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Effects of a Strong Electron-Withdrawing *N*-Boryl Substituent on the Stability of Nitrilimines: Surprising Dimerization Involving the Nitrilimine Heteroatom Substituents with Formation of (Fused) Bicyclic [3.3.0] and [4.3.0] Derivatives

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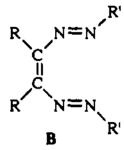
Summary: The lithium salts of [bis(diisopropylamino)-phosphino]diazomethane **1a** *and [bis(diisopropylamino)thioxophosphoranyl]diazomethane* **1b** *react with dicyclohexylchloroborane giving transient N-borylnitrilimines* **2a** *and* **2b**, *which dimerize affording (fused) heterobicyclic [3.3.0] and [4.3.0] derivatives* **4** *and* **6**, *respectively. Base induced hydrolysis of* **6** *leads to 1,4-dihydro-1,2,4,5-tetrazine* **9**.

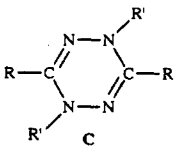
Nitrilimines **A** are important reagents in organic synthesis,[1] but most of them are only stable at low temperatures (T < 80 K) or in the gas phase.[2] In the absence of dipolarophiles, these 1,3-dipoles usually give rise to complex mixtures of products.[1,2] However, two types of dimers have been isolated: bis(azo)ethylenes **B**, which can be considered as "carbene" dimers,[3] and 1,4-dihydro-1,2,4,5-tetrazines **C**, the formal head-to-tail 3 + 3 dimers.[4] Recently, we have shown that, providing bulky substituents are used, monomeric nitrilimines could exist as stable compounds in the liquid and solid states.[5] Dimerization did not occur. Experimental and theoretical studies have shown that nucleophilic nitrilimines have a bent, nonplanar, allenic type structure.[6,7] Geometric changes in the direction of propargylic structures were expected,[7] and observed only to some extent, for electrophilic nitrilimines.[8] We report here the unexpected dimerization of nitrilimines induced by strongly acidic boryl substituents.


$R-\overset{+}{C}=N-\overset{-}{N}-R'$

A



B



C

Stable *N*-borylnitrilimines of type **2** (R = R′ = iPr$_2$N, X = S or lone pair) have been obtained earlier by reacting bis(diisopropylamino)chloroborane with the lithium salts of [bis(diisopropylamino)phosphino]diazomethane (**1a**) and [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**1b**).[9] However, the presence of amino groups strongly decreases the Lewis acid character of boron, and thus it was tempting to use dialkylhalogenoboranes. Addition of dicyclohexylchloroborane to a THF solution of **1a** at −78 °C results in rapid formation of derivative **4**, which was isolated as a violet oil, in 90% yield. The mass spectroscopic data were in agreement with a dimerization of the transient *N*-borylnitrilimine **2a**. In the ^{11}B NMR spectrum, a broad signal at +52.5 ppm was consistent with the presence of a boryl group, but a sharp signal at +5.5 ppm indicated a borate moiety, excluding the formation of symmetrical dimers of types **B** or **C**. The ^{31}P NMR spectrum of **4** showed an AB system (δ_P +36.2 and +36.7) with a large coupling constant (J_{PP} = 159.9 Hz), arguing for a PCP sequence, which was confirmed by the ^{13}C NMR spectrum where the two quaternary carbons appeared as two doublets of doublets (δ_C 122.8, J_{PC} = 78.4 and 12.8 Hz and 144.4, J_{PC} = 167.0 and 21.7 Hz). Since derivative **4** was reluctant to crystallize, and in order to have more insight into its actual structure, it was treated with 1 equiv of elemental sulfur. After filtration on silica gel and recrystallization from toluene–pentane, compound **5** was isolated as orange crystals (mp 210 °C, 85% yield). Comparison of the analytical data for **4** and **5** clearly indicated that no major changes occurred except that the boryl group has been cleaved, probably by hydrolysis on silica gel, and one of the phosphorus atoms has been oxidized by sulfur. The ORTEP drawing of **5** (Figure 1) shows that this compound has a zwitterionic bicyclic[3.3.0] structure, each of the fused five-membered rings being nearly planar (maximum deviation = 0.016 Å) with a dihedral angle [P(1)–C(1)–N(1)–N(2)–C(2)]–[N(2)–C(2)–N(3)–N(4)–B] of 7.7(6)°.

The mechanism rationalizing the formation of compound **4** is of special interest. It formally involves two different resonance forms of transient nitrilimine **2a**, one of which features a boron–nitrogen double bond due to the strongly acidic character of boron. In the first step the CNN skeleton of one molecule of **2a** reacts with the boron–nitrogen multiple bond of a second one by a [2 + 3] cycloaddition reaction,[10] giving a transient zwitterion

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1994.

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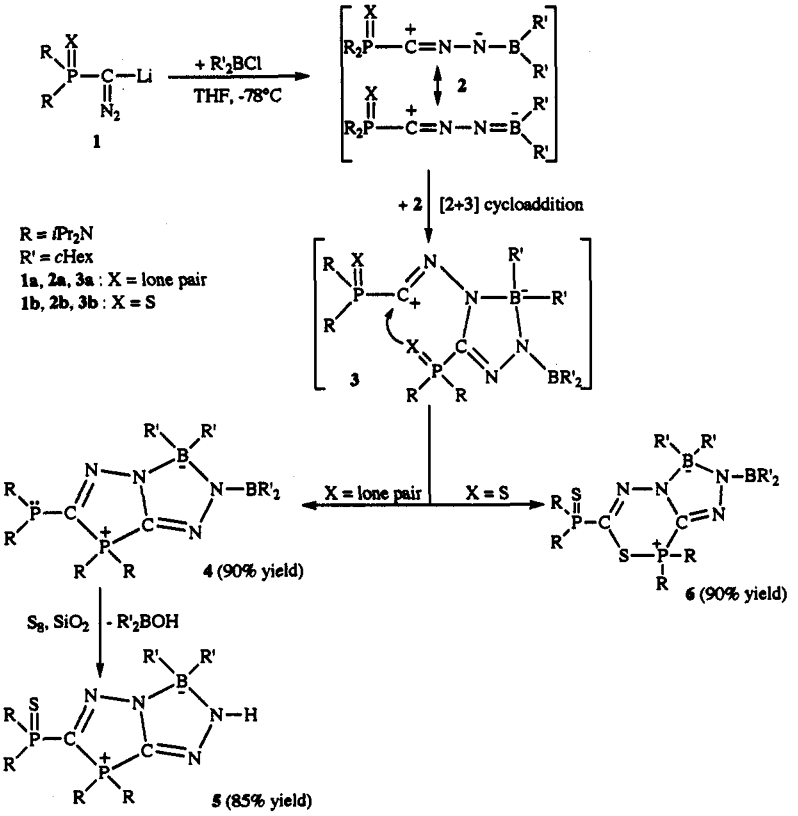
Scheme 1



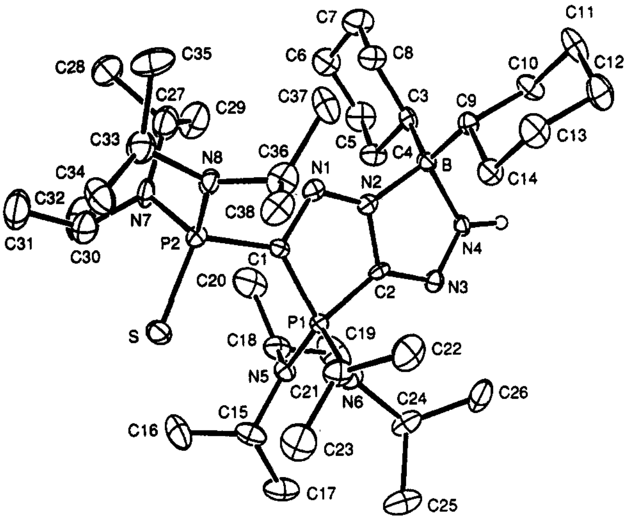


Figure 1. Molecular structure of **5** (ORTEP). H atoms are not shown for clarity, except for NH. Selected bond lengths (Å) and bond angles (deg): P(1)–C(1) 1.777(4), P(1)–C(2) 1.764(5), C(1)–N(1) 1.366(6), C(2)–N(2) 1.385(6), N(1)–N(2) 1.328(5), B–N(2) 1.584(6), B–N(4) 1.596(6), N(3)–N(4) 1.307(5), C(2)–N(3) 1.336(6); C(1)–P(1)–C(2) 87.3(2), P(1)–C(1)–N(1) 113.2(3), C(1)–N(1)–N(2) 112.9(3), N(1)–N(2)–C(2) 115.0(4), P(1)–C(2)–N(2) 111.7(3), N(2)–C(2)–N(3) 112.6(4), C(2)–N(3)–N(4) 108.5(4), N(3)–N(4)–B 116.3(3), N(2)–B–N(4) 91.8(3).

3a. In a second step, **3a** undergoes a ring closure by nucleophilic addition of the phosphorus lone pair to the carbocation.

A similar result was observed when dicyclohexylchloroborane was added at -78 °C to a THF solution of lithium salt **1b**. Compound **6**, featuring fused five- and six-membered rings, was isolated as an orange oil in 90% yield. The structure of compound **6** was easily found by comparing its spectroscopic data with those observed for **4** and **5**. In particular, there were two signals in the ^{11}B NMR spectrum at δ_B +6.8 (sharp) and +52.5 (broad), the two quaternary carbon signals appeared as doublets of doublets [δ_C 115.9, J_{PC} = 173.8 and 5.6 Hz, and 129.1, J_{PC} = 163.6 and 1.1 Hz] in the ^{13}C NMR spectrum, and an AX system at δ_P +29.5 and +64.3 with a small phosphorus–phosphorus coupling constant (J_{PP} = 26.0 Hz) was observed in the ^{31}P NMR spectrum. From a mechanistic point of view, the only difference from the previous reaction is the attack at the cationic center by the sulfur lone pair.

Surprisingly, base induced hydrolysis of **6** led to 1,4-dihydro-1,2,4,5-tetrazine **9**, the formal 3 + 3 dimer (type C) of the *N*-hydrogeno-*C*-[bis(diisopropylamino)thioxophosphoranyl]nitrilimine. Compound **9** has been fully characterized, including a single-crystal X-ray study; the ORTEP view shows that **9** has a twist conformation (Figure 2). A possible mechanism for this reaction could be the hydrolysis of the boryl group leading to **7**, which, in the presence of a base, would be in equilibrium with the open form **8**. Nucleophilic attack of the amide at the ring carbon atom then leads to **9** (Scheme 2).

These results are additional proof[11] that the scope of application of dipoles having a nitrilium betaine structure can be enlarged enormously by introducing heteroatom substituents.

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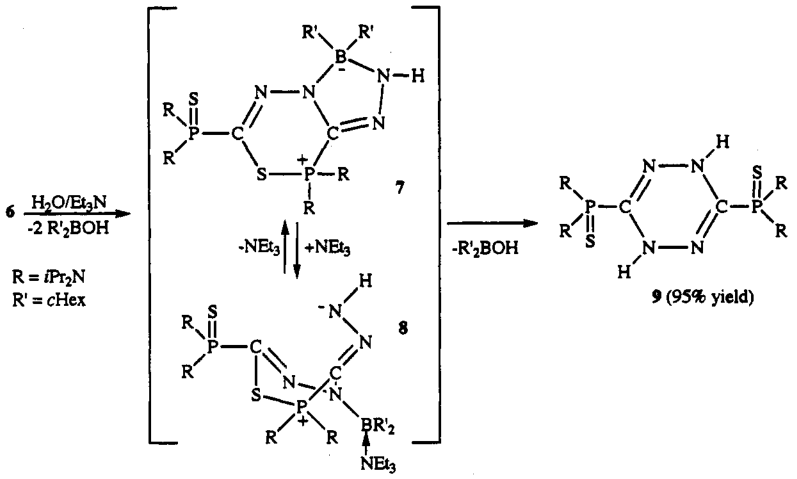
Scheme 2



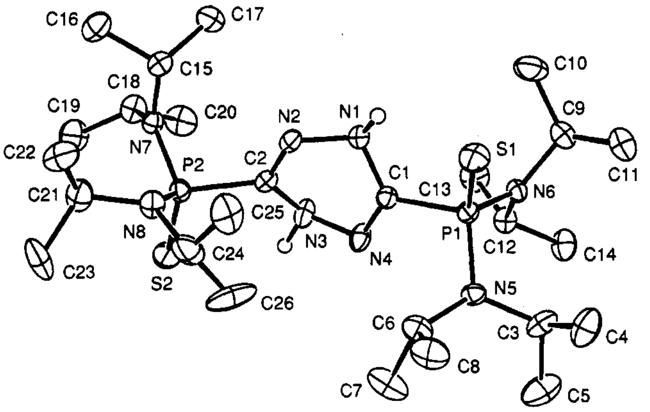


Figure 2. Molecular structure of **9** (ORTEP). H atoms are not shown for clarity, except for NH. Selected bond lengths (Å) and torsion angles (deg): P(1)–C(1) 1.846(3), C(1)–N(1) 1.396(3), C(1)–N(4) 1.267(4), N(1)–N(2) 1.427(3), N(3)–N(4) 1.435(3), C(2)–N(2) 1.268(4), C(2)–N(3) 1.387(3), P(2)–C(2) 1.844(2); C(1)–N(1)–N(2)–C(2) –42.4(3), N(1)–N(2)–C(2)–N(3) 0.5(4), N(2)–C(2)–N(3)–N(4) 42.9(3), C(2)–N(3)–N(4)–C(1) –42.1(3), N(3)–N(4)–C(1)–N(1) 0.2(3), N(4)–C(1)–N(1)–N(2) 43.1(3).

Table 1. Experimental Data for the X-ray Diffraction Studies

	5	**9**
formula	$C_{38}H_{79}BN_8P_2S$	$C_{26}H_{58}N_8P_2S_2$
mol wt	752.9	608.9
measurement temp, K	173	293
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	11.638(2)	15.766(1)
b, Å	21.109(4)	13.246(1)
c, Å	18.058(3)	18.660(2)
β, deg	90.92(2)	114.58(1)
cell vol, $Å^3$	4436(2)	3543.8(8)
Z	4	4
$F(000)$	1656	1328
d_{calcd}, $g{\cdot}cm^{-3}$	1.127	1.141
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	0.17	0.26
scan mode	ω–2θ	ω–2θ
scan with, deg	$0.90 + 0.35 \tan\theta$	$0.80 + 0.35 \tan\theta$
scan range, 2θ, deg	3–44	3–50
no. of meas refl	5743	5217
no. of obs refl, NO	3078 $[F_o^2 > 2\sigma(F_o^2)]$	3660 $[F_o^2 > 3\sigma(F_o^2)]$
no. of refined param, NV	452	349
R^a	0.044	0.027
R_w^b	0.054	0.030
S^c	1.39	1.01
$(\Delta/\sigma)_{max}$	0.018	0.010
max residual peak, $e{\cdot}Å^{-3}$	0.44	0.15

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $S = [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ with $w = [\sigma^2(F_o) + 0.0008F_o^2]^{-1}$ for **5** and $w = 1$ for **9**.

Experimental Section

Heterobicyclic[3.3.0] Derivative 4. To a THF solution (30 mL) of diazolithium salt **1a**[12] (2 mmol) at –78 °C was added a THF solution (10 mL) of dicyclohexylchloroborane (0.42 g, 2 mmol). After the solution had warmed to room temperature, the solvent was removed under vacuum, and the residue was treated with pentane and filtered. After evaporation of the pentane, compound **4** was obtained as a violet oil (1.61 g, 90% yield). ^{31}P NMR ($CDCl_3$): δ_P +36.2 and +36.7 (J(PP) = 159.9 Hz). ^{11}B NMR ($CDCl_3$): δ_B +52.5 and +5.5. ^1H NMR ($CDCl_3$): δ 1.16–1.33 (m, 92 H, CH_3CH and *c*Hex), 3.78 (sept d, J(HH) = 6.4 Hz, J(HP) = 12.8 Hz, 4 H, CHN), 4.13 (sept d, J(HH) = 7.5 Hz, J(HP) = 15.0 Hz, 4 H, CHN). ^{13}C NMR ($CDCl_3$): δ_C 24.6 (d, J(PC) = 7.0 Hz, CH_3CH), 24.8 (d, J(PC) = 19.1 Hz, CH_3CH), 25.3 (d, J(PC) = 7.0 Hz, CH_3CH), 26.1 (d, J(PC) = 4.5 Hz, CH_3CH), 28.4–30.5 (CH_2), 32.5 and 34.7 (s broad, CHB), 48.9 (d, J(PC) = 5.5 Hz, CHN), 50.0 (d, J(PC) = 12.5 Hz, CHN), 122.8 (dd, J(PC) = 12.8 and 78.4 Hz, PCP), 144.4 (dd, J(PC) = 167.0 and 21.7 Hz, PCPC). Mass spectrum: m/z 897 (M + 1). Anal. Calcd for $C_{50}H_{100}B_2N_8P_2$: C, 66.95; H, 11.24; N, 12.49. Found: C, 67.05; H, 11.26; N, 12.44.

Heterobicyclic[3.3.0] Derivative 5. To a THF solution (40 mL) of **4** (1.80 g, 2 mmol) was added an excess of sulfur. After stirring for 2 h at room temperature, the mixture was filtered on silica gel and the solvent evaporated. On crystallization from toluene–pentane, compound **5** was obtained as orange crystals (1.28 g, 85% yield). Mp: 210 °C. ^{31}P NMR ($CDCl_3$): δ_P +32.8 and +63.4 (J(PP) = 91.0 Hz). ^{11}B NMR ($CDCl_3$): δ_B +1.7. ^1H NMR ($CDCl_3$): δ 1.29–1.36 (m, 70 H, CH_3CH and *c*Hex), 3.95 (sept d, J(HH) = 7.1 Hz, J(HP) = 14.0 Hz, 4 H, CHN), 4.30 (sept d, J(HH) = 6.7 Hz, J(HP) = 14.3 Hz, 4 H, CHN), 7.65 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ_C 24.4 (d, J(PC) = 4.5 Hz, CH_3CH), 24.6 (d, J(PC) = 4.0 Hz, CH_3CH), 25.0 (d, J(PC) = 3.5 Hz, CH_3CH), 25.2 (d, J(PC) = 4.5 Hz, CH_3CH), 27.4–29.6 (s, CH_2), 31.6 (s broad, CHB), 47.2 (d, J(PC) = 6.9 Hz, CHN), 48.5 (d, J(PC) = 7.4 Hz, CHN), 113.7 (dd, J(PC) = 175.5 and 107.4 Hz, PCP), 136.3 (dd, J(PC) = 190.0 and 10.1 Hz, PCPC). Anal. Calcd for $C_{38}H_{79}BN_8P_2S$: C, 60.61; H, 10.58; N, 14.88. Found: C, 60.98; H, 11.08; N, 15.00.

Heterobicyclic[4.3.0] Derivative 6. To a THF solution (30 mL) of diazolithium salt **1b**[13] (2 mmol) at –78 °C was added

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Table 2. Fractional Atomic Coordinates and Isotropic Equivalent Temperature Factors (Å^2 × 100) with Esds in Parentheses for 5

atom	x	y	z	U_{eq}[a]
S	0.7807(1)	0.74976(6)	0.72792(8)	3.29(8)
P(1)	0.8124(1)	0.58442(6)	0.70297(7)	1.94(7)
P(2)	0.6912(1)	0.69645(6)	0.79481(7)	2.07(7)
N(1)	0.6608(3)	0.5703(2)	0.8084(2)	2.3(2)
N(2)	0.6913(3)	0.5119(2)	0.7894(2)	2.0(2)
N(3)	0.7910(3)	0.4491(2)	0.7118(2)	2.3(2)
N(4)	0.7235(3)	0.4113(2)	0.7485(2)	2.1(2)
N(5)	0.9526(3)	0.5943(2)	0.7099(2)	2.3(2)
N(6)	0.7809(3)	0.5969(2)	0.6147(2)	2.6(2)
N(7)	0.7278(3)	0.7088(2)	0.8834(2)	3.0(3)
N(8)	0.5492(3)	0.7073(2)	0.7899(2)	2.6(2)
B	0.6413(5)	0.4439(2)	0.8072(3)	2.2(3)
C(1)	0.7160(4)	0.6159(2)	0.7689(2)	1.9(3)
C(2)	0.7716(4)	0.5085(2)	0.7338(2)	1.9(3)
C(3)	0.6715(4)	0.4175(2)	0.8889(3)	2.5(3)
C(4)	0.7986(4)	0.4221(3)	0.9110(3)	3.3(3)
C(5)	0.8245(4)	0.3956(3)	0.9876(3)	4.6(4)
C(6)	0.7530(4)	0.4267(3)	1.0447(3)	4.6(4)
C(7)	0.6262(4)	0.4214(3)	1.0256(3)	4.6(4)
C(8)	0.5981(4)	0.4475(3)	0.9487(3)	3.5(3)
C(9)	0.5082(4)	0.4401(2)	0.7809(2)	2.2(3)
C(10)	0.4583(4)	0.3733(2)	0.7883(3)	3.3(3)
C(11)	0.3323(4)	0.3698(2)	0.7644(3)	4.2(3)
C(12)	0.3130(4)	0.3941(3)	0.6866(3)	4.4(4)
C(13)	0.3600(4)	0.4602(2)	0.6787(3)	3.9(3)
C(14)	0.4871(4)	0.4635(2)	0.7011(3)	2.9(3)
C(15)	1.0163(4)	0.6410(3)	0.6663(3)	3.8(3)
C(16)	1.0662(4)	0.6955(2)	0.7116(3)	5.1(4)
C(17)	1.1117(4)	0.6096(3)	0.6213(3)	5.3(4)
C(18)	1.0240(4)	0.5634(2)	0.7699(3)	3.5(3)
C(19)	1.0543(5)	0.4958(3)	0.7533(4)	6.4(5)
C(20)	0.9719(5)	0.5707(3)	0.8458(3)	5.9(4)
C(21)	0.6888(4)	0.6412(2)	0.5913(3)	3.3(3)
C(22)	0.5856(4)	0.6086(3)	0.5545(3)	4.6(4)
C(23)	0.7301(5)	0.6956(3)	0.5440(3)	5.0(4)
C(24)	0.8324(5)	0.5499(2)	0.5630(3)	3.6(3)
C(25)	0.8817(5)	0.5793(3)	0.4929(3)	5.3(4)
C(26)	0.7521(5)	0.4947(2)	0.5427(3)	4.5(4)
C(27)	0.6667(5)	0.6740(2)	0.9419(3)	5.0(4)
C(28)	0.6188(5)	0.7181(3)	1.0019(3)	6.1(4)
C(29)	0.7342(5)	0.6188(3)	0.9766(3)	6.0(4)
C(30)	0.8235(4)	0.7537(2)	0.9017(3)	5.3(4)
C(31)	0.7806(6)	0.8199(2)	0.9221(3)	6.6(5)
C(32)	0.9104(5)	0.7281(3)	0.9583(3)	7.4(5)
C(33)	0.5055(4)	0.7657(2)	0.8257(3)	4.8(4)
C(34)	0.5019(5)	0.8231(2)	0.7734(3)	5.4(4)
C(35)	0.3900(4)	0.7550(3)	0.8638(3)	6.6(5)
C(36)	0.4769(4)	0.6694(2)	0.7382(3)	4.6(4)
C(37)	0.3928(4)	0.6252(2)	0.7749(3)	4.4(4)
C(38)	0.4203(5)	0.7110(3)	0.6784(3)	6.6(5)

[a] $U_{eq} = {}^1/_3[U11 + U22 + U33]$.

Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2 × 100) with Esds in Parentheses for 9

atom	x	y	z	U_{eq}[a]
S(1)	0.39002(5)	0.17278(6)	0.65856(4)	5.41(4)
S(2)	0.89168(5)	0.35636(6)	0.71605(5)	6.50(5)
P(1)	0.41789(4)	0.24919(5)	0.58204(3)	3.23(3)
P(2)	0.84470(4)	0.24970(5)	0.76152(4)	3.67(3)
C(1)	0.5443(2)	0.2356(2)	0.6101(1)	3.6(1)
N(1)	0.5855(1)	0.1455(2)	0.6470(1)	4.5(1)
N(2)	0.6754(1)	0.1606(2)	0.7096(1)	4.2(1)
C(2)	0.7236(2)	0.2237(2)	0.6913(1)	3.8(1)
N(3)	0.6870(1)	0.2696(2)	0.6178(1)	4.7(1)
N(4)	0.5921(1)	0.3013(2)	0.5940(1)	4.5(1)
N(5)	0.3989(1)	0.3728(1)	0.5786(1)	3.8(1)
N(6)	0.3694(1)	0.2084(1)	0.4904(1)	3.5(1)
N(7)	0.9019(1)	0.1422(2)	0.7761(1)	3.7(1)
N(8)	0.8366(1)	0.2754(2)	0.8456(1)	4.5(1)
C(3)	0.3042(2)	0.4087(2)	0.5250(2)	5.3(2)
C(4)	0.2319(2)	0.4039(3)	0.5583(2)	8.6(3)
C(5)	0.3055(3)	0.5115(3)	0.4896(2)	9.2(3)
C(6)	0.4588(2)	0.4290(2)	0.6517(2)	5.5(2)
C(7)	0.5060(3)	0.5189(3)	0.6340(2)	9.5(3)
C(8)	0.4159(3)	0.4548(3)	0.7073(2)	8.5(3)
C(9)	0.3099(2)	0.1164(2)	0.4634(2)	5.0(2)
C(10)	0.3600(2)	0.0177(2)	0.5004(2)	7.2(2)
C(11)	0.2172(2)	0.1297(2)	0.4680(2)	6.9(2)
C(12)	0.4009(2)	0.2544(2)	0.4326(1)	4.3(1)
C(13)	0.4659(2)	0.1833(2)	0.4138(2)	7.0(2)
C(14)	0.3187(2)	0.2872(2)	0.3568(1)	5.7(2)
C(15)	0.8722(2)	0.0543(2)	0.8100(1)	4.3(2)
C(16)	0.9538(2)	0.0069(2)	0.8788(2)	6.0(2)
C(17)	0.8234(2)	−0.0267(2)	0.7489(2)	5.9(2)
C(18)	0.9704(2)	0.1166(2)	0.7428(2)	5.6(2)
C(19)	1.0635(2)	0.1684(3)	0.7844(2)	8.9(3)
C(20)	0.9313(3)	0.1249(3)	0.6532(2)	9.6(3)
(C21)	0.9238(2)	0.2706(2)	0.9183(2)	5.9(2)
C(22)	0.9087(3)	0.2177(3)	0.9850(2)	8.4(2)
C(23)	0.9716(2)	0.3716(3)	0.9438(2)	8.2(2)
C(24)	0.7602(2)	0.3392(3)	0.8480(3)	9.3(3)
C(25)	0.6869(2)	0.2817(3)	0.8625(2)	10.5(3)
C(26)	0.7180(3)	0.4069(3)	0.7787(3)	13.0(4)

[a] $U_{eq} = {}^1/_3\ [U11 + U22 + U33]$.

dicyclohexylchloroborane (0.42 g, 2 mmol) in THF (10 mL). The solution was warmed to room temperature, the solvent was evaporated, and the residue was treated with pentane and filtered. After evaporation of the pentane, compound 6 was obtained as an orange oil (1.73 g, 90% yield). ^{31}P NMR (CDCl$_3$): δ_P +29.5 and +64.3 (J(PP) = 26.0 Hz). ^{11}B NMR (CDCl$_3$): δ_B +52.5 and +6.8. ^{1}H NMR (CDCl$_3$): δ 1.11–1.60 (m, 92 H, C*H*$_3$CH and *c*Hex), 3.72 (sept d, J(HH) = 6.9 Hz, J(PH) = 17.6 Hz, 4 H, CHN), 4.04 (sept d, J(HH) = 6.9 Hz, J(PH) = 16.4 Hz, 4 H, CHN). ^{13}C NMR (CDCl$_3$): δ_C 23.1 (d, J(PC) = 3.1 Hz, *C*H$_3$CH), 23.9 (d, J(PC) = 2.5 Hz, *C*H$_3$CH), 24.1 (d, J(PC) = 3.1 Hz, *C*H$_3$CH), 24.6 (d, J(PC) = 1.8 Hz, *C*H$_3$CH), 26.9–30.4 (s, *C*H$_2$), 31.3 and 32.5 (s broad, CHB), 47.9 (d, J(PC) = 5.5 Hz, CHN), 49.6 (d, J(PC) = 4.9 Hz, CHN), 115.9 (dd, J(PC) = 173.8 and 5.6 Hz, PCP), 129.1 (dd, J(PC) = 163.6 and 1.1 Hz, PCP*C*). Mass spectrum: m/z 961 (M + 1). Anal. Calcd for $C_{50}H_{100}B_2N_8P_2S_2$: C, 62.48; H, 10.49; N, 11.66. Found: C, 62.55; H, 10.56; N, 11.60.

1,4-Dihydro-1,2,4,5-tetrazine 9. To a THF solution (40 mL) of 6 (0.96 g, 1 mmol) was added an excess of wet Et$_3$N (2 mL). After stirring for 2 h at room temperature, the solvent was removed and compound 6 was obtained after crystallization from pentane as orange crystals (0.57 g, 95% yield). Mp: 208 °C. ^{31}P NMR (CDCl$_3$): δ_P +54.8. ^{1}H NMR (CDCl$_3$): δ 1.28 (d, J(HH) = 6.8 Hz, 24 H, C*H*$_3$CH), 1.28 (d, J(HH) = 6.8 Hz, 24 H, C*H*$_3$CH), 3.82 (sept d, J(HH) = 6.8 Hz, J(HP) = 18.0 Hz, 8 H, CHN), 8.29 (s broad, 2 H, NH). ^{13}C NMR (CDCl$_3$): δ_C 23.0 (d, J(PC) = 1.8 Hz, *C*H$_3$CH), 47.2 (d, J(PC) = 2.6 Hz, CHN), 47.3 (d, J(PC) = 2.7 Hz, CHN), 145.4 (d, J(PC) = 145.8 Hz, PCN). Anal. Calcd for $C_{26}H_{58}N_8P_2S_2$: C, 51.29; H, 9.60; N, 18.40. Found: C, 51.19; H, 9.70; N, 18.46.

X-ray Crystallographic Studies. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å), at 173 K for 5 and 293 K for 9. Unit cells were obtained from the least-squares fit of the setting angles of 25 reflections. During data collection, three standard reflections were checked every 2 h, showing no significative variations. No absorption corrections were made. Crystal data and details of data collection are given in Table 1. Atomic coordinates are given in Tables 2 and 3.

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Supplementary Material Available: Listings of crystal and intensity collection data, positional and thermal parameters, interatomic distances and angles, and least-squares planes equations for 5 and 9 (17 pages). Ordering information is given on any current masthead page.

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