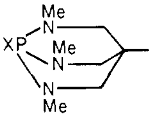
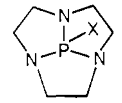
Synthesis and Crystal Structure of a Stable Bis(borane)aminophosphane Adduct: The Unusually Strong Basic Character of a Nitrogen Atom Bound to Phosphorus

Sir:

It is now well-established that a nitrogen atom bound to phosphorus loses most or all of its donor character, while the P-N bond length becomes shorter than what is normally expected for a single σ bond, and while the nitrogen adopts a coplanar arrangement with its substituents;[1,2] this is usually interpreted as resulting from the involvement of the nitrogen lone pair into π bonding to the π-acid phosphorus atom. Thus, when aminophosphanes are allowed to react with diborane, only one BH_3 group is usually coordinated, and that is to phosphorus.[2] The very few exceptions known[3] to this general behavior concern constrained structures of types **1** and **2**. The bicyclic compound **1a** has been found to add a second BH_3 group on one—and only one—of the nitrogen atoms, to form an adduct which readily loses BH_3 to give **1a** back.[4] Other N-bonded adducts, generally unstable in solution, have been obtained with compounds **1b** and **1c**[4,5] while the acyclic $XP(NMe_2)_3$ analogues of **1a** and **1b** do not add BH_3 on nitrogen,[2] nor does the phosphoramide $P_4(NCH_3)_6$.[6] Furthermore, no N-bonded BH_3 adducts were obtained with compounds **2a**, although the nitrogen atoms are forced to adopt pyramidal conformations (which is not the case in **1**). Only in the case of **2b** could evidence for the formation of a bisborane adduct be obtained, although the coordination sites have not been established yet.[7] Even the harder BF_3 acid yielded only an unstable nitrogen-bound adduct with $F_2P\text{-}NMe_2$,[8] but a more stable one has been reported with $\mathrm{F\overline{PN(Me)(CH_2)_2N}Me}$.[9] Although no satisfying interpretation has been offered for these differences, it is clear that particular constraints can drastically change the nitrogen's ligating ability in these systems.[2,5,7] No diffraction data have yet been reported on a nitrogen-coordinated aminophosphane adduct.

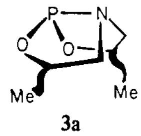


1a, X = BH_3
b, X = O, S, Se
c, X = $M(CO)_n$; M = Cr, Mo, W (n = 5), Fe (n = 4), Ni (n = 3)

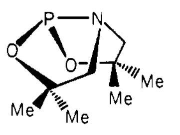


2a, X = lone pair
b, X = S

Bicyclic aminophosphanes **3a** and **3b** were attractive to us because their bicyclic structure and the pyramidal phosphorus atom force the nitrogen atom to stay pyramidal. We expected this to hinder the $p_\pi\text{-}d_\pi$ interaction, and to restore the nitrogen atom's donor properties.



3a



3b

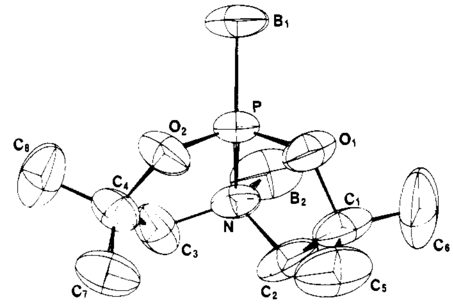


Figure 1. Molecular structure of complex **5b**. Selected bond lengths (Å) and angles (deg): $P\text{-}B_1$ 1.873 (7), $N\text{-}B_2$ 1.655 (8), P-N 1.757 (4), $P\text{-}O_1$ 1.550 (4), $P\text{-}O_2$ 1.564 (4), $O_1\text{-}C_1$ 1.472 (6), $O_2\text{-}C_4$ 1.468 (6), $N\text{-}C_2$ 1.495 (7), $N\text{-}C_3$ 1.547 (6) Å. $B_1\text{-}P\text{-}O_2$ 112.9 (3), $B_1\text{-}P\text{-}O_1$ 113.9 (3), $O_1\text{-}P\text{-}O_1$ 113.9 (3), $O_1\text{-}P\text{-}N$ 95.0 (2), $O_2\text{-}P\text{-}N$ 97.7 (2), $N\text{-}P\text{-}B_1$ 125.4 (3), $C_3\text{-}N\text{-}B_2$ 110.1 (5), $C_2\text{-}N\text{-}B_2$ 111.7 (5), $C_2\text{-}N\text{-}C_3$ 113.3 (4), $C_2\text{-}N\text{-}P$ 104.5 (3), $P\text{-}O_1\text{-}C_1$ 118.2 (3), $P\text{-}O_2\text{-}C_4$ 117.5 (4)°.

When **3a** and **3b** were allowed to react with 0.5 and then 1 molar equiv of diborane at room temperature in toluene, we indeed obtained, successively and very easily, the adducts $\mathbf{3}\cdot BH_3$ (**4**) and

$$\mathbf{3} \xrightarrow[\text{toluene, }-30\ ^\circ\text{C}]{{}^1/_2B_2H_6} \underset{\mathbf{4}}{\mathbf{3}\cdot(BH_3)} \xrightarrow[\text{toluene, }-30\ ^\circ\text{C}]{{}^1/_2B_2H_6} \underset{\mathbf{5}}{\mathbf{3}\cdot(BH_3)_2}$$

$\mathbf{3}\cdot(BH_3)_2$(**5**) in high yields. The coordination of BH_3 to phosphorus in **4a** and **4b** was established by the presence of quartets at 143.2 and 152.4 ppm, respectively (J_{P-B} = 88 Hz), in the $^{31}P\{^1H\}$ NMR spectra, and of doublets at −42 and −39 ppm, respectively (J_{B-P} = 88 Hz), in the $^{11}B\{^1H\}$ NMR spectra. Additional broader signals appear at −10 ppm in the ^{11}B spectra of adducts **5a** and **5b**, together with downfield shifts (1-2 ppm) of the ^{31}P resonances. The elemental analysis and infrared, mass, and ^1H NMR spectra are also consistent with these formulations.[11]

The unusual stability of the bisborane adducts **5a** and **5b** is illustrated by their rather high decomposition points (115 and 110 °C, respectively), which are higher than those of the monoborane adducts **3a** and **3b** (85 and 75 °C, respectively), and by the appearance of the molecular peaks in their mass spectra at 150 °C and 15 eV. Compounds **4** and **5** can be stored at room temperature under argon for at least 2 months without noticeable changes; **5b** is even air stable. No evolution of B_2H_6 was detected in their CH_2Cl_2 solutions.

Another surprising observation is that in the case of ligand **3a**, which initially consists of two diastereoisomers in an 80:20 ratio (meso and racemic, respectively),[10] one observes the formation of the BH_3 adducts of the meso form only. The observations that NMR monitoring of the reaction shows that both isomers are consumed with only the adducts of the meso isomers being detected in the resulting solutions and that these adducts were isolated in 90 and 85% yields in the case of **4a** and **5a**, respectively, strongly suggest that BH_3 coordination provokes rapid epimerization of the bicyclic frame, which implies the breaking of a C-O, C-C, or C-H bond.

The isolation of stable crystals of **5b** allowed the first X-ray diffraction data to be obtained on a P-bound N atom coordinated to BH_3. The space group ($P2_1/n$) was determined for **5b** from Weissenberg photographs with Cu Kα radiation. The unit-cell parameters are a = 7.803 (1), b = 16.650 (1), c = 10.431 (1) Å;

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(3) The formation of $Me_2P(BH_3)\text{-}NMe_2(BH_3)$ has been claimed, but no evidence has been offered to establish this formulation: Burg, A. B.; Slota, P. J. *J. Am. Chem. Soc.* **1960**, *82*, 2145.

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(11) Mass spectrum (MS), m/e^+ for compound **3a** at 70 eV and 90 °C: $LH\cdot BH_3$ (35%), LH (63%), $L\text{-}CH_3$ (19%), $L\text{-}C_2H_6$ (47%), C_4H_8NOP (100%). MS for compound **4a** at 15 eV and 150 °C: $L\cdot 2BH_3$ (7.5%), $L\cdot BH_3$ (8.4%), L (9%), $L\text{-}CH_3$ (9%), $C_6H_{12}NO_2B$ (100%). IR (Nujol, main absorption bands, ν (B-H) cm^{-1}) for **3a**: 2400 (vs), 2395 (sh), 2350 (s). IR (Nujol, cm^{-1}) for **3b**: 2400 (vs), 2345 (s). IR (Nujol, cm^{-1}) for compound **4a**: ν [P(B-H)] 2395 (vs), 2330 (s); ν[N(B-H)] 2460 (s), 2280 (m). IR (Nujol, cm^{-1}) for compound **4b**: ν[P(B-H)] 2400 (vs), 2350 (s); ν[N(B-H)] 2460 (s), 2290 (m). NMR spectra in CD_3CN at −20 °C, chemical shifts are given positively to lower fields relative to 85% H_3PO_4 or neat $BF_3\cdot OEt_2$ as external references.

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$\beta = 95.1$ (1)°; $V = 1349.7$ Å^3, $M_P = 217.87$, $d_{\text{calcd}} = 1.068$ g cm^{-3}, $d_{\text{obsd}} = 1.07$ g cm^{-3}, $Z = 4$. The measurements could be taken at room temperature, although a time-dependent decay of the intensities, which amounted to ~25% at the end of data collection, was observed, and corrected for. Of the 2662 measured reflections, 1758 were used for the refinement of the structure ($R = 8.7\%$).

The structure (Figure 1) unambiguously shows the location of the two B atoms on P and N. It is noteworthy that the N–B bond length [1.655 (8) Å] is comparable to that found in the only normal amine–borane adduct whose structure has been determined to our knowledge, namely, $Me_3N{\cdot}BH_3$ (1.638 ± 0.010 Å by microwave spectroscopy[12]). The P–B bond length [1.873 (7) Å] is short but comparable to those found in other adducts in which phosphorus has electronegative substituents.[2] The P–N bond [1.757 (4) Å] is as expected in the absence of π bonding.[13]

When BF_3 is allowed to react with **3a**, the first equivalent of BF_3 is probably coordinated to the nitrogen atom, as suggested by the low, $J_{BP} = 4.5$ Hz and $J_{PF} = 27$ Hz, couplings. This is further evidence for the strong donor character of the N atom.

In summary, all these observations indicate that the phosphorus and nitrogen atoms of these aminophosphanes behave as independent donors of comparable strengths. The behavior of these ligands with relation to transition-metal derivatives is under investigation.

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

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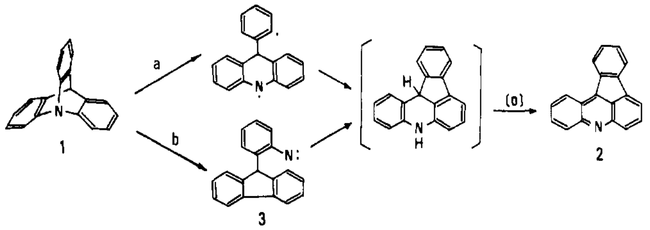
Formation of *o*-(9-Fluorenyl)phenylnitrene in the Photoisomerization of 1-Azatriptycene

Sir:

In view of the recent interest in the polar effects of substituents on the di-π-methane rearrangement[1] and the intriguing diversion therefrom of the the photorearrangement of triptycenes to give carbene intermediates,[2] it seemed to be high time to investigate the photochemical behavior of 1-azatriptycene (**1**), the first example of the di-π-methane system carrying the heteroatom at the methane position. An intriguing question about **1** is which end of the *o*-benzeno moieties will take part in the bridging: in other words, is a carbene or nitrene species formed from the bridgehead atom?

Scheme I



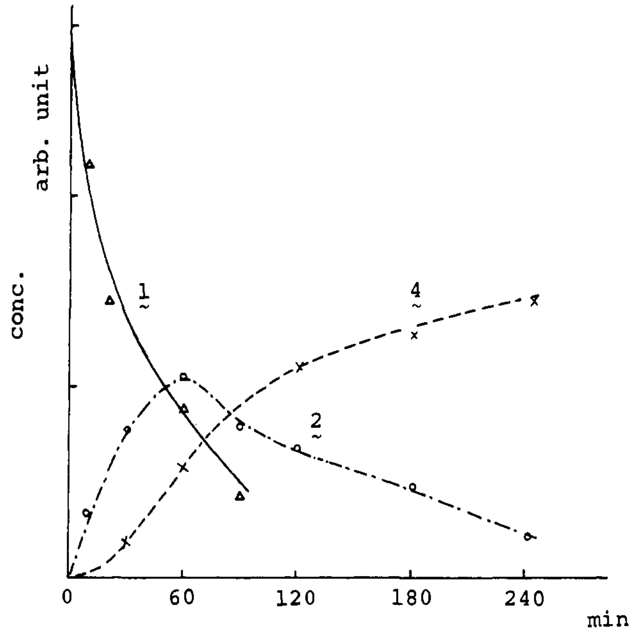


Figure 1. The appearance of products and disappearance of the starting material during the irradiation of **1** in acetic acid (0.51 mM) vs. time.

In 1964, **1** was prepared via the internal nucleophilic addition to a benzyne and subjected to UV irradiation by Wittig and Steinhoff.[3] Indenoacridine (**2**) was obtained inefficiently in acetic acid and interpreted as arising from C–N bond cleavage followed by free-radical phenylation (route a in Scheme I). We have investigated the photoreaction under various conditions, found a number of new products due to nitrene **3** in these reactions, and therefore suggest route b for **2** as well. The results are summarized in Table I.

The irradiation of **1** in acetic acid with a low-pressure mercury lamp in an immersion apparatus was monitored by high-performance LC to give the results shown in Figure 1. Formation of **2** as described in the literature[3] was reproduced except that **2** was photolabile under these conditions, giving 12b-methyl-5,12b-dihydro derivative **4**, mp 151–153 °C, as a secondary product: IR (Nujol) 3370, 1580, 1290, and 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (3 H, s), 6.30 (1 H, br s), and 6.8–8.0 (11 H, m). Apparently, Wittig and Steinhoff stopped the reaction at low conversion. According to the known photochemical behavior of acridines,[4] **4** can be reasoned as being formed from the ion pair consisting of the conjugate acid of **2** and acetate anion produced from the photoexcited state of **2**. Electron transfer followed by decarboxylation and recombination would give **4**.

In dilute methanolic sodium methoxide, azepine derivative **5** was isolated as orange needles, mp 162–164 °C dec, in 69% yield. In acetonitrile in the presence of TCNE, adduct **6**, colorless plates, mp 183–185 °C dec, was obtained. Structures **5** and **6** were unequivocally established by spectral data. The mass spectra of **5** and **6** showed parent peaks at m/e 255 and 383 [base peak at m/e 255 = M$^+$ − 128 (TCNE)], respectively. The 100-MHz ^{1}H NMR of **5** showed three olefinic protons, A, B, and C, at δ 4.7 (m, 10 and 4.5 Hz coupling with the C and D signals, respectively), 6.3 (t, 4.2 Hz coupling with D), and 6.7 (d, 10 Hz coupling with

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