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for **12**, evaluated by means of isodesmic reactions, eq 1 and 2 (with $\Delta H_f{}^{\circ}{}_{298}$ values in kcal/mol given in parentheses), which tend to

$$\begin{array}{ccccccc}
(\mathrm{CH})_3{}^+ & + & \mathrm{CH_3C{\equiv}CH} & \rightarrow & (\mathrm{CH})_2\mathrm{CC{\equiv}CH^+} & + & \mathrm{CH_4} \\
\text{cyclopropenium} & & (44.3^{16}) & & \mathbf{11} & & (-17.9^{16}) \\
\text{ion} & & & & (311\ \text{calcd}) & & \\
(257^{16}) & & & & & &
\end{array}$$

$$-8.2\ \text{kcal/mol (3-21G//3-21G)} \qquad (1)$$

$$\begin{array}{ccccccc}
\mathrm{HC{\equiv}CCH_2}{}^+ & + & \mathrm{CH_3C{\equiv}CH} & \rightarrow & \mathrm{HC{\equiv}CC{\equiv}CCH_2}{}^+ & + & \mathrm{CH_4} \\
\text{propargyl} & & (44.3^{16}) & & \mathbf{12} & & (-17.9^{16}) \\
\text{cation} & & & & (326\ \text{calcd}) & & \\
(281^{16}) & & & & & &
\end{array}$$

$$-17.6\ \text{kcal/mol (3-21G//3-21G)} \qquad (2)$$

cancel errors. An experimental upper limit of 342 kcal/mol for the heat of formation of $C_5H_3{}^+$ of unknown structure[17] is in general agreement.

Based on the estimated $\Delta H_f{}^{\circ}$ for **11**, the experimental value for $CH_3{}^+$, and the calculated energy of eq 3, $\Delta H_f{}^{\circ} = 601$ kcal/mol for the geometry-optimized $D_{2h}$ singlet benzene dication is obtained as shown in eq 3 ($\Delta H_f{}^{\circ}{}_{298}$ values in kcal/mol given in parentheses).

$$\begin{array}{ccccc}
\mathrm{C_6H_6}{}^{2+} & \rightarrow & \mathrm{CH_3}{}^+ & + & \mathrm{C_5H_3}{}^+ \\
\mathbf{4}\text{, singlet,} & & (262^{16}) & & \mathbf{11} \\
D_{2h} & & & & (311\ \text{calcd,} \\
(601\ \text{calcd}) & & & & \text{eq 1)}
\end{array} \qquad (3)$$

$$-28.0\ \text{kcal/mol}$$

Like **11**, **12** and **13** can also be formed by $CH_3{}^+$ elimination from $C_6H_6{}^{2+}$ precursors, e.g., **11** from **6**, **12** from **7**, and **13** from **10**. Both **7** and **10** have unbranched carbon skeletons which might have been formed by opening of the benzene dication ring followed by hydrogen migrations. Likewise, **2** might give **6** prior to fragmentation. Three-membered rings are often produced in carbocationic processes, and **2** might arise via cleavage of a bicyclo[3.1.0]hexenediyl dication intermediate. There is some precedent in the mechanism of the photochemical rearrangements of benzene.[18]

Since **10** is a rather unstable $C_6H_6{}^{2+}$ isomer, we regard **6** and **7** to be more likely metastable fragmentation precursors. The energetically more favorable process, exothermic by 47 kcal/mol (3-21G), involves fragmentation of **6** into **11** and $CH_3{}^+$. This is related to, but does not correspond directly to, the experimental process which releases 2.6 eV (60 kcal/mol) of translational energy. The energy difference between the fragmentation transition state (e.g., **6**$^{\ddagger}$ rather than **6**) and the products (e.g., **11** and $CH_3{}^+$) may be involved. Decomposition of dications into two monocations typically requires activation, even though such transformations may be very favorable thermodynamically.[1] Assuming this also to be true for the decomposition of **6**, the 47 kcal/mol exothermicity would only have to be augmented by a modest activation energy to agree with the experimental energy release value of 60 kcal/mol.

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**Registry No. 1**, 84253-83-8; **2**, 84237-96-7; **3**, 84237-97-8; **4**, 15157-23-0; **5**, 55574-89-5; **6**, 84237-98-9; **7**, 84237-94-5; **8**, 84237-99-0; **9**, 81932-71-0; **10**, 84237-95-6; **11**, 84238-00-6; **12**, 81932-80-1; **13**, 79530-50-0.

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# Bis(borane)-Cyclenphosphorane: A Stable Adduct in Which Two Phosphorus(V)-Bonded Nitrogen Atoms Display Donor Character

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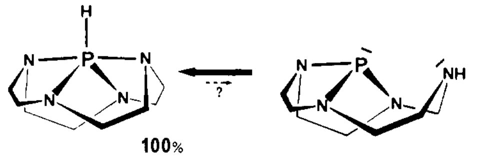
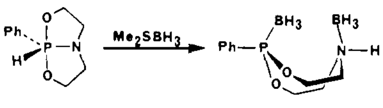
Phosphorus-bonded tricoordinated Nitrogen atoms usually show little donor capacity. The few known $BH_3$ adducts derive from constrained structures and are usually unstable.[1] The unique behavior reported here of cyclenphosphorane **1a** toward diborane



1a 1b (1)

is therefore remarkable. It provides the first example of a stable $H_3B$–N–P–N–$BH_3$ sequence and adds a new facet to the already rich chemistry of phosphoranes derived from macrocyclic tetraamines.[2-4]

Aside from homocyclen, cyclenphosphorane is the only member of the family of tetracyclic tetraaminophosphoranes for which the open-form phosphane tautomer **1b** has not been detected in solution. It was therefore of interest to investigate the possibility of revealing such an open form and of displacing the tautomeric equilibrium 1 under the action of a Lewis acid capable of coordinating the phosphane and/or amine sites of **1b**. Such behavior has previously been observed in the case of bicyclic aminophosphoranes of type **2**, for which the open form is usually not



2 3

present either and which, under the action of transition-metal derivatives[5] or diborane,[6] convert to adducts such as **3**. The coordination of the nitrogen site in the phosphorus-bound form **2** has never been observed.

Cyclenphosphorane was found to react readily with diborane on the vacuum line and to add 2 equiv of $BH_3$. The reaction product, which was isolated in near-quantitative yield as a white crystalline powder, proved, quite unexpectedly, not to be the open-form analogue of **3** but the bis-adduct **4**, in which no rearrangement of the initial structure had occurred.

Even more surprising is the outstanding stability of **4**, as illustrated by its high melting point (with decomposition) at 200

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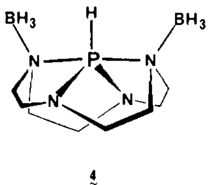
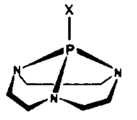


4

°C, absence of air-sensitivity, and absence of evolution of $B_2H_6$ on dissolution. The elemental analysis and mass spectrum, which exhibits the molecular peak, support its formulation.

The $^{31}$P NMR spectrum of 4 in $CDCl_3$ solution exhibits a single sharp doublet at −28 ppm, characteristic of 5-connected phosphorus, with $J_{\text{P-H}}$ = 790 Hz, confirming that the proton has not undergone the expected tautomeric shift to the nitrogen atom with concomitant P–N bond opening. The $^{11}$B NMR spectrum consists of a quartet at −15.7 ppm ($J_{\text{B-H}}$ = 100 Hz), a position usually found for N-coordinated $BH_3$ groups.[7] The $^{13}$C NMR spectrum consists only of two signals of equal intensity, at +41.2 and +50.2 ppm; this can only be consistent with the presence of the two $BH_3$ groups on two nitrogen atoms symmetrically located in the macrocycle. The available structural data on fluorocyclenphosphorane,[8] bis(cyclenphosphorane),[2d] and molybdenum cyclamphosphoranide[4] all show the tendency of the pentavalent phosphorus atom to adopt a nearly perfect trigonal bipyramidal arrangement, in spite of the constraint imposed by the cycles; there is therefore a strong precedent to proposing that 4 adopts a similar arrangement. The $BH_3$ groups are then likely, both on kinetic and thermodynamic grounds, to be coordinated to the apical nitrogen atoms: these have been shown to undergo less pπ–dπ interaction with phosphorus than those in equatorial positions[9] and hence are likely to manifest the greater basicity;[2e] then, even if the attack of the $BH_3$ groups were to occur on the equatorial nitrogen atoms, we would expect the structure to rearrange itself so as to bring the uncoordinated nitrogen atoms into the equatorial plane in which pπ–dπ interactions are favored and the $BH_3$ coordinated nitrogen atoms, which have no electron left for back donation, into the apical positions.

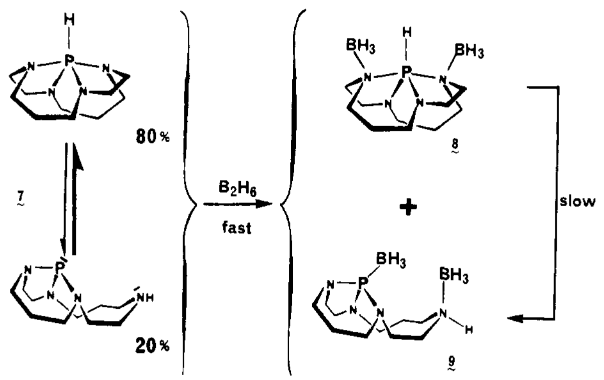
Compound 4 is to our knowledge the first for which the $BH_3$–N–P–N–$BH_3$ pattern is established. Of two close analogues of 1a, one, the tricyclic triaminophosphane 5, was reported not to react with diborane; a solution of the other, 6, the sulfide of 5, was observed to absorb 1.85 equiv of $BH_3$; however, the nature of the crude insoluble (soluble but unstable in dimethylformamide) product isolated could not be established.[10] The gross difference in behavior of 1a and 2 can probably be assigned both to a strong macrocyclic effect,[11] which in the former case favors the closed form, and to the presence in 1a of apical N atoms, which are more basic in character.



5: X = lone pair
6: X = S

The mono(borane) adduct of 1a was not detected. Only the bis(borane) adduct 4 is formed even if only 0.5 mol equiv of $B_2H_6$ is used; half of the starting material is then recovered unreacted.

Preliminary investigations on cyclamphosphorane 7, which is known to be in equilibrium with an open form in solution, reveal a more complex behavior: in comparable working conditions the addition of 1 mol equiv of $B_2H_6$ leads to a mixture from which 40% of closed bis(borane)–cyclamphosphorane 8, analogous to 4, and 15% of *open* bis(borane)–cyclamphosphane 9, were isolated.



Their mass and NMR spectra support these formulations unambiguously [8, $^{31}$P δ −45 ($J_{\text{P-H}}$ = 780 Hz), $^{11}$B δ −14.5; 9, $^{31}$P δ +115 ($J_{\text{P-B}}$ = 95 Hz), $^{11}$B δ −14.5, 43.0 Hz ($J_{\text{B-P}}$ = 95 Hz)]. Both compounds are quite stable, as evidenced by their melting points: 117 °C for 8 and 147 °C, with decomposition, for 9. Both compounds can be stored in the solid state for months without noticeable changes, but when 8 is left at room temperature in a sealed tube in $CD_2Cl_2$ solution, it converts, slowly but totally, to 9 in a matter of a few weeks.

**Acknowledgment.** We are grateful to Prof. J. E. Richman for a sample of cyclen.

**Registry No.** 1a, 64317-97-1; 4, 84237-90-1; 7 (isomer 1), 64317-99-3; 7 (isomer 2), 71089-76-4; 8, 84237-91-2; 9, 84237-92-3; diborane, 19287-45-7.

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## 1,1-Bis(benzenesulfonyl)cyclopropane: A Synthon for a Propylene 1,3-Dipole

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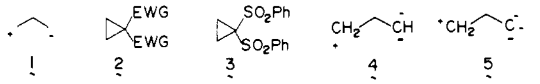
The development of 1,3-dipoles as basic building blocks have mainly focused on unsaturated systems. Trimethylenemethane[1] and oxatrimethylenemethane[2] synthons have been particularly fruitful. Their success stems from their inhibition toward self-annihilation either because of great strain or by π complexation to transition metals. The development of saturated analogues such as 1 becomes more devious since steric inhibition for closure to a cyclopropane does not exist nor is stabilization by metal complexation easily available. Introduction of electron-withdrawing groups on the cyclopropane (i.e., 2) facilitates the opening of this closed form of the dipole by nucleophiles[3-5]—thus making C(2)



EWG = electron withdrawing group

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