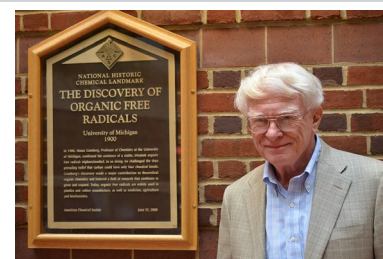


Low-Coordinate Phosphorus Compounds

The Route to Phosphabenzene and Beyond

Arthur J. Ashe III*[a]

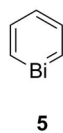
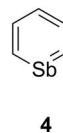
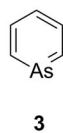
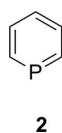
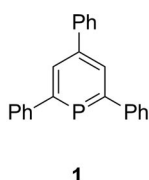


Abstract: This article presents the background of the author's synthesis of phosphabenzene in 1971. It also expands to tell the story behind the syntheses of the heavier group 15 hetero-

benzenes: arsabenzene, stibabenzene, and bismabenzene, which were prepared nearly at the same time and by a largely similar route.

In 1966 Gottfried Märkl reported the synthesis of 2,4,6-triphenylphosphabenzene (**1**), which is a stable yellow crystalline compound.^[1] To put the synthesis of **1** in its proper historical perspective, one should recall that prior to the 1970s it was widely felt that, "...*p-p* π -bonding is of little importance in the third and higher period elements...".^[2] Yet 2,4,6-triphenylphosphabenzene must contain a phosphorus-carbon (3p-2p) π -bond! Presumably, the aromaticity of **1**, or perhaps the heavy substitution, compensated for any lability of this bond. It is highly appropriate to commemorate Märkl's seminal breakthrough on its 50th anniversary.

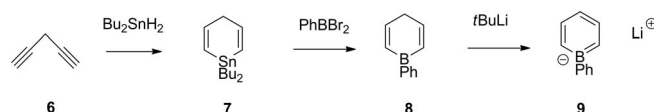
Professor Müller has asked me to write an article about the background of our 1971 synthesis of the parent phosphabenzene (**2**).^[3] I am pleased to do so but have expanded the coverage to all of the heavier group 15 heterobenzenes: arsabenzene (**3**),^[3] stibabenzene (**4**),^[4] and bismabenzene (**5**),^[5] since they were prepared at essentially the same time as **2** and by a largely similar route. It is also important to note that the bonding in **3**, **4**, and **5** place that of phosphabenzene in context.



I was trained as a physical organic chemist at Yale University in Kenneth B. Wiberg's laboratory. At that time inorganic chemistry was not a big part of the curriculum, and indeed I never took a formal course in it. One thing I did take away from that education was a fascination with molecules of theoretical inter

est, particularly those without perturbing substituents. My 1966 Ph.D. dissertation concerned carbocation rearrangements of bicyclic tosylates, an aspect of the then popular "non-classical carbocation problem."^[6] After I arrived at the University of Michigan in the fall of 1966, I recall feeling that the field of carbocation rearrangements had become a bit crowded. Perhaps it might be prudent to try to find another research area. I then made a small step towards main-group organometallic chemistry by examining sigmatropic rearrangements of trimethylsilylcyclopentadienes.^[7]

I also became interested in preparing lithium 1-phenylboratabenzene (**9**). It seemed to me that the novel **9** might be an aromatic anion with cyclopentadienide-like properties. Although **9** was unknown when we initiated this work, Herberich and coworkers reported a cobalt complex of **9** in 1970.^[8] In late 1968, I interested my first graduate student, Paul Shu, in preparing **9**. We selected a route (**6** through **9**), in which one of the key steps involved a boron/tin exchange. By the end of 1970, Paul had finished enough of the work so that it was in publishable form (see Scheme 1).^[9]

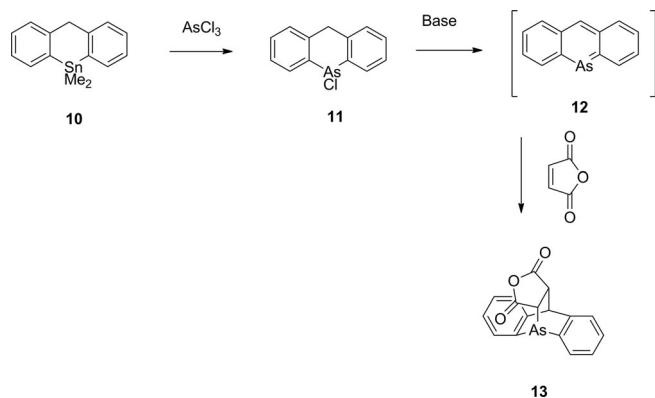


Scheme 1. The synthesis of lithium 1-phenylboratabenzene (**9**).

In 1969, two back-to-back papers in *Angew. Chem.*, one by Jutzki and Deuchert^[10] and the other by Bickelhaupt and Vermeer,^[11] attracted my attention in a very compelling way. It was reported that tin compound **10** underwent a facile arsenic/tin exchange reaction with arsenic trichloride to afford **11**. Treating **11** with base effected HCl elimination to give 9-arsanthracene (**12**). Although **12** is too reactive to be isolated, it could be detected by using UV spectroscopy and chemical trapping (see Scheme 2).

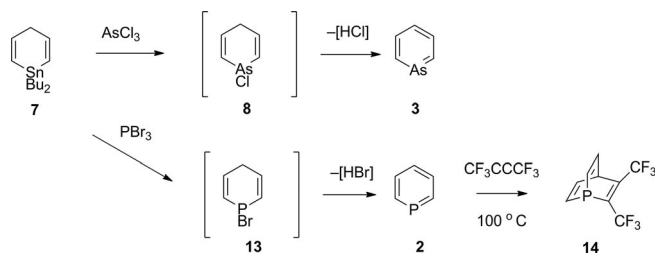
It was clear to me (and I suspect to knowledgeable readers of our 1971 *J. Am. Chem. Soc.* communication^[9]) that **7** was an ideal precursor for the parent arsabenzene. Of course its stability was unknown, but it seemed likely that it might be de-

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Scheme 2. The synthesis of 9-arsanthracene.

tected/trapped in a similar manner to 9-arsanthracene above. Therefore, I knew that our laboratory had to try reactions that lead from **7** to **3** (Scheme 3) before another laboratory did so. It seemed unfair to divert Paul from his productive thesis work, and since there were no other coworkers I did the work myself.



Scheme 3. The syntheses of arsabenzene (**3**) and phosphabenzene (**2**).

In March 1971 I carried out the reaction of **7** with arsenic trichloride (Scheme 3). It was surprising and very exciting that the product was not precursor **8** but arsabenzene itself! Most surprising was the fact that arsabenzene was a stable distillable liquid. Encouraged by this result, I tried the reaction of **7** with phosphorus tribromide the next week (March 24, 1971 to be precise). Again the reaction gave phosphabenzene directly as a distillable liquid. Although phosphabenzene is oxygen-sensitive, it seemed to be remarkably unreactive. Later we noted that it needed a temperature of 100 °C for phosphabenzene to undergo the Diels–Alder reaction with the reactive dienophile hexafluorobutylene.^[5] For comparison, the more reactive arsabenzene reacts with hexafluorobutylene at 25 °C to give an analogous adduct.^[5]

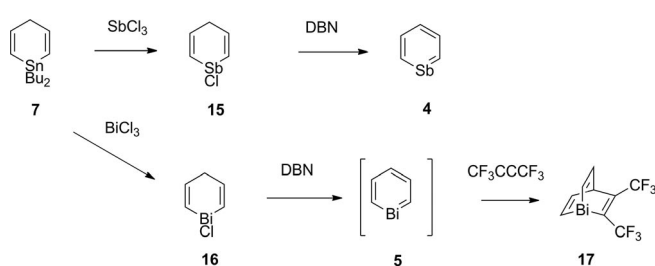
It was relatively easy to extend these syntheses to stibabenzene (**4**)^[4] and bismabenzene (**5**)^[5,12] as illustrated in Scheme 4. The reaction of **7** with antimony trichloride gave 1-chloro-1-stibacyclohexa-2,5-diene (**15**) as a crystalline solid. On treatment with base, **15** was converted to the highly labile but isolable stibabenzene. Similarly, the reaction of **7** with bismuth trichloride afforded the crystalline 1-chloro-1-bismacyclohexa-2,5-diene (**16**). Treating **16** with base effected HCl elimination to afford solutions of bismabenzene, which could be detected

spectroscopically^[12] and by chemical trapping, for example, to give **17**.^[5]

These facile syntheses afforded a unique series of group 15 heterobenzenes. Taken together with pyridine, the series consists of aromatic compounds in which carbon is π -bonded to an entire column of group 15 elements. A preliminary inspection of routine spectra [even in 1971] seemed to require that p–p π -bonding be the central feature of the structures of the group 15 heterobenzenes. At this point, I felt it was important to collaborate with a group of physical chemists/spectroscopists who could apply more sophisticated spectroscopic tools to this important problem.

It was particularly easy to collaborate with my excellent colleagues at the University of Michigan. Professor Robert Kuczkowski and coworkers measured the microwave spectra of **2**, **3**, and **4** from which it was established that the molecules are planar with C_{2v} symmetry.^[13] Professor Lawrence Bartell and T. C. Wong evaluated the electron diffraction of **2** and **3**, which allowed them to determine these structures in the gas phase.^[14] Professor Robert Sharp and J. Tolan analyzed the NMR spectra of **2**, **3**, and **4**, which allowed them to determine the effects of the diamagnetic ring currents and hence their aromaticity.^[15] Finally, Professor Edgar Heilbronner and coworkers at the Physical Chemical Institute of the University of Basel measured the UV photoelectron spectra of **2**, **3**, **4**, and **5**.^[16] Analysis of the spectra allowed them to follow trends in ionization potentials of the molecules. The great similarities of the photoelectron spectra of all of the heterobenzenes is indicative of great similarities in π -bonding in the series.

The chemistry of the group 15 heterobenzenes has been reviewed^[17] and is beyond the scope of this essay. However, returning to the quotation in the first paragraph, it can be concluded that p–p π -bonding may be important even for the heaviest of elements.



Scheme 4. The syntheses of stibabenzene (**4**) and bismabenzene (**5**).

Acknowledgments

It is a pleasure to acknowledge the contributions of my colleagues and coworkers. I am especially grateful to Dr. Paul Shu who originally prepared the key synthon stannacyclohexadiene **7**.

Keywords: Aromaticity · Group 15 elements · Heterocycles · π -Bonding

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