phosphonium ions has been reported[7] 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.

Acknowledgment. The support of this research by the National Science Foundation (CHE8402135) is gratefully acknowledged.

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

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Received May 21, 1986

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 ($RN{\equiv}BR'$).[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*-$Bu_3C_6H_2$), (ii) detection of novel anions of the type $[(tmp)(R)B\rightharpoonup PAr]^-$ which also appear to exhibit phosphorus-boron multiple bonding, and (iii) a new synthetic approach to diphosphadiboretanes.[4]

Equimolar quantities of $(tmp)BCl_2$[3b] and $ArP(SiMe_3)Li$[5] were allowed to react in Et_2O 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 ^{31}P 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 than those in the less sterically emcumbered analogue $[(tmp)BP(mesityl)]_2$ (**3**, 1.916 (3) Å)[4c], (ii) the P_2B_2 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).

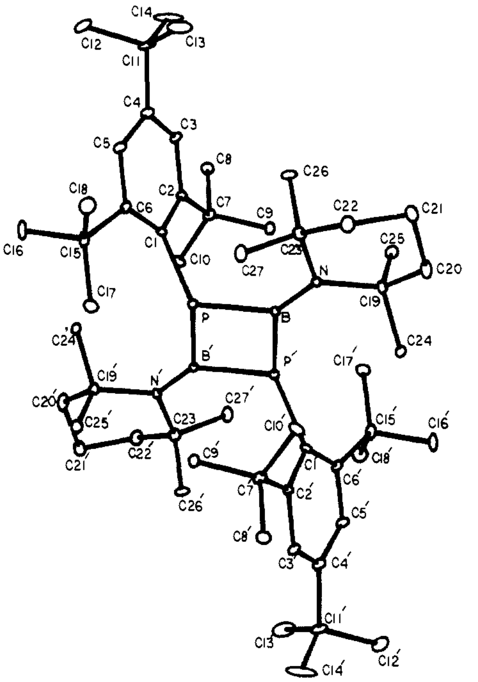
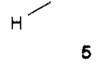


Figure 1. View of **2** showing the atom numbering scheme. The molecule resides on a center of symmetry. Important parameters: P–B 1.96 (2) Å, B–N 1.39 (2) Å, P–C(1) 1.891 (13) Å, B–P–B′ 86.9 (8)°, P–B–P′ 93.1 (8)°, P–B–N 136.4 (6)°, P′–B–N 136.7 (6)°, B–P–C(1) 119.0 (6)°, B′–P–C(1) 127.8 (6)°.

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 $C_{27}H_{47}BNP$, 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 calculations[8] 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.



5

6

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 Et_2O 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 Et_2O):

$$ArPH_2 \xrightarrow{n\text{-BuLi}} ArPHLi \xrightarrow{Me_3SiCl} ArP(H)(SiMe_3) \xrightarrow{n\text{-BuLi}} ArP(SiMe_3)Li$$

(6) Crystal data for **2**: $C_{54}H_{94}B_2N_2P_2$, M_r = 854.94, monoclinic, space group $P2_1/c$ (No. 14), a = 10.840 (1) Å, b = 11.736 (2) Å, c = 21.034 (3) Å, β = 91.23 (1)°; V = 2625.3 Å^3, 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 ($3.00 \leqslant 2\theta \leqslant 48.0°$). 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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(8) Pulay, P. *Theor. Chim. Acta* **1979**, *50*, 299. Pulay, P; Fogaras, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550. Pulay, P. *Chem. Phys. Lett.* **1980**, *73*, 393.

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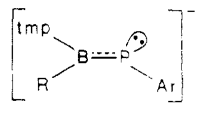
resulted in novel phosphide anions, **8a**,**b**. The identities of these



8a, R = Me
b, R = *t*-Bu

anions were proved by, e.g., reaction with H^+ to form (tmp)(R)BP(Ar)(H) (R = Me, *t*-Bu) which have been prepared by an independent route. The ^{31}P NMR chemical shifts are unusual (**8a** (THF) δ + 72; **8b** (THF) δ +85, +87). Normally, phosphide anions exhibit negative ^{31}P chemical shifts (e.g., δ -148 for $[ArP(SiMe_3)]^-$).[5] We attribute the substantial deshielding in the case of **8a**,**b** to partial donation of a phosphorus lone pair into a vacant boron orbital. In turn, the development of phosphorus-boron multiple-bond character, together with the increased steric bulk, explains the observation of two ^{31}P chemical shifts for **8b** (tmp group syn and anti to the phosphorus lone pair).

Studies of the reactivity and coordination chemistry of **1** are in progress. Indeed, very recently we have found that **1** (but not **2**) will react with $Fe_2(CO)_9$.

Acknowledgment. We are grateful to the Texas Advanced Technology Research Program for financial support.

Note Added in Proof. Professor Philip P. Power has informed us that his group has obtained X-ray crystallographic data on the following phosphinideneborate species: $[Li(Et_2O)_2PRB(mesityl)_2]$ (R = C_6H_{11}, mesityl) and $[Li(12\text{-crown-}4)_2][(mesityl)PB(mesityl)_2]\cdot THF$. The P-B bond lengths fall in the range 1.823 (7)-1.835 (13) Å and are thus consistent with phosphorus-boron multiple bonding. Moreover, the boron and phosphorus centers are planar in all three compounds. We are most grateful to Prof. Power for sending a preprint of his manuscript.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for **2** (6 pages). Ordering information is given on any current masthead page.

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(9) ^{31}P NMR data for **7** (32.38 MHz, THF): s, δ -96, $^1J_{PH}$ = 225 Hz. MS (70 eV): *m/e* 463 (12%, M^+), 277 (100%, $[ArPH]^+$), 186 (49%, $[(tmp)BCl]^+$.

Photochemical Preparation of Luminescent Platinum(IV) Complexes via Oxidative Addition on Luminescent Platinum(II) Complexes

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Received April 3, 1986

We have recently reported[4,5] the preparation and characterization (including absorption spectra, emission spectra, and excited state lifetimes) of the orthometalated Pt(II) complexes $Pt(Phpy)_2$ and $Pt(Thpy)_2$, which contain the ligands shown in Figure 1 ($Phpy^-$ and $Thpy^-$ are the C-deprotonated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine). We have now found that such complexes are photosensitive in several organic solvents, giving rise to oxidative addition reactions which lead to the formation of new luminescent orthometalated Pt(IV) complexes.

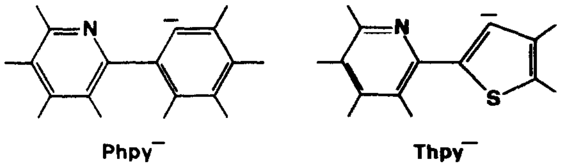

Figure 1. Structural formulas of the ligands.

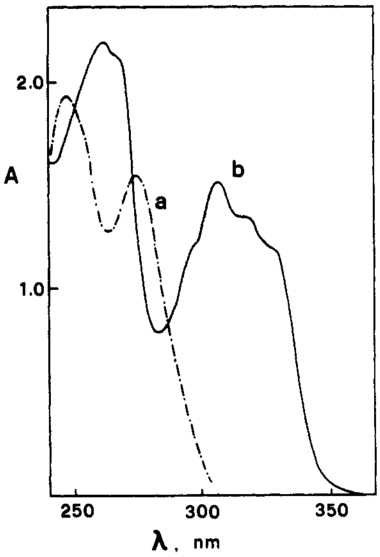

Figure 2. Absorption spectra of PhpyH 1.1 × 10^{-4} M (a) and $Pt(Phpy)_2(CH_2Cl)Cl$ 9.6 × 10^{-5} M (b) in CH_2Cl_2 at room temperature.

In a typical experiment, a 2.0 × 10^{-4} M solution of $Pt(Thpy)_2$ in deaerated CH_2Cl_2 was irradiated with light of a medium-pressure Hg lamp (λ > 400 nm). Irradiation caused the disappearance of the metal-to-ligand charge-transfer band of $Pt(Thpy)_2$ with λ_{max} = 420 nm[4,5] and other spectral changes, with clean isosbestic points.[6] At the end of the photoreaction, NMR analysis of the solution showed that only one species was present.[6] Evaporation of the solution yielded a light yellow powder that was recrystallized from CH_2Cl_2. Elemental analysis and NMR spectroscopy showed that this product corresponds to the formula $Pt(Thpy)_2(CH_2Cl)Cl$, indicating that the observed photochemical reaction is a simple photooxidative addition:

$$Pt(Thpy)_2 + CH_2Cl_2 \xrightarrow{h\nu} Pt(Thpy)_2(CH_2Cl)Cl$$

Similar reactions have been recently reported[7-9] for other Pt(II) complexes. A completely analogous photochemical reaction takes place with $Pt(Thpy)_2$ in $CHCl_3$ and with $Pt(Phpy)_2$ in CH_2Cl_2 or $CHCl_3$, as shown by the characterization of the reaction products. $Pt(Thpy)_2$ and $Pt(Phpy)_2$, as well other orthometalated Pt(II) complexes recently prepared in our laboratory, are photosensitive in several solvents, suggesting that photochemical oxidative addition might be a convenient route to prepare a variety of orthometalated Pt(IV) complexes. Detailed photochemical results and a discussion of the photochemical mechanism will be reported elsewhere.

The Pt(IV) complexes obtained via the photochemical oxidative addition reaction described above have a cis configuration, as shown by NMR spectra.[6] Their electronic absorption spectra (Table I; Figure 2) show intense bands in the near-UV spectral

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