeded in preparing π metal complexes of phosphabenzene, but both arsabenzene and stibabenzene give stable π - $Mo(CO)_3$ adducts **12d,e**.⁴⁰ Production of **12e** was particularly gratifying since the complex appears more stable than stibabenzene itself. Apparently, as in $Fe(CO)_3$ -cyclobutadiene, the transition metal stabilizes the high-energy π system.⁴⁸ We now have great hope that the even more labile bismabenzene can be similarly stabilized.

While the heteroatoms of the heterobenzenes are nonbasic, we have found evidence for C-protonation in

(34) J. Colburn, Ph.D. Thesis, The University of Michigan, 1977.

(41) H. Oehling and A. Schweig, *Tetrahedron Lett.*, 4941 (1970).

(42) For structures of phosphonium and arsonium salts see: R. M. Wing, *J. Am. Chem. Soc.*, 90, 4828 (1968), and J. Drummond and J. S. Wood, *J. Chem. Soc. A*, 226 (1970).

(43) The calculated low basicity of phosphabenzene is not inconsistent with this argument since the geometry was assumed not to change on protonation: H. Oehling and A. Schweig, *Phosphorus*, 1, 203 (1970), and ref 32.

(44) For a triphenylphosphine complex see: S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965).

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(46) R. B. King, “Transition-Metal Organometallic Chemistry”, Academic Press, New York, N.Y., 1969, pp 68–69.

(47) J. Deberitz and H. Noeth, *Ber.*, 103, 2541 (1970); 106, 2222 (1973); H. Vahrenkamp and H. Noeth, *Ber.*, 105, 1148 (1972).

(48) See F. A. Cotton, “Chemical Applications of Group Theory”, Wiley, New York, N.Y., 1963, pp 132, 180.

(34) R. S. H. Liu, *J. Am. Chem. Soc.*, 90, 215 (1968).

(35) R. Huisgen, *Top. Heterocycl. Chem.*, 223 (1969).

(36) G. Maerkl and F. Lieb, *Angew. Chem., Int. Ed. Engl.*, 7, 733 (1968).

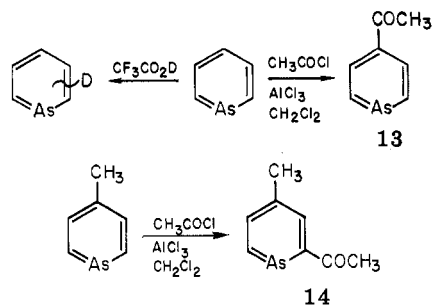
(37) A. Streitwieser, Jr., “Molecular Orbital Theory for Organic Chemistry”, Wiley, New York, N.Y., 1961, pp 432–438.

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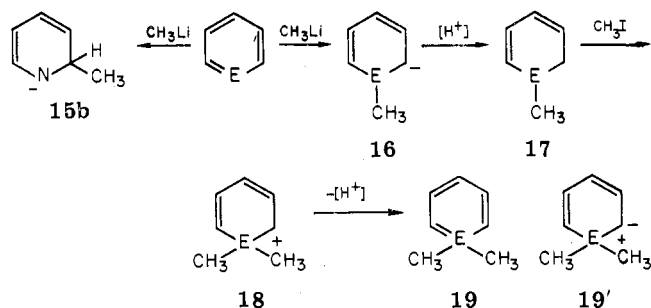
arsabenzene. Deuteriotrifluoroacetic acid converts arsabenzene to a mixture of arsabenzene-*d*₁ and -*d*₂.³⁹ At present, we do not know the position of substitution on the ring, although competition experiments with benzene indicate arsabenzene is more reactive. Since this reaction represents the prototype for electrophilic aromatic substitution, we intend to look at it in detail.

Encouraged by the deuterium-exchange experiments, we have examined more classical aromatic substitution reactions. Indeed, Friedel-Crafts acylation of arsabenzene gave a 75% yield of 4-acetylarsabenzene (13),



while 4-methylarsabenzene gave only a low yield of the 2-acetyl derivative 14.³⁹ Qualitatively, arsabenzene is more reactive than benzene. As yet, we have not explored substitution reactions of the other heterobenzenes.

Reactions with Lewis Bases; Synthesis of λ⁵-Heterobenzenes. It is well-known that strong bases such as alkyl lithium reagents attack pyridine at its most electropositive atom, the α carbon, to give the charge delocalized anion 15b.⁴⁹ On the other hand, methyl-



lithium adds to the more electropositive heteroatoms of the heavier heterobenzenes to yield the corresponding lithium 1-methylheterocyclohexadienides 16c-e.^{50,51} These anions show ¹H and ¹³C NMR spectra which are typical for pentadienyl carbanions.⁵² They may be reversibly quenched to the methyl heterocyclohexadienes 17c,d.

In the case of the arsenic and phosphorus compounds, dienes 17 could be easily converted into the corresponding λ⁵-heterobenzenes. Thus, quaternization with methyl iodide followed by deprotonation with dimethyl anion gave 1,1-dimethyl-λ⁵-phosphabenzene (19c) and

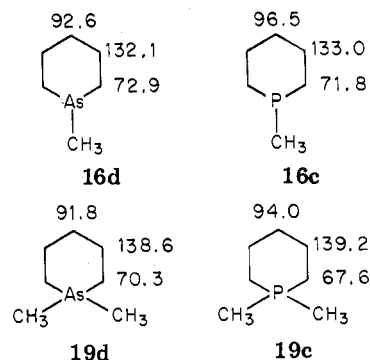


Figure 3. ¹³C NMR chemical shift values for the ring carbon atoms of the lithium heterocyclohexadienides and the corresponding 1,1-dimethyl-λ⁵-heterobenzenes.^{51,53}

the first λ⁵-arsabenzene, 19d.⁵³

Should we regard these λ⁵-heterobenzenes as aromatic systems (structure 19), or are they better regarded as delocalized ylides (structure 19')? NMR spectroscopy provides an unambiguous answer. The H₂, H₄, and H₆ protons of 19 have chemical shift values well upfield from the aromatic region. Although the H₃ and H₅ protons of 19 are more highly shielded, even they occur upfield from the corresponding H₃ protons of conjugate acid 18. These upfield shifts suggest that there are no appreciable ring-current effects in λ⁵-phosphabenzene and λ⁵-arsabenzene. In fact, the strong shielding of H₂, H₄, and H₆ indicates that these protons bear a high electron density. The ¹³C NMR spectra of 19 further support this conclusion. Signals for C₂ and C₆ occur more than 60 ppm upfield from the normal aromatic/olefinic absorption region. It is particularly striking that the chemical shift values of ylides 19 are nearly identical with those of anions 16 (Figure 3). Thus, we must view the ring carbon atoms as favoring a pentadienyl anion structure which is stabilized largely by electrostatic interaction with positive heteroatoms. In contrast to the aromatic λ³-heterobenzenes, the λ⁵-heterobenzenes appear to be ylidic in character.⁵⁴

Summary

Clearly much work remains to be done, but in the broad outline the properties of the λ³-heterobenzenes are clear. Phosphabenzene and particularly arsabenzene resemble their more familiar benzocyclic relatives, while even the more labile stibabenzene and bismabenzene seem qualitatively similar. At first it appears somewhat disconcerting to the organic chemist that elements as different from carbon as phosphorus, arsenic, antimony, and bismuth can take part in aromatic π bonding. However, it is ultimately reassuring that our venerable concept of aromaticity has a greater generality than we had suspected.

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