

dodecapeptide **5** does not seem to follow this trend, which may suggest that secondary interactions exist between the terpenoid and peptide moieties.

Although we still need to perform many experiments to develop a reliable mechanistic model to explain the observed phenomenon, our preliminary observations show an interesting potential in this area and investigation along this line is in progress in our laboratories.

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Supplementary Material Available: Experimental details for the synthesis of **2-5**, ^1H NMR spectra of the key compounds, and ^1H NMR spectra for the determination of asymmetric induction (18 pages). Ordering information is given on any current masthead page.

"Quaternary Ammonium Amalgams" as Zintl Ion Salts and Their Use in the Synthesis of Novel Quaternary Ammonium Salts

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We propose that "quaternary ammonium amalgams" are Zintl ion salts of empirical formula $\text{R}_4\text{N}^+\text{Hg}_4^-$ and that these salts, upon treatment with NaA, can be used to synthesize less easily prepared quaternary ammonium salts, $\text{R}_4\text{N}^+\text{A}^-$. Production of "ammonium amalgams"¹ and quaternary ammonium amalgams²⁻⁵ by reductions of salts at a mercury electrode have been reported many times, although a clear characterization of the nature of the "amalgam" produced and the presumed reduced ammonium species has not been obtained. An alternative description of these species can be given within the Zintl ion framework,⁶ i.e., as ammonium salts of an anionic mercury species. To investigate this possibility, we undertook a study of the stoichiometry of the electroreduction reaction and the regeneration of the R_4N^+ from the product upon chemical oxidation. A mercury electrode consisting of a weighed amount of Hg in a glass cup contacted

by a small (area, ca. 0.2 mm²) Pt wire was used to electrolyze 30 mL of a 1.5 M $\text{TBA}^+\text{PF}_6^-$ (where TBA^+ is tetra-*n*-butylammonium)-acetonitrile (MeCN) solution at -20 °C, with the Hg maintained at -4.5 V vs. a silver wire quasi-reference electrode immersed in the same solution and held in a separate reference electrode chamber. The electrolysis was carried out until 50-100 C were passed. During electrolysis the Hg surface was covered with a black layer, and finely divided particles of product were dispersed into solution. The unreacted Hg was washed with pure solvent, dried with a tissue, and weighed. For three trials, the moles of Hg reacted per faraday was 4.1 ± 0.2 . Thus, the reduction reaction can be written as



Note, however, that in earlier papers, on the basis of analyses of the product isolated after electrolysis, quaternary ammonium/Hg ratios of 1:12-13³ and 1:11.6-14.4⁴ were proposed. One problem with isolation and analysis of product is its high reactivity with O₂ and moisture.

To study the regeneration of the quaternary ammonium ion from the product and the use of an electrolysis procedure to convert an easily obtainable salt, e.g., TBABr , to one with a different anion, e.g., TBAPF_6 , bulk electrolysis at a large area (3 cm²) Hg pool was undertaken. The cell was a three-compartment cell, with two fine-porosity sintered-glass disks separating the working and counter electrodes. The solution, 0.1 M TBABr -MeCN held at -20 °C, showed an interelectrode resistance initially of 2-3 kΩ. A potential of -10.0 V vs. Ag quasi-reference electrode was applied to the Hg pool; this value was chosen to be sufficiently negative that the actual potential drop at the Hg/solution interface would be maintained at the background reduction level as the solution resistance increased. After 2.5 h of electrolysis, the current, initially about 3.5 mA, decayed to 3.2 μA, and the interelectrode resistance increased to about 3 MΩ (as compared to 5-10 MΩ for pure MeCN in the cell). Thus, electrolysis had depleted the electrolyte via the reaction in eq 1 at the Hg pool and Br⁻ migration to the counter electrode chamber, where it was oxidized. The rest potential of the Hg pool after electrolysis was about 3.6-3.9 V more negative than the initial value. During electrolysis the Hg pool became covered with a black layer, and black, finely divided particles dispersed in the solution and eventually settled to the bottom of the cell. The addition of a sodium salt, NaA (A = PF_6^- , F⁻), caused disappearance of the black material, via the proposed reaction



where Na(Hg) represents sodium amalgam. A cyclic voltammogram of the MeCN solution after this procedure at a Pt electrode showed only a small wave for residual bromide ion (equivalent to ca. 4 mM), with the oxidation background occurring at potentials about 1 V more positive (PF_6^- and F⁻ oxidation vs. Br⁻ oxidation). This indicates better than 90% conversion of the Br⁻ salt to the A⁻ form. The product quaternary ammonium salt could be isolated by precipitation with ethyl ether, followed by filtration of the crystals. The NMR of the Bu_4N^+ in the product in deuteriochloroform was essentially the same as that for the starting material, $\text{Bu}_4\text{N}^+\text{Br}^-$, indicating regeneration of the cation upon oxidation of the reduction product. No products from solvent reduction⁹ or tri-*n*-butylamine (characteristic of decomposition of TBA^+) was observed by NMR or IR spectroscopy, suggesting that side reactions that would compromise the coulometric measurement are not important. This electrochemical method should prove useful in preparing less easily obtainable quaternary ammonium salts from R_4NBr .

The electrochemical production of Zintl anions of mercury and other metals as salts of different cations appears promising. Indeed, reduction at an Hg pool in the presence of sulfonium and

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phosphonium ions has been reported⁷ to produce the corresponding "amalgams"; these are probably also the corresponding Zintl anion salts. Similarly, the products of "reduction of tetraalkylammonium ions" on other metals (e.g., Pb, Sn, Sb, and Bi)⁸ probably also leads to the Zintl ion salts.

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Production of a Boraphosphene (RB=PR') in the Vapor Phase by Thermolysis of a Sterically Encumbered Diphosphadiboretane

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Significant recent effort has been devoted to the preparation of compounds exhibiting multiple bonding between the heavier main-group elements, particularly those from groups 14 and 15.^{1,2} Much less is known, however, about the multiple bonding capabilities of the group 13 elements. There are, for example, no heavier congeners of the iminoboranes (RN=BR').³ We report (i) mass spectrometric evidence for the first boraphosphene, (tmp)B=P(Ar) (**1**) (tmp = 2,2,6,6-tetramethylpiperidino; Ar = 2,4,6-*t*-Bu₃C₆H₂), (ii) detection of novel anions of the type [(tmp)(R)B=P(Ar)]⁻ which also appear to exhibit phosphorus-boron multiple bonding, and (iii) a new synthetic approach to diphosphadiboretanes.⁴

Equimolar quantities of (tmp)BCl₂^{3b} and ArP(SiMe₃)Li⁵ were allowed to react in Et₂O at 0 °C then warm to 25 °C. Pale lemon crystals of [(tmp)BP(Ar)]₂ (**2**) formed upon cooling the filtered and concentrated reaction mixture to -20 °C. The 32.38-MHz ³¹P NMR spectrum of **2** (s, -90) was indicative of a four-membered ring.^{4c} This was confirmed by X-ray crystallography (Figure 1).⁶ Considerable strain is apparent in the molecule as evidenced by the following: (i) the P-B bonds in **2** (1.96 (2) Å) are longer

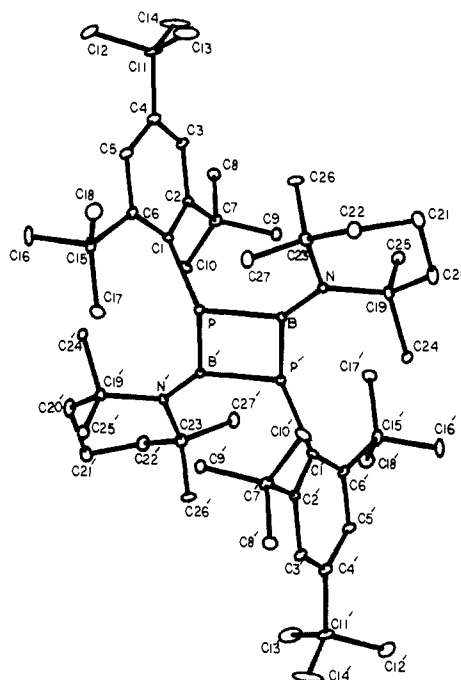


Figure 1. View of **2** showing the atom numbering scheme. The molecule resides on a center of symmetry. Important parameters: P-B 1.96 (2) Å, B-N 1.39 (2) Å, P-C(1) 1.891 (13) Å, B-P-B' 86.9 (8)°, P-B-P' 93.1 (8)°, P-B-N 136.4 (6)°, P'-B-N 136.7 (6)°, B-P-C(1) 119.0 (6)°, B'-P-C(1) 127.8 (6)°.

than those in the less sterically encumbered analogue [(tmp)BP(mesityl)]₂ (**3**, 1.916 (3) Å)^{4c}, (ii) the P₂B₂ moiety of **2** is rhombic while that of **3** is square, (iii) the P-aryl groups of **2** are "bent" in the sense that each phosphorus atom is ~0.7 Å out of the respective aryl plane, and (iv) the phosphorus pyramid of **2** is flatter than that of **3** (sums of angles at P = 329.0° and 339.9° in **2** and **3**, respectively).

Thermolysis of **2** at 250 °C results in the clean production of the boraphosphene (tmp)B=P(Ar) (**1**) in the vapor phase. The highest mass peak in the medium-resolution EI MS (70 eV) of **1** appears at *m/e* 427. The identity of this peak was confirmed by HRMS: calcd for C₂₇H₄₇BNP, 427.3539; found, 427.3551. A chemical ionization MS experiment revealed that even at 120 °C, <1% of the dimer **2** is detectable. Of particular significance is the fact that the fragmentation pattern of **1** is completely different from those of diphosphadiboretanes with less bulky substituents. For example, the 100% intensity peak in the EI MS (70 eV) of **3** occurs at *m/e* 602 and thus corresponds to the parent peak of the dimer. A prominent peak (45%) is also evident at *m/e* 451 and is attributable to loss of a (tmp)B unit from the dimer.

In order to gain some insight into the structure of **1**, ab initio MO calculations⁸ were performed on the model boraphosphene, HBPH, using the 6-31G basis set. At this level of theory the minimum energy corresponds to structure **5** with a P-B distance



of 1.756 Å and H-P-B and P-B-H angles of 94.5° and 175.0°, respectively. In contrast to the iminoboranes,³ the triple-bonded structure of **6** (computed P-B distance = 1.649 Å) is significantly (23.1 kcal/mol) less stable than the double-bonded structure **5**. The dimerization energy of **5** was computed to be -54.2 kcal/mol.

Finally, we note that attempts to prepare **2** via the reaction of MeLi or *t*-BuLi with (tmp)B(Cl)P(H)Ar (**7**)⁹ in Et₂O at 25 °C

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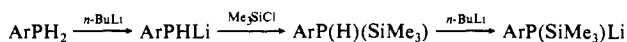
(1) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III → 3 and 13.)

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(5) Prepared in situ by the sequence of reactions (in Et₂O):



(6) Crystal data for **2**: C₃₄H₉₄B₂N₂P₂, *M_r* = 854.94, monoclinic, space group *P*2₁/*c* (No. 14), *a* = 10.840 (1) Å, *b* = 11.736 (2) Å, *c* = 21.034 (3) Å, β = 91.23 (1)°; *V* = 2625.3 Å³, *Z* = 2; *D_c* = 1.061 g cm⁻³; λ(Mo Kα) = 0.7107 Å, μ(Mo Kα) = 1.12 cm⁻¹. No decay (<1%) or absorption corrections were applied. The intensities of 4433 unique reflections were measured in an Enraf-Nonius CAD-4F diffractometer at room temperature (3.00 ≤ 2θ ≤ 48.0°). The structure was solved by direct methods and refined by full-matrix least squares using 1308 unique reflections with *I* > 3.0(*I*). The final residuals were *R* = 0.751 and *R* = 0.0792. All calculations were performed by using the SDP-Plus program package.⁷

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