ity between the behavior of acetylene and nitrogen in nitrogenase and the model systems indicates that both are reduced at a molybdenum-containing active site.

Acknowledgment. This work was supported by Grant No. GP 12324 from the National Science Foundation and an equipment grant from the Committee on Research of the Academic Senate, University of California, San Diego.

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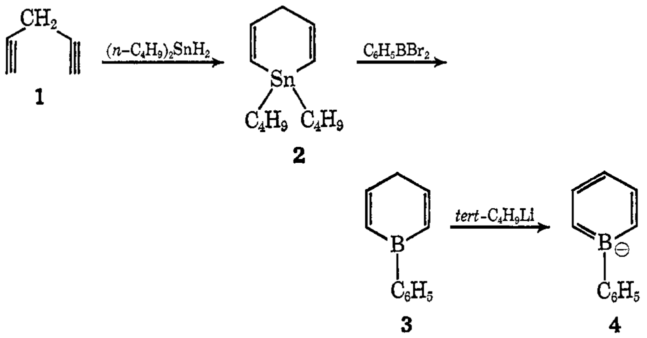
Received November 12, 1970

The 1-Phenylborabenzene Anion

Sir:

The extensive investigations of the chemistry of borazarenes have shown that replacement of carbon atoms of "normal aromatic compounds" by the isoelectronic B^- and N^+ leads to aromatic systems of considerable stability.[1] However, there have been no known aromatic compounds in which B^- alone replaces a carbon atom. The simplest of such systems, the 1-phenylborabenzene anion **4**, was recently reported as the ligand of a transition metal π complex.[2] We now wish to report the synthesis and some properties of the parent anion.



Our synthesis has relied heavily on the elegant conversions of 1,5-diacetylenes to borepin derivatives through organotin intermediates.[3] The necessary starting material, diethynylmethane (**1**), was prepared by the coupling of propargyl bromide with acetylenemagnesium bromide.[4] This highly reactive liquid could be isolated in 20% yield from the tetrahydrofuran solution. The structure follows from spectroscopic evidence: nmr (CCl_4) τ 6.7 (t, J = 2.5 Hz, 2 H), 8.16 (t, J = 2.5 Hz, 2 H); ir (CCl_4) 3350 (s), 2970 (s), 2150 cm^{-1} (m); mass spectrum M^+ 64 (base peak).

Stannohydration of **1** with dibutyltin hydride in refluxing heptane followed by heating to 200° gave 40% of 1,4-dihydro-1,1-dibutylstannobenzene (**2**). The molecular ion was not observed in the mass spectrum of **2**. The base peak at m/e 243 (M − 57) corresponded to loss of a butyl group from $C_{12}H_{24}{}^{120}Sn$. Divinyldibutylstannane shows similar behavior.[5] The pmr spectrum showed a broad peak due to the 18 protons of the n-butyl groups at τ 7.5–9.0, a 2-proton multiplet at τ 6.55 due to the diallylic protons and the 4 vinylic protons as an AB pattern (J_{AB} = 14 Hz) at τ 3.48 and 3.06 (each peak was split into a triplet; J_{AC} = 2 Hz and J_{BC} = 3.5 Hz, respectively).

Reaction of **2** with phenylboron dibromide gave dibutyltin dibromide and 1-phenyl-1,4-dihydroborabenzene (**3**), which could be separated by distillation in 50% yield. The mass spectrum of **3** gave a base peak at m/e 154 (the molecular ion for $C_{11}H_{11}{}^{11}B$). Nmr (THF-d_8, external TMS) showed a two-proton diallylic signal at τ 6.52 split by the two groups of two vinyl protons (J_{AX} = 3 Hz, J_{BX} = 1.5 Hz) and half of a four-vinyl-proton AB pattern (J_{AB} = 13 Hz) at τ 2.56, which was split into triplets (J_{BX} = 1.5 Hz) (the other half of the AB pattern and three of the phenyl protons occur as a complex pattern at τ 2.2–2.45; the two remaining phenyl protons occur as multiplet at τ 1.6–1.75). The ^{11}B nmr shows a signal +37 ppm from external trimethylborane, close to that of trivinylborane at +31.2 ppm.[6] Treatment of **3** with acetic acid gave benzene and 1,4-pentadiene.

3 could be deprotonated by lithium triphenylmethide in THF or more conveniently by the method of Bates using *tert*-butyllithium in pentane–THF.[7] Treating these solutions of **4** with excess acetic acid gave 1,4-pentadiene, *cis*-1,3-pentadiene, and benzene. The presence of anion **4** was established by examining the products of deuteration by acetic acid-d_1. The mass spectrum of the *cis*-1,3-pentadiene showed a molecular ion at m/e 71, indicating incorporation of three deuterium atoms. The nmr spectrum of **4** in THF-d_8 (external TMS) is quite characteristic: the proton at C_4 occurs as a triplet (J = 6.5 Hz) at τ 3.66; the protons at C_2 and C_6 occur as half of an AB pattern at τ 3.05 (J_{AB} = 10 Hz), while the protons at C_3 and C_5 as well as three of the phenyl protons form a complex pattern at τ 2.4–2.8 The remaining two phenyl protons are a multiplet at τ 1.9–2.

The chemical shift values of protons of aromatic systems are sensitive to the charge density at adjacent carbon and to ring-current effects.[8] Peak positions for **4** occur at relatively low field compared to those of the corresponding pentadienyl anions.[9] This is consistent with substantial ring-current effects and/or diminished negative charge at carbon. In either case the result suggests considerable electron donation to boron. Additional evidence for this comes from the ^{11}B nmr spectrum of **4**, which consists of a broad band

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centered +59 ppm from external trimethylborane. The upfield shift from the conjugate acid is large, and indeed such a shift is characteristic of negatively charged boron.[10,11]

The smaller alternation of peak positions of adjacent CH groups of **4** relative to that of pentadienyl anions is consistent with a more even charge distribution in **4**. As expected from examination of classical resonance structures, the protons at C_4, C_2, and C_6 are more highly shielded than those at C_3 and C_5. That C_4 may have the greatest charge density is suggested by its highest field peak.

While spectra suggest significant aromatic properties for the borabenzene anion, further studies, now in progress, are necessary to better define this stabilization.

Acknowledgment. We wish to acknowledge partial support of this work by a Rackham Faculty Grant of the University of Michigan and to thank the National Science Foundation for a grant (No. GP-8345) to the University of Michigan for the purchase of an MS-9 mass spectrometer.

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(11) G. R. Eaton and W. N. Lipscomb, "Nmr Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969, pp 437–516, 562.

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Received December 23, 1970

The Barrier to Pyramidal Inversion in Acylphosphines[1]

Sir:

The amide functionality, due in part to its biological import, has been extensively studied. With regard to molecular structure and dynamics, amides are known to be planar or to possess low barriers (*ca.* 1 kcal/mol) to pyramidal inversion,[2] and relatively high (*ca.* 20 kcal/mol) torsional barriers[3] about the nitrogen–carbonyl bond. No comparable information is available for the congeneric structures formed by replacement of nitrogen by phosphorus or other group Va elements. We now report our finding that, in contradistinction to amides, the rate-limiting conformational exchange process in acylphosphines, as represented by acetylisopropylphenylphosphine (**1**), is pyramidal inversion. The magnitude of the barrier ($\Delta G^{\ddagger}_{110}$), *ca.* 19.4 kcal/mol, is markedly lower than that found for sundry acyclic diarylalkyl- and dialkylarylphosphines.[4]

The synthesis of **1** was accomplished by condensation of acetyl chloride with the sodium salt of isopropylphenylphosphine according to the procedure of Issleib and Priebe.[5] The crude reaction mixture was purified by chromatography (silica gel, benzene) followed by rapid distillation (kugelrohr, *ca.* 60° (0.02 mm)). The ir spectrum shows a low-frequency carbonyl stretch at *ca.* 1675 cm^{-1},[6] and the pmr spectrum (a *ca.* 20 v/v % solution in CF_2Cl_2 with *ca.* 1 v/v % tetramethylsilane) is consistent with the assigned structure: δ 7.9–7.2 (m, C_6H_5), 2.7–2.0 (m, $CH(CH_3)_2$), 2.0 (d, J_{PH} = 6.0 Hz, $C(O)CH_3$), 1.22 (q, J_{PH} = 17.8 Hz, J_{HH} = 6.8 Hz, $CH(CH_{3(A)})$), 0.80 (q, J_{PH} = 13.4 Hz, J_{HH} = 7.0 Hz, $CH(CH_{3(B)})$).

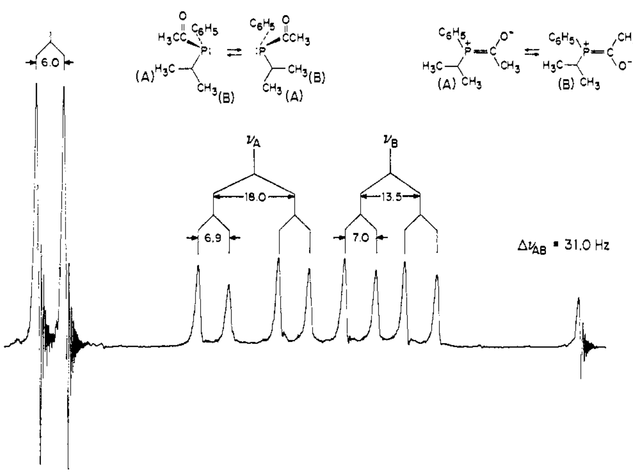
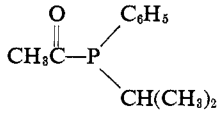
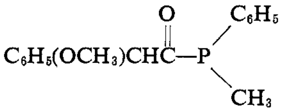


Figure 1. 60-MHz spectrum of the methyl region of **1** (*ca.* 25 v/v % solution in 1-bromonaphthalene with *ca.* 1 v/v % $(Si(CH_3)_3)_2$ as internal standard) at 45°.



$CH_3C(O)P(C_6H_5)CH(CH_3)_2$

1



$C_6H_5(OCH_3)CHC(O)P(C_6H_5)CH_3$

2

The methyl portion of the pmr spectrum of **1** in 1-bromonaphthalene (see Figure 1) is compatible with a conformationally restricted phosphine. The isopropyl methyl resonances exhibit a temperature dependence, broadening with increasing temperature to a coalescence at *ca.* 110°; further heating results in a quartet. The acetyl methyl signal remains as a sharp doublet over the entire range of temperature (45–150°). Substitution of the rate constant derived from the Gutowsky–Holm equation into the Eyring equation (assuming a transmission coefficient of unity)[7] yielded the above cited $\Delta G^{\ddagger}$. Cooling a sample of the phosphine (CF_2Cl_2 solvent) to *ca.* −100° produces only a severe broadening of all the resonances of **1**, while tetramethylsilane remains relatively sharp. However, no new resonances were observed.

These observations are accommodated by two alternative interpretations, suggested by analogy to related processes in phosphines and amides: either the phosphorus atom is pyramidal, and the interconversion is one of enantiomers, by inversion (limiting case I), or the phosphorus moiety is planar, and the interconversion is one of diastereomers, *i.e.*, cis and trans forms, by rotation (limiting case II); see Figure 1.

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(1) This work was supported by grants from the Air Force Office of Scientific Research (AF-AFOSR-1188-B) and the National Science Foundation (GP-22542).

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