λ^5-Phosphonitriles–λ^3-Phosphinonitrenes: Evidence for Nitrene–Lewis Acid Adducts

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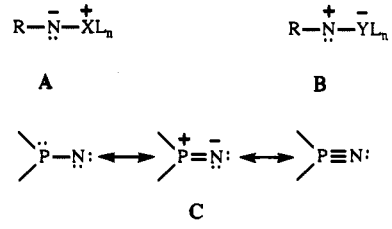
Abstract: Photolysis of bis(diisopropylamino)- and bis(dicyclohexylamino)phosphanyl azides **1a** and **1b** with dimesitylfluoroborane leads to *P*-fluoro-*N*-boryliminophosphoranes **3a** and **3b**, in 80% yields; according to an X-ray crystal diffraction study, **3b** has a pseudo-allene structure. Thermolysis of azide **1b** with dimesitylmethyl- and dimesitylethylborane affords *N*-boryl-*N*-mesityl-*N*-phosphanylamines **7** and **15** in 85 and 90% yield, respectively. Photolysis of **1a** and **1b** with triethyl- or tricyclohexylborane gives rise to *P*-hydrogeno-*N*-boryliminophosphoranes **8a,b** or **9a,b**, in good yields, along with ethylene or cyclohexene. It is shown that no interaction occurs between the boranes and the azides used. All the results are rationalized by the transient formation of phosphanylnitrene–borane adducts, possessing a PN multiple bond, which undergo either a 1,2-migration of a boron substituent to the "nitrene" center or a retro-ene type reaction.

Introduction

Since the end of the last century, nitrenes have attracted considerable attention.[1] They are neutral reactive intermediates and possess a sextet of electrons in their outer shell. From the electronic configuration of singlet nitrenes, one would expect that they manifest both electrophilic (unoccupied orbital) and nucleophilic (electron pair) properties. The stabilization of these species by complexation with Lewis bases (XL_n) leading to ylidic complexes of type **A** (Scheme 1) is indeed well documented.[1] In contrast, to the best of our knowledge, no examples of the reverse type of nitrene complexes **B**, with Lewis acids (YL_n), have been reported so far, although nucleophilic nitrenes such as oxynitrenes[2,3] and aminonitrenes[3,4] have been extensively studied. Note that the first carbene–Lewis acid adducts have only very recently been reported.[5]

Calculations[6] and experimental results[7] have shown that phosphanylnitrenes **C** are best formulated as multiply-bonded λ^5-phosphonitriles due to the delocalization of the phosphorus and nitrogen lone pairs. In other words, they can be considered as singlet nucleophilic nitrenes and are therefore good candidates for this study. Moreover, since λ^5-phosphonitriles are the monomers corresponding to the well-known family of polyphosphazenes,[8] and since Lewis acids are often used to catalyze polymerization, the study of the reactivity of these species with Lewis acids presents a further interest.

Scheme 1



Here we report our results concerning the reactivity of two phosphanylnitrenes, namely the bis(diisopropylamino)- and bis(dicyclohexylamino)phosphanylnitrenes **2a** and **2b** with a variety of organoboranes.

Results and Discussion

We have already shown that the bis(diisopropylamino)phosphanylnitrene **2a** can be generated by photolysis (λ = 250 nm) of the corresponding azide **1a**.[7a] In the same way bis(dicyclohexylamino)phosphanylnitrene **2b** is formed under irradiation but also by thermolysis (refluxing toluene) of phosphanyl azide **1b**. Three types of boranes were chosen: a halogenoborane (Mes_2BF), trialkylboranes (Et_3B and c-Hex_3B), and (diaryl)alkylboranes (Mes_2B–Me and Mes_2B–Et). The reactions were performed using equimolar quantities of organoboranes and phosphanyl azides **1**.

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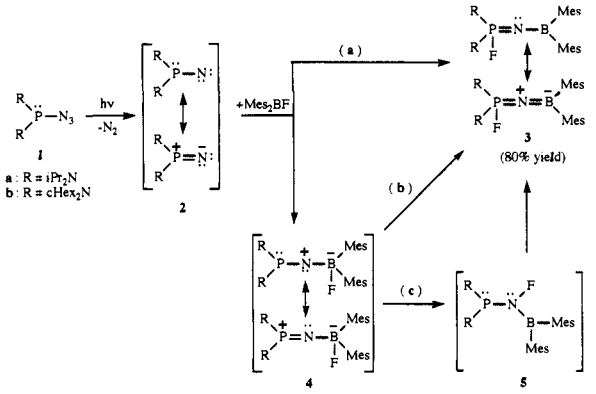
Scheme 2



The reaction of organoboranes with organic azides leading to secondary amines is well-known.[9] Brown has clearly demonstrated that this reaction does not involve an initial decomposition of the azide into the nitrene but a reversible coordination of the azide with the borane.[9b] In our case, no reaction occurs at room temperature, in the absence of irradiation, between the boranes and the azides used. The kinetics of decomposition of **1b**, under heating, are not modified by the presence of the reagents excluding any interaction of the boranes with the starting azide **1b** (except for the fluoroborane, vide infra). Under irradiation, the rates of decomposition of **1a** and **1b** are not altered by trialkylboranes and are even reduced by the presence of mesitylborane derivatives (due to the absorption of the aromatic ring). Although these experimental observations seem surprising, it should be noted that **1a** and **1b** are reluctant to undergo Staudinger reactions or even [2 + 3]-cycloaddition reactions. The rationalization of the inertness of the azido group of **1** is not obvious, but in any case, it is clear that the reactions reported hereafter involve the phosphanylnitrenes **2**.

Irradiation of azides **1a** and **1b** with dimesitylfluoroborane led to *P*-fluoro-*N*-(dimesitylboryl)iminophosphoranes **3a** and **3b**, which were isolated as white crystals in 80% yields (Scheme 2).

Numerous so-called stabilized phosphorus ylides have been studied in which the negative charge is delocalized into an organic,[10] organometallic,[11] or heteroatomic[12] framework including boron.[13] In contrast, only little attention has been devoted to the analogous iminophosphorane derivatives,[14] and no X-ray crystal study has been done for *N*-borylated iminophosphoranes. These compounds are of interest, since they can also be considered as "inorganic allenes" and thus can be compared with the only structurally characterized bis(boryl)amide ($Mes_2BNBMes_2$, Li) reported by Power et al.[15] Derivative **3b** was subjected to an

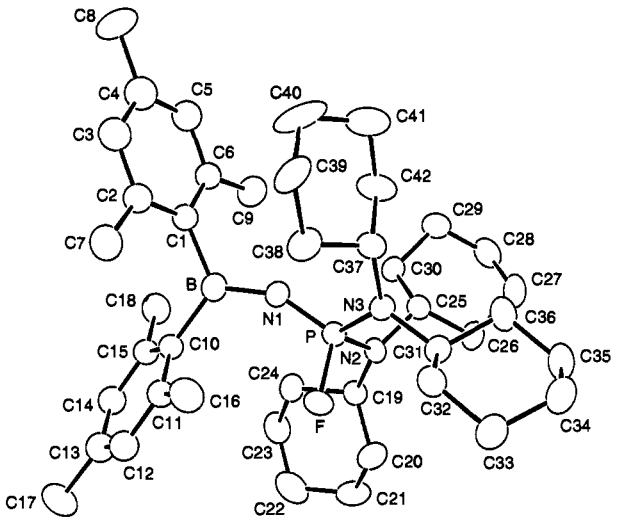


Figure 1. ORTEP drawing of *P*-fluoroiminophosphorane (**3b**).

Table 1. Selected Bond Lengths (Å) and Angles (deg), with esd's in Parentheses, for *P*-Fluoroiminophosphorane (3b)

P–F	1.574(2)	B–N(1)	1.393(6)
P–N(1)	1.520(3)	B–C(1)	1.642(4)
P–N(2)	1.650(3)	B–C(10)	1.631(6)
P–N(3)	1.638(4)		
F–P–N(1)	113.1(2)	N(1)–P–N(2)	119.1(2)
F–P–N(2)	99.0(1)	N(1)–P–N(3)	112.8(2)
F–P–N(3)	103.1(1)	N(2)–P–N(3)	107.9(2)
P–N(1)–B	150.2(3)	N(1)–B–C(10)	120.4(3)
N(1)–B–C(1)	118.1(4)	C(1)–B–C(10)	121.4(3)

X-ray crystal study. The atom-labeling scheme for **3b** is given on the ORTEP view of the molecule (Figure 1). Selected bond lengths and angles are given in Table 1. Of particular interest is the PN(1) bond distance (1.520(3) Å), which lies near the lower limit of all known values for PN bonds (1.467 Å in Ar—N≡P^+),[16] excluding any significant weight of the polar resonance form ≻P^+–N^-–. The value of the BN(1) bond length (1.393(6) Å) is within the range of those observed for amino-[17] or iminodimesitylboranes (≈1.40 Å),[18] indicating a double-bond character. However, the value of this BN bond length and the value of the PNB angle (150.2(3)°) are larger and smaller, respectively, than those observed in $Mes_2BNBMes_2$, Li (1.343 Å; 176°).[15] The deviation from a pure allene geometry is the consequence of the replacement of the p orbital of boron by the σ^* orbital of phosphorus.

In solution, a similar picture emerges from NMR spectroscopy. The high-field ^{31}P NMR chemical shift (**3a**, +5.9; **3b**, +15.5) is in good agreement with an iminophosphorane structure, and the broad boron NMR signal (**3a**, +49.4; **3b**, +45.0), in the range of dimesitylaminoboranes.[19]

Derivatives **3** formally result from a 1,2-addition of the fluoroborane to the phosphorus–nitrogen multiple bond of phosphinonitrene **2** (pathway a). However, the primary formation of the desired phosphinonitrene–borane adduct **4**, followed by a 1,3-migration of the fluorine atom from the electron-rich boron to the electron-poor phosphorus, cannot be ruled out (pathway b). Alternatively, a mechanism involving two successive 1,2-

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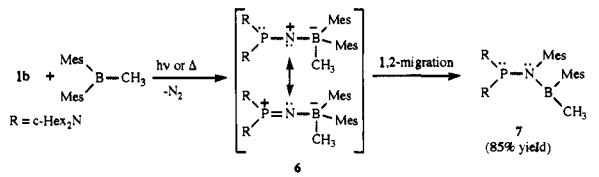
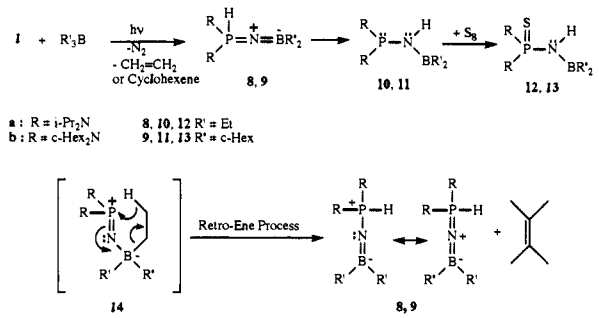
Scheme 3



Scheme 4



migrations of fluorine is also possible (pathway c); indeed since the phosphorus–fluorine bond is very strong, it is quite likely that if it is formed, the fluoramine **5** would rearrange into **3** (Scheme 2). Note that when the azide **1b** was thermolyzed in the presence of dimesitylfluoroborane, two competitive reactions occurred: (i) the formation of nitrene **2b** leading to iminophosphorane **3b** and (ii) an exchange process affording bis(diisopropylamino)phosphoranyl fluoride and dimesitylazidoborane.

To have more insight into the mechanism, phosphanylnitrene **2b** was generated in the presence of dimesitylmethylborane. The *N*-phosphanyl-*N*-boryl-*N*-mesitylamine **7** was obtained in 85% yield. The low-field ^{31}P NMR chemical shift (+122.2) and the broad ^{11}B NMR signal (+54.6, $\nu_{1/2}$ = 461 Hz) indicate the presence of tricoordinated phosphorus and boron atoms. On the ^{13}C NMR spectrum a broad signal at 11.1 indicates that the methyl group is still bonded to boron, and there are two sets of signals for the two mesityl groups; of particular interest, one of the ipso-carbons (bonded to boron) appeared as a broad singlet (142.5) and the other as a well-resolved doublet (146.6, J_{PC} = 5.7 Hz) (Scheme 3).

At this point, it seemed clear that the first-formed nitrene–borane adduct **6** undergoes a 1,2-migration of a boron substituent to nitrogen. It is known, that the migrating ability of substituents in the borates is dictated both by steric and electronic factors.[20] Thus, it is not surprising that, with dimesitylfluoroborane, the very electronegative fluorine and, with dimesitylmethylborane, the bulky mesityl group are the migrating groups, respectively (Scheme 3). Note that product **7** is of the same type as the postulated intermediate **5**, arguing for pathway c in Scheme 2.

Since the alkyl group of dimesitylmethylborane did not migrate, it was tempting to use trialkylboranes. Surprisingly, irradiation of azides **1** in the presence of triethylborane led to *P*-hydrogeno-*N*-boryliminophosphorane **8** in nearly quantitative yield, along with the corresponding amount of dinitrogen and ethylene. A similar reaction occurred with tricyclohexylborane, leading to **9**, dinitrogen, and cyclohexene (Scheme 4).

The structure of adducts **8** and **9** was clear from the rather shielded doublet of quintets on the ^{31}P NMR spectra (**8a**: −7.2, J_{PH} = 485.0 and 14.0 Hz. **8b**: −5.8, J_{PH} = 492.5 and 16.8 Hz. **9a**: −8.3, J_{PH} = 493.0 and 16.9 Hz. **9b**: −7.4, J_{PH} = 500.8 and 17.0 Hz.) and the broad boron signal on the ^{11}B NMR spectra (**8a**, +51.6; **8b**, +50.0; **9a**, +51.0; **9b**, +49.5). In solution, compounds **8** and **9** rearrange (over a week at room temperature in pentane or spontaneously in polar solvents), by a classical

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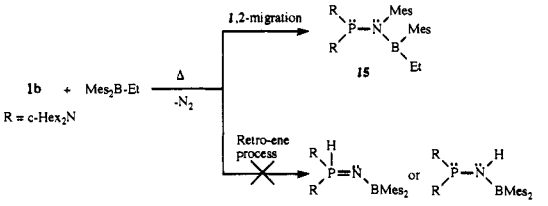
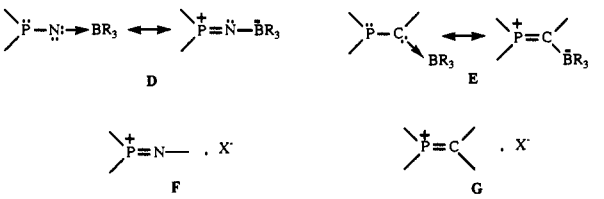
Scheme 5



Scheme 6



prototropic process,[21] into the isomeric phosphanes **10** and **11**. Obviously, when phosphanylnitrene **2b** was generated by thermolysis, **10b** and **11b** were directly obtained. Compounds **10** and **11** were isolated in good yields as thiophosphoranyl derivatives **12** and **13**, after treatment with elemental sulfur. (Scheme 4).

The most reasonable mechanism for the formation of compounds **8** and **9**, along with the corresponding alkenes, is to postulate the formation of the nitrene–borane adduct **14**, which would undergo a retro-ene type reaction[22] (Scheme 4). It is important to note that, in contrast with most retro-ene reactions, formation of **8** and **9** occurs even when the photolysis is performed at −40 °C.

Lastly, when phosphanyl azide **1b** was heated in the presence of dimesitylethylborane, the formation of the *N*-mesitylamine **15** was observed (90% yield), and no trace of the possible retro-ene type derivatives was detected. It is thus clear that the 1,2-migration of a mesityl group is easier than the retro-ene type process (Scheme 5).

Conclusions

Except the thermolysis reaction of phosphanyl azide **1b** with dimesitylfluoroborane, where a competitive exchange reaction was observed, all the boranes used in this study do not react with phosphanyl azides **1** but with the corresponding phosphanylnitrenes **2**. All the results can be rationalized by the primary formation of a transient nitrene–borane complex. However, these adducts are unstable; they either rearrange by 1,2-migration of a boron substituent to nitrogen or undergo a retro-ene type reaction. This last reaction indicates that the multiple-bond character of the free phosphanylnitrene is preserved in the complex **D** (Scheme 6). It is stricking to note that analogous phosphanylcarbene–boron adducts **E** have recently been described.[5b] This corroborates the fact that, although some methylenephosphonium salts **G** are stable,[23] all attempts to characterize iminophosphonium salts **F** failed, so far.[24]

Experimental Section

All experiments were performed in an atmosphere of dry argon or nitrogen. Melting points were obtained on a Electrothermal capillary apparatus and were not corrected. ^{1}H, ^{31}P, ^{13}C, and ^{11}B NMR spectra were recorded on Bruker AC80, AC200, or WM250 spectrometers. ^{1}H

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and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P and ^{11}B downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 and $BF_3{\cdot}OEt_2$, respectively. Infrared spectra were recorded on a Perkin-Elmer lattice spectrometer (Mol 597). Mass spectra were obtained on a Ribermag R10 10E instrument. Photochemical reactions were performed in quartz tubes with a Rayonnet photochemical reactor. Conventional glassware was used.

Synthesis of Bis(dicyclohexylamino)phosphanyl Azide (1b). To a dichloromethane solution (50 mL) of bis(dicyclohexylamino)chlorophosphine (10 g, 23.4 mmol) was added sodium azide (2.28 g, 35.1 mmol) and dibenzo-18-crown-6 (0.84 g, 2.3 mmol). The suspension was stirred for 24 h at room temperature. The solvent was removed under vacuum, and pentane was added. After filtration and evaporation of pentane, azide **1b** was purified by crystallization (Et_2O/CH_3CN) and obtained as white crystals (8.0 g, 79% yield): mp 119 °C dec; ^{31}P NMR ($CDCl_3$) 109.4; ^{13}C NMR ($CDCl_3$) 25.0 (s, NCCC*C*), 26.1 and 26.3 (s, NCC*C*), 34.2–34.8 (m, NC*C*), 55.2 (d, J_{PC} = 10.4 Hz, N*C*); IR ($CDCl_3$) 2100 cm^{-1} (N_3). Anal. Calcd for $C_{24}H_{44}N_5P$: C, 66.47; H, 10.23; N, 16.15. Found: C, 66.52; H, 10.20; N, 16.18.

Synthesis of *P*-Fluoroiminophosphoranes 3a and 3b. A toluene solution (15 mL) of phosphanyl azide **1a** or **1b** (2.5 mmol) and dimesitylfluoroborane (0.67 g, 2.5 mmol) was irradiated at 300 nm for 36 h at room temperature. After evaporation of the solvent, the white residue was slowly recrystallized from pentane to afford iminophosphanes **3a** or **3b** as white crystals.

3a (1.08 g, 80% yield): mp 155 °C; ^{31}P NMR (C_6D_6) 5.9 (d, J_{PF} = 1005.0 Hz); ^{11}B NMR (C_6D_6) 49.4; ^{1}H NMR (C_6D_6) 1.08 (d, J_{HH} = 6.7 Hz, 12 H, NC(CH_3)$_2$), 1.15 (d, J_{HH} = 6.7 Hz, 12 H, NC(CH_3)$_2$), 2.21 (s, 6H, *p*-CH_3), 2.30 (s, 12 H, *o*-CH_3), 3.53 (sept d, J_{HH} = 6.7 Hz, J_{PH} = 19.0 Hz, 4 H, NCH), 6.66 (s, 4 H, H_{arom}); ^{13}C NMR (C_6D_6) 20.9 (s, *p*-CH_3), 21.7 and 21.8 (d, J_{PC} = 2.2 Hz, NC*C*), 22.71 (d, J_{PC} = 1.3 Hz, NC*C*), 22.8 (s, *o*-CH_3), 45.9 (d, J_{PC} = 1.2 Hz, N*C*), 46.0 (d, J_{PC} = 1.2 Hz, N*C*), 127.3 (s, C_m), 137.1 (s, C_p), 139.5 (s, C_o), MS *m/e* 524 (M^+). Anal. Calcd for $C_{30}H_{50}BN_3PF$: C, 70.16; H, 9.81; N, 8.18. Found: C, 69.99; H, 9.84; N, 8.14.

3b (1.34 g, 80% yield): mp 140 °C; ^{31}P NMR (C_6D_6) 15.5 (d, J_{PF} = 1004.6 Hz); ^{11}B NMR (C_6D_6) 45.0; ^{13}C NMR (C_6D_6) 20.8 (s, *p*-CH_3), 22.6 (s, *o*-CH_3), 25.0 (s, NCC*C*), 26.4 (s, NCCC*C*), 32.1 (s, NC*C*), 33.2 (s, NC*C*), 55.3 (d, J_{PC} = 5.3 Hz, N*C*), 55.4 (d, J_{PC} = 5.4 Hz, N*C*), 127.2 (s, C_m), 135.0 (s, C_p), 139.3 (s, C_o), 143.7 (broad s, C_i); MS *m/e* 673 (M^+). Anal. Calcd for $C_{42}H_{66}BN_3PF$: C, 74.87; H, 9.87; N, 6.24. Found: C, 74.89; H, 9.90; N, 6.21.

Synthesis of *N*-Mesitylphosphane (7). A toluene solution (10 mL) of phosphanyl azide **1b** (1.79 g, 4.13 mmol) and dimesitylmethylborane (1.09 g, 4.13 mmol) was heated at 110 °C for 16 h. After evaporation of the solvent, phosphane **7** was obtained as a white powder (2.35 g, 85% yield): mp 158 °C; ^{31}P NMR ($CDCl_3$) 122.2; ^{11}B NMR (C_7D_8, 66 °C) 54.6 ($\nu_{1/2}$ = 461 Hz); ^{13}C NMR ($CDCl_3$) 11.1 (broad s, BCH_3), 20.4 and 20.8 (s, *p*-CH_3), 21.7, 21.8, 23.8, and 24.1 (s, *o*-CH_3), 25.9 (s, NCC*C*), 27.3 and 27.4 (s, NCCC*C*), 35.7 and 35.9 (s, NC*C*), 59.8 and 60.2 (s, N*C*), 127.6 and 129.3 (s, C_m), 133.4 and 135.8 (s, C_p), 135.2 and 137.9 (s, C_O), 142.5 (broad, C_i), 146.6 (d, J_{PC} = 5.7 Hz, C_i); MS *m/e* 669 (M^+). Anal. Calcd for $C_{43}H_{69}BN_3P$: C, 77.10; H, 10.38; N, 6.27. Found: C, 77.00; H, 1.43; N, 6.22.

Synthesis of *P*-Hydrogeno-*N*-boryliminophosphoranes 8a, 8b, 9a, and 9b. A toluene solution (4 mL) of phosphanyl azide **1a** or **1b** (1.2 mmol) and triethyl- or tricyclohexylborane (1.2 mmol) was irradiated at 300 nm for 36 h at room temperature. After evaporation of the solvent, the corresponding *P*-hydrogenoiminophosphoranes **8** and **9** were obtained as yellow oils in near quantitative yields. Due to their instability in solution, only **8a** has been fully spectroscopically characterized. **8a**: ^{31}P NMR (C_6D_6) −7.2 (d, J_{PH} = 485 Hz); ^{11}B NMR (C_6D_6) 51.6; ^{1}H NMR (C_6D_6) 1.03 (d, J_{HH} = 6.9 Hz, 12 H, NCCH_3), 1.20 (d, J_{HH} = 6.9 Hz, 12 H, NCCH_3), 0.93–1.45 (m, 10 H, CH_2CH_3), 3.43 (sept d, J_{HH} = 6.9 Hz, J_{PH} = 14.0 Hz, 4 H, NCH), 7.67 (d, J_{PH} = 485.0 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) 8.6 (s, BC*C*), 20.0 (broad s, B*C*), 23.3 (d, J_{PC} = 8.1 Hz, NC*C*), 23.5 (d, J_{PC} = 7.9 Hz, NC*C*), 44.2 (d, J_{PC} = 5.9 Hz, N*C*).

Rearrangement of *P*-Hydrogeno-*N*-boryliminophosphoranes 8 and 9 into Aminophosphanes 10 and 11. Derivatives **8** and **9**, obtained as described above, spontaneously rearranged in chloroform solution into the corresponding aminophosphanes **10** and **11**. **10a**: ^{31}P NMR (C_6D_6) 74.2; ^{11}B NMR (C_6D_6) 48.2; ^{1}H NMR ($CDCl_3$) 0.78–0.95 (m, 10 H, BCH_2CH_3), 1.09 (d, J_{HH} = 7.0 Hz, 12 H, NCCH_3), 1.12 (d, J_{HH} = 7.4 Hz, 12 H, NCCH_3), 3.4 (sept d, J_{HH} = 7.0 Hz, J_{PH} = 10.9 Hz, 4 H, NCH), 4.8 (broad s, 1 H, NH); ^{13}C NMR ($CDCl_3$) 8.28 (s, BC*C*), 16.34 (broad s, B*C*), 23.28 (d, J_{PC} = 5.6 Hz, NC*C*), 24.29 (d, J_{PC} = 7.4 Hz, NC*C*), 44.65 (d, J_{PC} = 11.8 Hz, N*C*). **10b**: ^{31}P NMR (C_6D_6) 73.1; ^{11}B NMR (C_6D_6) 47.4. **11a**: ^{31}P NMR (C_6D_6) 68.5; ^{11}B NMR (C_6D_6) 50.8. **11b**: ^{31}P NMR (C_6D_6) 71.9; ^{11}B NMR (C_6D_6) 49.0.

Synthesis of *N*-Boryl-*N*-thioxophosphoranylamines 12 and 13. A chloroform solution of **10** and **11**, obtained as described above, and elemental sulfur was stirred for 1 h at room temperature. After filtration, evaporation, and several washes with cold pentane, derivatives **12** and **13** were obtained as pale-yellow, low-melting solids (mp < 25 °C).

12a: ^{31}P NMR ($CDCl_3$) 62.0; ^{11}B NMR ($CDCl_3$) 53.1; ^{1}H NMR ($CDCl_3$) 0.78–1.00 (m, 10 H, BCH_2CH_3), 1.14 (d, J_{HH} = 6.9 Hz, 12 H, NCCH_3), 1.25 (d, J_{HH} = 6.9 Hz, 12 H, NCCH_3), 3.70 (sept d, J_{HH} = 7.0 Hz, J_{PH} = 17.4 Hz, 4 H, NCH), 5.05 (broad s, 1 H, NH); ^{13}C NMR ($CDCl_3$) 8.18 (s, BC*C*), 13.00 (broad s, B*C*), 23.45 and 22.01 (s, NC*C*), 46.24 (d, J_{PC} = 4.3 Hz, N*C*). Anal. Calcd for $C_{16}H_{39}BSN_3P$: C, 55.32; H, 11.32; N, 12.10. Found: C, 55.44; H, 11.23; N, 11.99.

12b: ^{31}P NMR ($CDCl_3$) 62.9; ^{11}B NMR ($CDCl_3$) 53.9; ^{1}H NMR ($CDCl_3$) 0.81–1.80 (m, 54 H, CH_2 and CH_3CH_2), 5.28 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) 8.6 (s, CH_2CH_3), 14.1 (broad s, CH_2CH_3), 25.8 (s, NCC*C*), 27.1 (s, NCCC*C*), 32.7 and 34.5 (s, NC*C*), 56.7 (d, J_{PC} = 5.7 Hz, N*C*); MS *m/e* 507 (M^+). Anal. Calcd for $C_{28}H_{55}BSN_3P$: C, 66.25; H, 10.92; N, 8.28. Found: C, 65.98; H, 10.87; N, 8.22.

13a: ^{31}P NMR ($CDCl_3$) 60.9; ^{11}B NMR ($CDCl_3$) 46.7; ^{1}H NMR ($CDCl_3$) 0.95–2.00 (m, 46 H, NCCH_3 and c-Hex), 3.70 (sept d, J_{HH} = 6.9 Hz, J_{PH} = 17.4 Hz, 4 H, NCH), 5.12 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) 22.6 (d, J_{PC} = 2.4 Hz, NC*C*), 24.5 (d, J_{PC} = 2.5 Hz, NC*C*), 27.3 and 27.9 (s, BCC*C*), 28.1 (s, BCCC*C*), 28.6 and 28.9 (s, BC*C*), 35.9 (broad s, B*C*), 47.1 (d, J_{PC} = 5.7 Hz, N*C*). Anal. Calcd for $C_{24}H_{51}BSN_3P$: C, 63.28; H, 11.28; N, 9.22. Found: C, 63.22; H, 11.28; N, 9.20.

13b: ^{31}P NMR ($CDCl_3$) 64.10; ^{11}B NMR ($CDCl_3$) 50.0; ^{1}H NMR ($CDCl_3$) 0.63–2.20 (m, 66 H, c-Hex-B and c-Hex-N), 5.18 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) 24.94 (s, NCC*C*), 25.57 (broad s, NCCC*C*), 26.89 and 26.31 (s, BCC*C*), 27.10 (s, BCCC*C*), 28.25 and 27.81 (s, BC*C*), 34.39 and 33.86 (s, NC*C*), 56.42 (d, J_{PC} = 5.4 Hz, N*C*). The B*C* signals are not observed; they are probably hidden by the NC*C* signals. Anal. Calcd for $C_{36}H_{67}BSN_3P$: C, 70.21; H, 10.97; N, 6.82. Found: C, 70.01; H, 11.05; N, 6.80.

Synthesis of *N*-Mesitylphosphane (15). A toluene solution (10 mL) of phosphanyl azide **1b** (1.95 g, 4.5 mmol) and dimesitylethylborane (1.25 g, 4.5 mmol) was heated at 110 °C for 16 h. After evaporation of the solvent, phosphane **15** was obtained as a white powder (2.67 g, 90% yield): mp 157 °C; ^{31}P NMR ($CDCl_3$) 123.2; ^{11}B NMR (C_6D_6) 43.1; ^{13}C NMR ($CDCl_3$) 9.7 (s, BCH_2CH_3), 16.3 (broad s, BCH_2CH$_3$), 20.6 and 21.0 (s, *p*-CH_3), 21.8 and 21.9 (s, *o*-CH_3), 23.9 and 24.1 (s, *o*-CH_3), 26.0 (s, NCC*C*), 27.5 and 27.6 (s, NCCC*C*), 36.0 (s, NC*C*), 59.7 and 59.8 (s, N*C*), 127.4 and 129.3 (s, C_m), 133.5 and 135.5 (s, C_p), 135.3 and 137.9 (s, C_o), 140.5 (broad s, C_i), 146.2 (d, J_{PC} = 5.9 Hz, C_i); MS *m/s* 683 (M^+). Anal. Calcd for $C_{44}H_{71}BN_3P$: C, 77.28; H, 10.47; N, 6.14. Found: C, 77.20; H, 10.49; N, 6.13.

Table 2. Crystallographic Data for *P*-Fluoroiminophosphorane (3b)

chemical formula	$BC_{42}FH_{66}N_3P$
formula weight	673.79
space group	$P2_1/c$ (no. 14)
Z	4
a, Å	19.869(2)
b, Å	9.271(1)
c, Å	23.344(3)
β, deg	109.40(1)
V, Å^3	4056(1)
ρ_{calcd}, g cm^{-3}	1.103
$\mu_{Mo\ K\alpha}$, cm^{-1}	1.0
cryst dimens, mm	0.50 × 0.40 × 0.20
temp, °C	21
radiation (monochromatic)	Mo, 0.710 73 Å (graphite)
scan type	$\omega/2\theta$
2θ range, deg	3–46
no. of data collected	5804
no. of unique data	4771 (R_{av} = 0.018)
no. of observed data $F_o^2 > 2\sigma(F_o^2)$	3138
no. of params varied	349
$R(F_o)$	0.045
$R_w(F_o)$	0.045
goodness of fit	1.5
max. parameter shift/esd	0.001

X-ray Structural Determination of *P*-Fluoroiminophosphorane (3b). A colorless crystal of **3b** was glued on a glass fiber and placed on the CAD4 diffractometer. Twenty-five reflections with values of θ between 10° and 19° were centered and used for cell determination. Data were collected in a *P* monoclinic crystal system with absences consistent with space group $P2_1/c$. Solution by direct methods using the SHELX program allowed placement of most atoms, and least-squares refinement followed by difference-Fourier map, using the SHELX-76 program, allowed the location of all remaining atoms. In the final model, hydrogens were placed in idealized positions and all non-hydrogen atoms were refined anisotropically. Data collection and refinement parameters are given in Table 2.

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Supplementary Material Available: Tables of fractional atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compound **3b** (5 pages); table of observed and calculated structure factors for compound **3b** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.