

# Novel [2 + 2] Cycloaddition Reactions of (Dimethylamino)bis(trifluoromethyl)borane, (CF<sub>3</sub>)<sub>2</sub>BNMe<sub>2</sub>, with *N*-Sulfinylsulfonamides, Aminoiminophosphines, Carbodiimides, and a Keteneimine<sup>†</sup>

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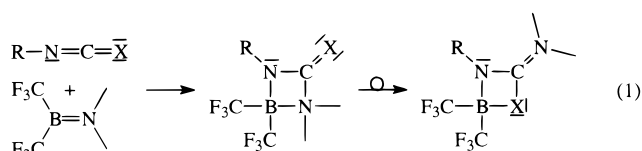
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Received March 27, 1997<sup>®</sup>

(Dimethylamino)bis(trifluoromethyl)borane, (CF<sub>3</sub>)<sub>2</sub>BNMe<sub>2</sub> (**1**), combines with *N*-sulfinylsulfonamides R–O<sub>2</sub>S–N=S=O in a [2 + 2] fashion to form (CF<sub>3</sub>)<sub>2</sub>B–NMe<sub>2</sub>–S(O)–N–SO<sub>2</sub>R (R = Me (**2a**), Et (**2b**), *i*Pr (**2c**), Ph (**2d**), and *p*Tol (**2e**)). Aminoiminophosphines RN=P–NR<sub>2</sub>' react with **1** analogously to yield the heterocycles (CF<sub>3</sub>)<sub>2</sub>B–NMe<sub>2</sub>–P(NR<sub>2</sub>')–NR (R = SiMe<sub>3</sub>, NR<sub>2</sub>' = N(SiMe<sub>3</sub>)<sub>2</sub> (**3a**), TMP (**3b**); R = *t*Bu, NR<sub>2</sub>' = N(SiMe<sub>3</sub>)*t*Bu (**3c**), N*i*Pr<sub>2</sub> (**3d**), TMP (**3e**)). Carbodiimides R–N=C=N–R add to the B=N bond of **1** to give unstable adducts (CF<sub>3</sub>)<sub>2</sub>B–NMe<sub>2</sub>–C(NR)–NR which rearrange at 20 °C to yield the four-membered heterocycles (CF<sub>3</sub>)<sub>2</sub>B–NR–C(NMe<sub>2</sub>)–NR (R = *i*Pr (**5a**), *c*C<sub>6</sub>H<sub>11</sub> (**5b**)). For carbodiimides with aryl substituents R = *p*XC<sub>6</sub>H<sub>4</sub>, this rearrangement competes with an internal electrophilic aromatic substitution reaction and mixtures of the two isomers (CF<sub>3</sub>)<sub>2</sub>B–NC<sub>6</sub>H<sub>4</sub>X–C(NMe<sub>2</sub>)–NC<sub>6</sub>H<sub>4</sub>X (X = H (**5c**), Me (**5d**), OMe (**5e**)) and (CF<sub>3</sub>)<sub>2</sub>B–CCHCXCHCHC–NH–C(NMe<sub>2</sub>)–N–(C<sub>6</sub>H<sub>4</sub>X) (X = H (**6c**), Me (**6d**), OMe (**6e**)) are obtained. Ph–N=C=CMe<sub>2</sub> combines with **1** to form the four-membered ring (CF<sub>3</sub>)<sub>2</sub>B–CMe<sub>2</sub>–C(NMe<sub>2</sub>)–NPh (**8**). F<sub>3</sub>C–CH<sub>2</sub>–N=S=O undergoes an ene-type reaction with **1** by which the dimethylamine borane (F<sub>3</sub>C–HC=N–S(=O))(CF<sub>3</sub>)<sub>2</sub>B·NHMe<sub>2</sub> (**9**) is formed. The constitution of the novel boron compounds has been deduced from multinuclear NMR, IR, and mass spectra. The structures of **2a**, **3c**, **5c**, **6d**, **6e**, and **8** have been investigated by single-crystal X-ray diffraction.

## Introduction

The remarkable reactivity of the B=N linkage in (dimethylamino)bis(trifluoromethyl)borane, (CF<sub>3</sub>)<sub>2</sub>BNMe<sub>2</sub> (**1**), is exemplified by the facile cycloaddition reactions which it undergoes with a variety of substrates to form novel heterocyclic ring systems.<sup>1</sup> Of particular interest are the [2 + 2] cycloaddition reactions of **1** with isocyanates and isothiocyanates R–N=C=X (X = O, S).<sup>2</sup> At low temperature, these cumulenes add with their N=C bond to the B=N double bond of **1** to yield four-membered heterocycles (CF<sub>3</sub>)<sub>2</sub>B–NMe<sub>2</sub>–C(X)–NR according to eq 1. Depending on the nature of R and X, some of these rings rearrange quantitatively to the isomers (CF<sub>3</sub>)<sub>2</sub>B–X–C(NMe<sub>2</sub>)–NR at ambient temperatures. In the present study, we will investigate [2 + 2] cycloaddition reactions of **1** with compounds containing N=S or N=P double bonds. Furthermore, we will



extend the reaction in eq 1 to reagents R–N=C=X in which X is an NR or a CMe<sub>2</sub> group.

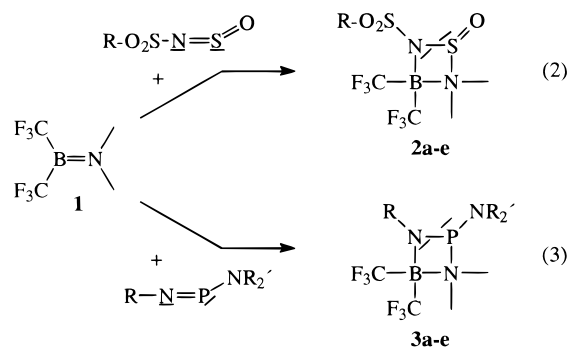
## Results

While Me–N=S=O reacts with **1** to form a colorless product at –30 °C, the product decomposes to reform the reactants upon warming to room temperature. However, *N*-sulfinylsulfonamides R–O<sub>2</sub>S–N=S=O (R = Me, Et, *i*Pr, Ph, and *p*Tol) add to **1** in a [2 + 2] fashion to form the moisture sensitive but thermally stable four-membered rings **2a–e**, eq 2. Despite their bulky substituents aminoiminophosphines R–N=P–NR<sub>2</sub>' combine similarly with **1** to yield the heterocycles **3a–e**, eq 3.

Although carbodiimides R–N=C=N–R bearing *t*Bu and SiMe<sub>3</sub> substituents do not react with **1**, derivatives with R = *i*Pr and *c*C<sub>6</sub>H<sub>11</sub> add at 60 and 20 °C, respectively, across the B=N double bond of **1**. In

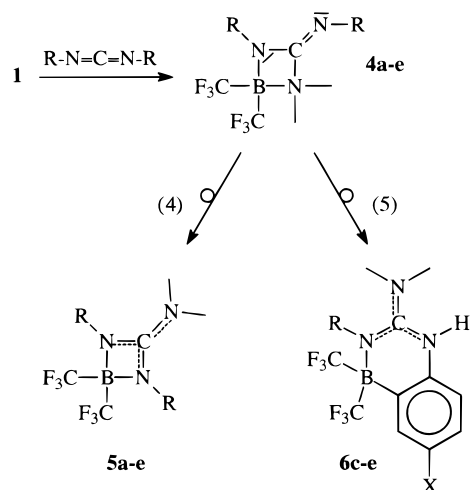
<sup>†</sup> Dedicated to Professor M. Weidenbruch on the occasion of his 60th birthday.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, October 1, 1997.  
 (1) Pawelke, G.; Bürger, H. *Appl. Organomet. Chem.* **1996**, *10*, 147.  
 (2) Ansoorge, A.; Brauer, D. J.; Bürger, H.; Dörrenbach, F.; Hagen, T.; Pawelke, G.; Weuter, W. *J. Organomet. Chem.* **1991**, *407*, 283.



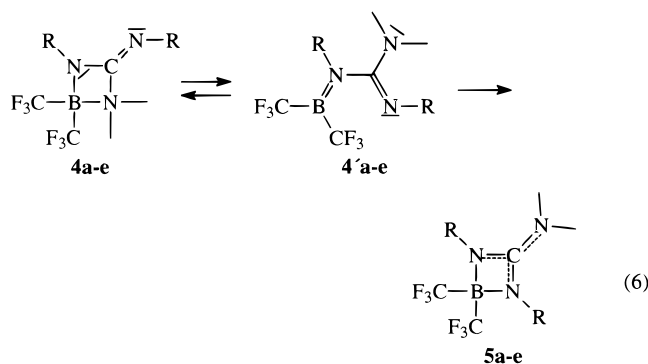
	R	3a	R	NR <sub>2</sub> '
2a	Me	3a	SiMe <sub>3</sub>	N(SiMe <sub>3</sub> ) <sub>2</sub>
2b	Et	3b	SiMe <sub>3</sub>	TMP
2c	<i>i</i> Pr	3c	<i>t</i> Bu	N(SiMe <sub>3</sub> )/ <i>t</i> Bu
2d	Ph	3d	<i>t</i> Bu	NiPr <sub>2</sub>
2e	<i>p</i> Tol	3e	<i>t</i> Bu	TMP

contrast to the above-mentioned behavior of the related isocyanates, the [2 + 2] cycloadducts **4a,b** could not be isolated as pure materials and we only have NMR spectroscopic evidence for their existence. These intermediates rearrange under the given reaction conditions to yield the respective, stable four-membered heterocycles **5a** and **5b**, eq 4. The reaction products of **1** with carbodiimides bearing aromatic substituents, R = *p*XC<sub>6</sub>H<sub>4</sub> (X = H, Me, OMe), show a more complex behavior. The initially formed [2 + 2] cycloadducts **4c–e** undergo two facile rearrangements. While one pathway is the same as that for **5a,b** and leads to species of type **5**, the other route leads to bicyclic heterocycles of type **6**, eq 5. Thus,

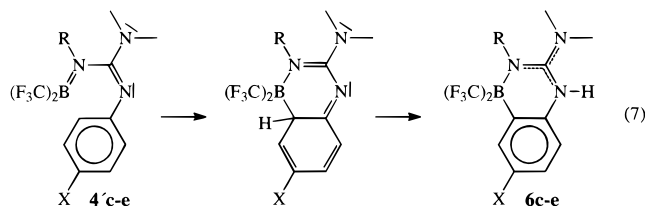


	R	6c	R	X
5a	<i>i</i> Pr	6c	Ph	H
5b	<i>c</i> C <sub>6</sub> H <sub>11</sub>	6d	<i>p</i> Tol	Me
5c	Ph	6e	<i>p</i> (MeO)C <sub>6</sub> H <sub>4</sub>	MeO
5d	<i>p</i> Tol			
5e	<i>p</i> (MeO)C <sub>6</sub> H <sub>4</sub>			

mixtures of **5c/6c**, **5d/6d**, and **5e/6e** are obtained—the molar ratios determined by NMR being 5:5, 3:7, and 2:8, respectively. The formation of these isomer pairs can be explained as follows. The initially formed four-membered cycloadducts **4a–e** are in equilibrium with acyclic isomers **4'a–e**, eq 6. In these isomers, the position of the NMe<sub>2</sub> and N–R groups can interchange by rotation about an N–C single bond. Ring closure

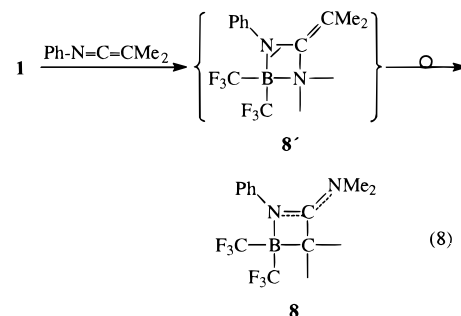


by the more electron rich N–R nitrogen forms the stable isomers **5a–e**. However, when R is a phenyl group, the phenyl ring in **4'c–e** may as well adopt an orientation which is favorable for an electrophilic aromatic substitution by the tricoordinate boron, eq 7. Electrophilic



attack by boron fuses a six-membered ring, and migration of a proton leads to the isomers **6c–e**.

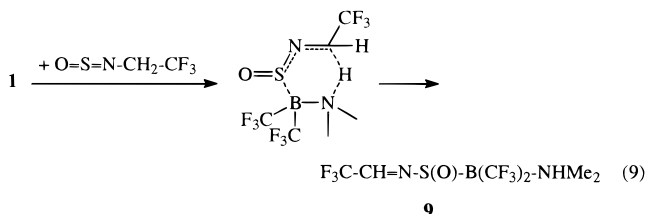
Keteneimines, RN=C=CR<sub>2</sub>, possess C=C and polar N=C linkages, only the latter being expected to enter into a [2 + 2] cycloaddition reaction with the B=N bond of **1**. We selected PhN=C=CMe<sub>2</sub> for a test because it is easily prepared, bears unobstructive substituents at carbon, and is relatively stable. However, instead of the expected [2 + 2] cycloaddition product **8'**, only a rearranged species **8** was obtained, eq 8. Its constitution



was elucidated by an X-ray structure investigation.

As mentioned above, electron-withdrawing *N*-sulfonyl substituents activate the N=S bond of sulfonylamines to such an extent that thermally stable [2 + 2] cycloaddition products with **1** could be isolated. Conceivably, the N=S bond of F<sub>3</sub>C–CH<sub>2</sub>–N=S=O might be activated analogously. However, its reaction with **1** followed an ene-type route (eq 9) to deliver the dimethylamine borane **9**—no [2 + 2] cycloaddition product being formed.

**Properties and Spectra.** The derivatives of novel heterocycles **2a–8** are colorless solids, the melting points of which are reported in the Experimental Section. While compounds **3a–e/b** and **5a–8** are stable to air and moisture, the species **2a–d** and **9** are sensitive to hydrolysis and, therefore, have to be handled in a dry atmosphere. All are soluble in polar organic solvents.



The <sup>1</sup>H, <sup>19</sup>F, <sup>11</sup>B, and <sup>13</sup>C NMR spectra of **2a–9** and the <sup>31</sup>P NMR spectra of **3a–e** were recorded. The chemical shifts and <sup>31</sup>P coupling constants (Table 1) are consistent with the proposed structures, and only a few comments will be necessary.

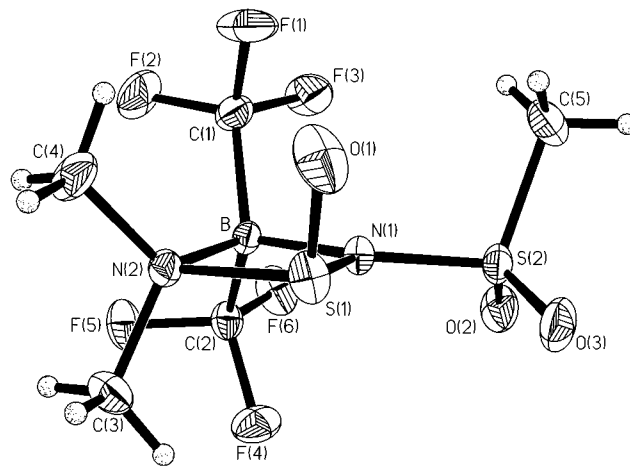
Compounds **3a–e** are sterically overcrowded, and the substituents attached to the four-membered ring possess only limited conformational freedom. This is underscored by the presence of magnetically nonequivalent SiMe<sub>3</sub> and *i*Pr groups bonded to the exocyclic nitrogen atoms of **3a** and **3d**, respectively; that is, no rotation about the exocyclic P–N bond occurs on the NMR time scale. Furthermore, 250 MHz <sup>1</sup>H NMR spectra of **3c** run between 325 and 225 K reveal that the rotation of the SiMe<sub>3</sub> group is hindered on the NMR time scale too. Free rotation is observed at 325 K, but at 230 K its proton resonance splits into three signals at 0.87, 0.43, and 0.36 ppm—the coalescence temperature being close to 300 K. Furthermore, the rather rigid framework of compounds **3a–e** leads to a wide range of element–<sup>31</sup>P coupling constants (Table 1) and in the <sup>13</sup>C NMR spectra to <sup>4</sup>J(CF) coupling constants (not listed) ranging from 4 to 1.5 Hz.

The IR spectra of **2a–9** were recorded in the 500–4000 cm<sup>-1</sup> region. These are dominated by the very strong absorptions of the CF<sub>3</sub> groups occurring between 1030 and 1120 cm<sup>-1</sup>. Identification of the isomers **6** is facilitated by the prominence of their ν(NH) vibration at 3430 cm<sup>-1</sup>. All novel species showed the expected absorptions belonging to their functional groups (ν(C=C), ν(C=N), ν(SO<sub>2</sub>), ν(PN/SiN)). The respective wavenumbers are given in the Experimental Section.

EI mass spectral data for **2a–9** are listed in Table 2. The peaks of the molecular ions [M]<sup>+</sup> for **2a–9** are weak if detectable at all—the ions [M–CF<sub>3</sub>]<sup>+</sup> and [M–C<sub>2</sub>F<sub>5</sub>]<sup>+</sup> being indicative of the molecular mass. The isomers **5c/6c**, **5d/6d**, and **5e/6e** show almost identical fragmentation patterns despite their different molecular frameworks. This observation does not refute the proposed structures because fragmentation pathways are conceivable for extracting the same observed ions from each isomer. For example, the base peaks of these spectra are assigned to the ion [XC<sub>6</sub>H<sub>4</sub>NCN(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (X = H, Me, OMe), and simple fragmentation pathways for the formation of these ions are suggested in Scheme 1. Because mass spectra do not distinguish between these isomers, Table 2 lists only the mass spectral data of the isomer mixtures **5c/6c–5e/6e**.

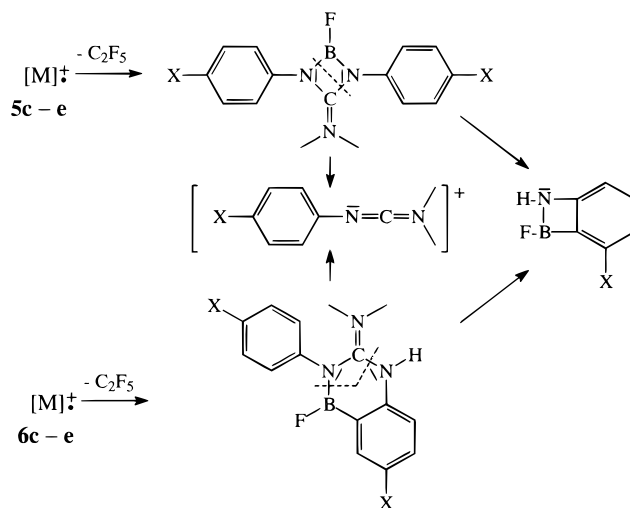
**Description of the Crystal Structures.** All of the crystals studied are composed of discrete monomeric molecules which form no unusual intermolecular contacts.

**Structures of 2a and 3c.** ORTEP drawings of **2a** and **3c** are displayed in Figures 1 and 2, and pertinent bond lengths and angles are listed in Tables 5 and 6. These compounds contain slightly folded four-membered rings—the folding along the N(1)⋯N(2) tieline of **2a**



**Figure 1.** Perspective drawing of (CF<sub>3</sub>)<sub>2</sub>B–NMe<sub>2</sub>–S(=O)–N–SO<sub>2</sub>Me (**2a**) with 20% probability thermal ellipsoids for the non-hydrogen atoms.

**Scheme 1. Fragmentation of Compounds 5c/6c–5e/6e, Formation of the Base Peak**



(7.2(3)°) being much less than that of **3c** (27.0(2)°). While the ring atoms S(1) in **2a** and P in **3c** exhibit pyramidal geometries, the 5.0(3)° larger valency angle sum for the latter may be due to its bulkier exocyclic substituent. In **3c**, the exocyclic N(3) atom lies only 0.050(3) Å from the plane defined by its substituents, and this plane forms a 71.1(1)° angle with the substituent plane of the P atom. This orientation minimizes steric congestion with the other ring substituents and repulsions between the lone pairs of the N(3) and P atoms. The steric congestion is underlined by the gearing of the groups bonded to the N(3) atom, as evident from Figure 2. While the tricoordinate N(1) atom of **2a** deviates only 0.021(2) Å from the plane through its substituent atoms, the corresponding deviation of the N(1) atom in **3c** is much larger (0.320(3) Å). Despite these differences, the bond lengths in the two four-membered rings are surprisingly similar.

The bonds formed by the three-coordinate N(1) atoms are shorter than those formed by the four-coordinate N(2) atoms. On the average, the difference amounts to 0.083(6) Å for the B–N bonds—a value which is similar to that (0.10(1) Å) found for the B–N bonds of (CF<sub>3</sub>)<sub>2</sub>B–NMe<sub>2</sub>–C(O)–N*t*Bu (**10**).<sup>2</sup> A greater dependency is





**Table 2.** Selected Electron Impact Mass Spectral Data in the Order of Decreasing Intensity ( $m/e$  (relative intensity) [fragment]<sup>+</sup>) for **2a–9**

<b>2a</b>	79 (100) [CH <sub>3</sub> SO <sub>2</sub> ] <sup>+</sup> ; 92 (80) [F <sub>2</sub> BN(=CH <sub>2</sub> )CH <sub>3</sub> ] <sup>+</sup> ; 44 (39) [N(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 74 (17) [FBN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 124 (7) [CF <sub>3</sub> BN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>
<b>2b</b>	92 (100) [F <sub>2</sub> BN(=CH <sub>2</sub> )CH <sub>3</sub> ] <sup>+</sup> ; 93 (73) [C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> ] <sup>+</sup> ; 74 (36) [FBN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 44 (33) [N(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 124 (27) [CF <sub>3</sub> BN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 279 (3) [M – CF <sub>3</sub> ] <sup>+</sup> ; 229 (2) [M – C <sub>2</sub> F <sub>5</sub> ] <sup>+</sup> ; 348 (1) [M] <sup>+</sup>
<b>2c</b>	44 (100) [N(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 92 (54) [F <sub>2</sub> BN(=CH <sub>2</sub> )CH <sub>3</sub> ] <sup>+</sup> ; 74 (13) [FBN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 124 (29) [CF <sub>3</sub> BN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 107 (3) [C <sub>3</sub> H <sub>7</sub> SO <sub>2</sub> ] <sup>+</sup>
<b>2d</b>	77 (100) [C <sub>6</sub> H <sub>5</sub> ] <sup>+</sup> ; 141 (83) [C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> ] <sup>+</sup> ; 92 (80) [F <sub>2</sub> BN(=CH <sub>2</sub> )CH <sub>3</sub> ] <sup>+</sup> ; 44 (19) [N(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 74 (17) [FBN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 124 (10) [CF <sub>3</sub> BN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 396 (3) [M] <sup>+</sup> ; 277 (3) [M – C <sub>2</sub> F <sub>5</sub> ] <sup>+</sup> ; 327 (1) [M – CF <sub>3</sub> ] <sup>+</sup>
<b>2e</b>	91 (100) [C <sub>7</sub> H <sub>7</sub> ] <sup>+</sup> ; 92 (94) [F <sub>2</sub> BN(=CH <sub>2</sub> )CH <sub>3</sub> ] <sup>+</sup> ; 155 (78) [C <sub>7</sub> H <sub>7</sub> SO <sub>2</sub> ] <sup>+</sup> ; 74 (15) [FBN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 124 (11) [CF <sub>3</sub> BN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 44 (2) [N(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 410 (2) [M] <sup>+</sup>
<b>3a</b>	73 (100) [Si(CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup> ; 278 (59) [(CH <sub>3</sub> ) <sub>3</sub> Si <sub>2</sub> NPNSi(CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup> ; 118 (48) [(CH <sub>3</sub> ) <sub>3</sub> SiNP] <sup>+</sup> ; 263 (22) [(CH <sub>3</sub> ) <sub>3</sub> Si <sub>2</sub> NPNSi(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 74 (18) [FBN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 371 (16) [M – C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup> ; 92 (14) [F <sub>2</sub> BN(=CH <sub>2</sub> )CH <sub>3</sub> ] <sup>+</sup> ; 471 (10) [M] <sup>+</sup> ; 94 (9) [F <sub>2</sub> BNH(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 352 (7) [M – C <sub>2</sub> F <sub>5</sub> ] <sup>+</sup> ; 235 (6) [(CH <sub>3</sub> ) <sub>3</sub> Si <sub>2</sub> NPN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 402 (3) [M – CF <sub>3</sub> ] <sup>+</sup>
<b>3b</b>	118 (100) [(CH <sub>3</sub> ) <sub>3</sub> SiNP] <sup>+</sup> ; 73 (76) [Si(CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup> ; 94 (52) [F <sub>2</sub> BNH(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 92 (43) [F <sub>2</sub> BN(=CH <sub>2</sub> )CH <sub>3</sub> ] <sup>+</sup> ; 74 (35) [FBN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 243 (27) [C <sub>8</sub> H <sub>15</sub> NPNSi(CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup> ; 211 (24) [M – C <sub>9</sub> H <sub>18</sub> N – C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup> ; 258 (13) [C <sub>9</sub> H <sub>18</sub> NPNSi(CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup> ; 382 (9) [M – CF <sub>3</sub> ] <sup>+</sup> ; 451 (7) [M] <sup>+</sup> ; 332 (5) [M – C <sub>2</sub> F <sub>5</sub> ] <sup>+</sup>
<b>3c</b>	57 (100) [C <sub>4</sub> H <sub>9</sub> ] <sup>+</sup> ; 282 (28) [M – C <sub>4</sub> H <sub>9</sub> – C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup> ; 368 (24) [M – C <sub>4</sub> H <sub>9</sub> N] <sup>+</sup> ; 73 (14) [Si(CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup> ; 439 (11) [M] <sup>+</sup> ; 118 (9) [Si(CH <sub>3</sub> ) <sub>3</sub> NP] <sup>+</sup> ; 92 (7) [F <sub>2</sub> BN(=CH <sub>2</sub> )CH <sub>3</sub> ] <sup>+</sup> ; 74 (5) [FBN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>
<b>3d</b>	57 (100) [C <sub>4</sub> H <sub>9</sub> ] <sup>+</sup> ; 187 (63) [(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> NPN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 270 (39) [M – C <sub>4</sub> H <sub>8</sub> – CF <sub>3</sub> ] <sup>+</sup> ; 100 (39) [(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> N] <sup>+</sup> ; 88 (25) [(CH <sub>3</sub> ) <sub>2</sub> CHNP] <sup>+</sup> ; 195 (20) [M – ((CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> N – C <sub>2</sub> F <sub>4</sub> )] <sup>+</sup> ; 395 (15) [M] <sup>+</sup> ; 94 (10) [F <sub>2</sub> BNH(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 238 (8) [M – C <sub>4</sub> H <sub>9</sub> – C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup>
<b>3e</b>	57 (100) [C <sub>4</sub> H <sub>9</sub> ] <sup>+</sup> ; 58 (21) [C <sub>3</sub> H <sub>8</sub> N] <sup>+</sup> ; 94 (19) [F <sub>2</sub> BNH(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 195 (19) [M – C <sub>9</sub> H <sub>18</sub> N – C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup> ; 245 (8) [M – C <sub>9</sub> H <sub>18</sub> N – CF <sub>2</sub> ] <sup>+</sup> ; 92 (7) [F <sub>2</sub> BN(=CH <sub>2</sub> )CH <sub>3</sub> ] <sup>+</sup> ; 435 (5) [M] <sup>+</sup>
<b>5a</b>	71 (100) [(H <sub>3</sub> C) <sub>2</sub> NCN(H)] <sup>+</sup> ; 204 (60) [M – CH <sub>3</sub> – C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup> ; 113 (48) [(H <sub>3</sub> C) <sub>2</sub> CHNCN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 200 (30) [M – C <sub>2</sub> F <sub>5</sub> ] <sup>+</sup> ; 304 (20) [M – CH <sub>3</sub> ] <sup>+</sup> ; 119 (17) [F <sub>2</sub> BNCN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 319 (11) [M] <sup>+</sup>
<b>5b</b>	399 (100) [M] <sup>+</sup> ; 55 (83) [C <sub>6</sub> H <sub>7</sub> ] <sup>+</sup> ; 71 (82) [(H <sub>3</sub> C) <sub>2</sub> NCN(H)] <sup>+</sup> ; 83 (71) [C <sub>6</sub> H <sub>11</sub> ] <sup>+</sup> ; 256 (52) [M – C <sub>3</sub> H <sub>7</sub> – C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup> ; 356 (45) [M – C <sub>3</sub> H <sub>7</sub> ] <sup>+</sup> ; 153 (44) [C <sub>6</sub> H <sub>11</sub> NCN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 280 (25) [M – C <sub>2</sub> F <sub>5</sub> ] <sup>+</sup> ; 119 (21) [F <sub>2</sub> BNCN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>
<b>5c/6c</b>	147 (100) [C <sub>6</sub> H <sub>5</sub> NCN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 194 (25) [C <sub>6</sub> H <sub>5</sub> NCNC <sub>6</sub> H <sub>5</sub> ] <sup>+</sup> ; 217 (19) [C <sub>13</sub> H <sub>8</sub> BN <sub>3</sub> ] <sup>+</sup> ; 387 (18) [M] <sup>+</sup> ; 268 (12) [M – C <sub>2</sub> F <sub>5</sub> ] <sup>+</sup> ; 287 (9) [M – C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup>
<b>5d/6d</b>	161 (100) [H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> NCN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 296 (44) [M – C <sub>2</sub> F <sub>5</sub> ] <sup>+</sup> ; 222 (39) [H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> NCNC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ] <sup>+</sup> ; 415 (28) [M] <sup>+</sup> ; 245 (21) [C <sub>15</sub> H <sub>12</sub> BN <sub>3</sub> ] <sup>+</sup> ; 346 (10) [M – CF <sub>3</sub> ] <sup>+</sup> ; 315 (9) [M – C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup>
<b>5e/6e</b>	177 (100) [H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> NCN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 254 (42) [H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> NCNC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ] <sup>+</sup> ; 147 (26) [C <sub>6</sub> H <sub>5</sub> NCN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 447 (25) [M] <sup>+</sup> ; 277 (15) [C <sub>15</sub> H <sub>12</sub> BN <sub>3</sub> O <sub>2</sub> ] <sup>+</sup> ; 347 (11) [M – C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup> ; 328 (4) [M – C <sub>2</sub> F <sub>5</sub> ] <sup>+</sup>
<b>8</b>	119 (100) [F <sub>2</sub> BNCN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 98 (87) [(CH <sub>3</sub> ) <sub>2</sub> NCC(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 145 (69) [C <sub>6</sub> H <sub>5</sub> NCC(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 238 (62) [M – C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup> ; 77 (43) [C <sub>6</sub> H <sub>5</sub> ] <sup>+</sup> ; 228 (22) [M – CF <sub>2</sub> ] <sup>+</sup> ; 338 (11) [M] <sup>+</sup>
<b>9</b>	94 (100) [F <sub>2</sub> BNH(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 92 (22) [F <sub>2</sub> BN(=CH <sub>2</sub> )CH <sub>3</sub> ] <sup>+</sup> ; 44 (19) [N(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 69 (8) [CF <sub>3</sub> ] <sup>+</sup> ; 338(7) [M] <sup>+</sup> ; 74 (5) [FBN(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> ; 128 (4) [F <sub>3</sub> CCH=NS] <sup>+</sup> ; 144 (2) [F <sub>3</sub> CCH=NSO] <sup>+</sup> ; 319 (1) [M – F] <sup>+</sup> ; 269 (1) [M – CF <sub>3</sub> ] <sup>+</sup>

**Table 3.** Elemental Analyses

compd	formula	anal. found: calcd		
		C	H	N
<b>2a</b>	C <sub>5</sub> H <sub>9</sub> BF <sub>6</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	17.6; 17.98	2.7; 2.72	8.4; 8.39
<b>2b</b>	C <sub>6</sub> H <sub>11</sub> BF <sub>6</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	20.9; 20.70	3.3; 3.19	8.0; 8.05
<b>2c</b>	C <sub>7</sub> H <sub>13</sub> BF <sub>6</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	23.4; 23.22	3.8; 3.62	7.5; 7.74
<b>2d</b>	C <sub>10</sub> H <sub>11</sub> BF <sub>6</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	30.0; 30.32	2.8; 2.80	7.2; 7.07
<b>2e</b>	C <sub>11</sub> H <sub>13</sub> BF <sub>6</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	31.9; 32.21	3.3; 3.19	6.9; 6.83
<b>3a</b>	C <sub>13</sub> H <sub>33</sub> BF <sub>6</sub> N <sub>3</sub> PSi <sub>3</sub>	32.8; 33.12	7.0; 7.06	8.9; 8.91
<b>3b</b>	C <sub>16</sub> H <sub>33</sub> BF <sub>6</sub> N <sub>3</sub> PSi	42.6; 42.58	7.7; 7.37	9.0; 9.31
<b>3c</b>	C <sub>15</sub> H <sub>33</sub> BF <sub>6</sub> N <sub>3</sub> PSi	40.7; 41.01	7.4; 7.57	9.2; 9.57
<b>3d</b>	C <sub>14</sub> H <sub>29</sub> BF <sub>6</sub> N <sub>3</sub> P	42.1; 42.55	7.4; 7.40	10.3; 10.63
<b>3e</b>	C <sub>17</sub> H <sub>33</sub> BF <sub>6</sub> N <sub>3</sub> P	46.6; 46.91	7.6; 7.64	9.4; 9.65
<b>5a</b>	C <sub>11</sub> H <sub>20</sub> BF <sub>6</sub> N <sub>3</sub>	40.7; 41.40	6.1; 6.32	12.8; 13.17
<b>5b</b>	C <sub>17</sub> H <sub>28</sub> BF <sub>6</sub> N <sub>3</sub>	51.3; 51.15	7.2; 7.07	10.2; 10.53
<b>5c/6c</b>	C <sub>17</sub> H <sub>16</sub> BF <sub>6</sub> N <sub>3</sub>	52.4; 52.74	4.1; 4.17	10.5; 10.85
<b>5d/6d</b>	C <sub>19</sub> H <sub>20</sub> BF <sub>6</sub> N <sub>3</sub>	54.8; 54.97	4.9; 4.86	9.9; 10.12
<b>5e/6e</b>	C <sub>19</sub> H <sub>20</sub> BF <sub>6</sub> N <sub>3</sub> O <sub>2</sub>	50.7; 51.03	4.5; 4.51	9.5; 9.40
<b>8</b>	C <sub>14</sub> H <sub>17</sub> BF <sub>6</sub> N <sub>2</sub>	49.6; 49.73	5.1; 5.07	8.3; 8.29
<b>9</b>	C <sub>6</sub> H <sub>8</sub> BF <sub>9</sub> N <sub>2</sub> OS	21.4; 21.32	2.50; 2.39	8.0; 8.29

found for the differences in the N–S (0.210(3) Å) and N–P (0.198(4) Å) bond lengths in **2a** and **3c**, respectively. The large difference might indicate a  $\pi$  component to the N(1)–S(1) and N(1)–P bonds similar to that proposed for the analogous N–C bond of **10**, which was found to be 0.21(1) Å shorter than the other endocyclic N–C linkage.<sup>2</sup>

**Structures of 5c and 8.** One of the two unique molecules of **5c** is depicted in Figure 3, and the molecular structure of **8** is shown in Figure 4. Selected bond lengths and angles are listed in Tables 7 and 8 for **5c** and **8**, respectively. Crystallographic symmetry is imposed on the molecules of **5c**; that is, the B(I)⋯C(I)–N(I) sequences of the two molecules ( $I = 1, 2$ ) in the asymmetric unit occupy sites of  $C_2$  symmetry. Since the bond lengths and angles of the two crystallographically independent molecules of **5c** agree quite

well, their average values will be quoted in the following. These compounds may be formulated as zwitterions (CF<sub>3</sub>)<sub>2</sub>B<sup>–</sup>–X–C<sup>+</sup>(NMe<sub>2</sub>)–NPh; X = NPh (**5c**), CMe<sub>2</sub> (**8**). The short C(1)–N bond lengths show that the formal positive charge on the C(1) atom is delocalized by  $\pi$  bonding to the adjacent nitrogen atoms. This  $\pi$  interaction explains the essentially planar substitution of the C(1), N(1), and N(2) atoms, the near (**8**) or exact (**5c**) planarity of the four-membered rings, and the small dihedral angles between the normals to the ring plane and the substituent plane of the exocyclic NMe<sub>2</sub> group—13.1(2)° (average) and 6.3(1)° in **5c** and **8**, respectively. Similar geometric details were observed for (CF<sub>3</sub>)<sub>2</sub>B<sup>–</sup>–S–C(NMe<sub>2</sub>)–NPh (**11**).<sup>2</sup>

The B–N distances in **5c**, **8**, and **11** (average 1.554(3), 1.559(3), and 1.557(9) Å, respectively) may have been lengthened by C(1)–N  $\pi$  bonding. Thus, these distances are significantly longer than the average value (1.500(6) Å) found for the ylid adduct Ph<sub>3</sub>P–CH<sub>2</sub>–(F<sub>3</sub>C)<sub>2</sub>B–NMe<sub>2</sub> (**12**),<sup>3</sup> but similar to that (1.541(4) Å) of (F<sub>3</sub>C)<sub>3</sub>B–NHCH–NMe<sub>2</sub> (**13**), which unlike **12** has delocalized C–N  $\pi$  bonding.<sup>4</sup>

The endocyclic B–C bond distance in **8** (1.662(3) Å) is significantly longer than the average B–CF<sub>3</sub> bond length (1.610(3) Å) but compares well with the B–CH<sub>2</sub>–PPh<sub>3</sub> linkage in **12** (average 1.661(6) Å)<sup>3</sup> or the endocyclic B–C bond (1.655(6) Å) in (**14**).<sup>5</sup>

**Structures of 6d and 6e.** The structures of **6d** and **6e** are shown in Figures 5 and 6, and important bond

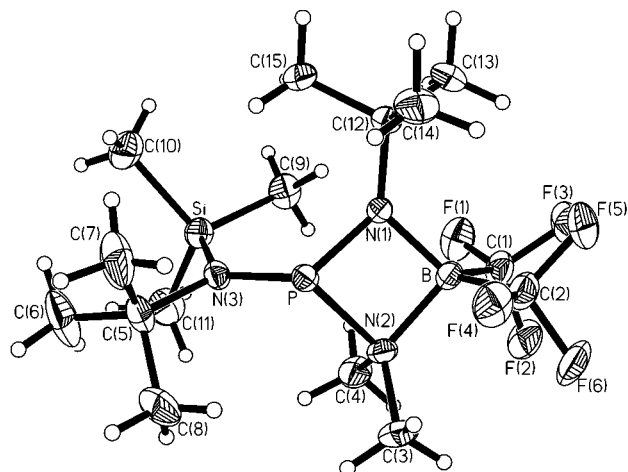
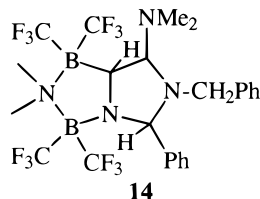
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(4) Ansoerge, A.; Brauer, D. J.; Bürger, H.; Krumm, B.; Pawelke, G. *J. Organomet. Chem.* **1993**, *446*, 25.

(5) Ansoerge, A.; Brauer, D. J.; Buchheim-Spiegel, S.; Bürger, H.; Hagen, T.; Pawelke, G. *J. Organomet. Chem.* **1995**, *501*, 347.

**Table 4. Crystal Data for 2a, 3c, 5c, 6d, 6e and 8**

	<b>2a</b>	<b>3c</b>	<b>5c</b>	<b>6e</b>	<b>6d</b>	<b>8</b>
formula	C <sub>5</sub> H <sub>9</sub> BF <sub>6</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub>	C <sub>15</sub> H <sub>33</sub> BF <sub>6</sub> N <sub>3</sub> PSi	C <sub>17</sub> H <sub>16</sub> BF <sub>6</sub> N <sub>3</sub>	C <sub>19</sub> H <sub>20</sub> BF <sub>6</sub> N <sub>3</sub> O <sub>2</sub>	C <sub>19</sub> H <sub>20</sub> BF <sub>6</sub> N <sub>3</sub>	C <sub>14</sub> H <sub>17</sub> BF <sub>6</sub> N <sub>2</sub>
<i>M<sub>r</sub></i>	334.06	439.31	387.13	447.19	415.19	338.10
cryst size (mm)	0.20 × 0.26 × 0.58	0.24 × 0.30 × 0.40	0.24 × 0.28 × 0.43	0.09 × 0.22 × 0.46	0.20 × 0.32 × 0.40	0.08 × 0.34 × 0.35
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	<i>C2</i>	<i>P2<sub>1</sub></i>	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	7.395(2)	10.804(2)	19.016(2)	7.4031(9)	15.916(1)	8.4476(9)
<i>b</i> (Å)	11.560(2)	13.371(1)	8.9928(7)	7.9373(9)	14.948(2)	16.826(2)
<i>c</i> (Å)	14.551(2)	15.760(1)	11.272(1)	17.659(2)	16.639(1)	11.3901(9)
<i>β</i> (deg)	93.59(2)		107.555(7)	100.310(9)		92.799(8)
<i>V</i> (Å <sup>3</sup> )	1241.5(4)	2276.7(5)	1837.8(3)	1020.9(2)	3958.6(6)	1617.0(3)
<i>Z</i>	4	4	4	2	8	4
<i>ρ</i> (g cm <sup>-3</sup> )	1.787	1.282	1.399	1.455	1.393	1.389
<i>T</i> (K)	299	293	295	293	298	296
<i>λ</i> (Å)	0.710 73	1.5405 62	1.541 84	1.541 84	1.541 84	1.541 84
2 $\theta$ range (deg)	2–25	8–150	4–138	5–138	9–138	9–138
index ranges	<i>h, ±k, ±l</i>	<i>h, k, l</i>	<i>±h, ±k, l</i>	<i>±h, ±k, l</i>	<i>h, k, l</i>	<i>h, k, ±l</i>
diffractometer	AED1	CAD4	P3	P3	P3	P3
no. of reflns measd	4740	2617	3832	3665	3694	3225
no. of unique reflns	2193	2617	3406	3308	3687	3014
<i>R</i> (int)	0.028		0.031	0.015	0.116	0.010
<i>μ</i> (λ) (mm <sup>-1</sup> )	0.509	2.068	1.107	1.151	1.065	1.149
transmission	0.877–0.922	0.506–0.653	0.620–0.836	0.733–0.913	0.711–0.815	0.713–0.913
ext param			0.0051(3)	0.0134(8)	0.0023(1)	0.0029(4)
no. of params varied	178	266	267	300	275	217
<i>R<sub>F</sub></i> (all)	0.053	0.040	0.038	0.036	0.074	0.066
<i>wR<sub>F</sub><sup>2</sup></i> (all)	0.113	0.108	0.103	0.088	0.119	0.124

**Figure 2.** Perspective drawing of (CF<sub>3</sub>)<sub>2</sub>B–NMe<sub>2</sub>–P(N(SiMe<sub>3</sub>)*t*Bu)–N*t*Bu (**3c**) with 20% probability thermal ellipsoids for the non-hydrogen atoms.

lengths and angles are tabulated in Tables 9 and 10. Their major structural features are quite similar. For example, their heterocyclic six-membered rings are folded along their B···N(2) tielines by 21.4(2)° in **6d** and 23.3(1)° in **6e**.

The C(1) atoms are the centers of formal positive charge in these zwitterionic compounds, and the lengths of the C(1)–N bonds indicate that the positive charge is delocalized to the three neighboring nitrogen atoms by  $\pi$  bonding. However, in each compound, the substitution plane of the exocyclic nitrogen atom forms a larger angle with the coordination plane of the C(1)

**Table 5. Selected Bond Lengths (Å) and Angles (deg) for (CF<sub>3</sub>)<sub>2</sub>B–NMe<sub>2</sub>–S(=O)–N–SO<sub>2</sub>Me (**2a**)**

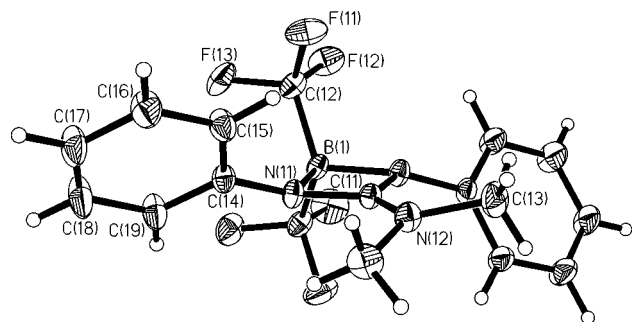
B–N(1)	1.532(3)	C(4)–N(2)	1.476(4)
B–N(2)	1.618(4)	N(1)–S(1)	1.684(2)
B–C(1)	1.623(4)	N(1)–S(2)	1.642(2)
B–C(2)	1.621(4)	N(2)–S(1)	1.894(2)
C(3)–N(2)	1.505(4)	S(1)–O(1)	1.434(3)
N(1)–B–N(2)	90.3(2)	B–N(2)–S(1)	90.4(1)
B–N(1)–S(1)	102.0(2)	N(1)–S(1)–N(2)	76.9(1)
B–N(1)–S(2)	138.5(2)	N(1)–S(1)–O(1)	110.8(2)
S(1)–N(1)–S(2)	119.5(1)	N(2)–S(1)–O(1)	108.0(2)

**Table 6. Selected Bond Lengths (Å) and Angles (deg) for (CF<sub>3</sub>)<sub>2</sub>B–NMe<sub>2</sub>–P(N(SiMe<sub>3</sub>)*t*Bu)–N*t*Bu (**3c**)**

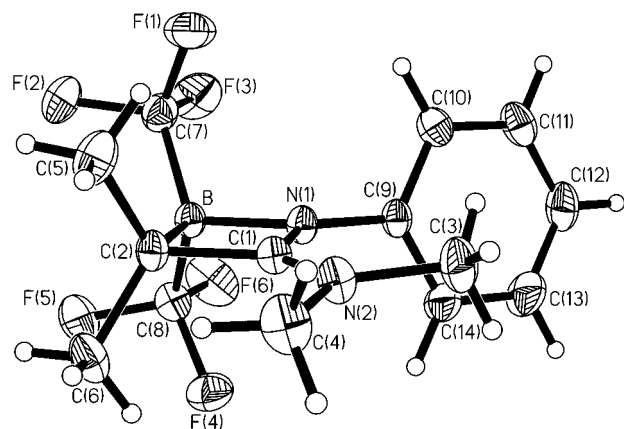
B–N(1)	1.534(4)	C(5)–N(3)	1.552(4)
B–N(2)	1.613(4)	C(12)–N(1)	1.486(3)
B–C(1)	1.651(5)	N(1)–P	1.691(2)
B–C(2)	1.631(5)	N(2)–P	1.889(3)
C(3)–N(2)	1.495(4)	N(3)–P	1.683(2)
C(4)–N(2)	1.484(4)	N(3)–Si	1.794(3)
N(1)–B–N(2)	92.2(2)	C(5)–N(3)–Si	118.8(2)
B–N(1)–C(12)	129.1(2)	P–N(3)–Si	132.6(2)
B–N(1)–P	96.3(2)	N(1)–P–N(2)	78.4(1)
C(12)–N(1)–P	121.5(2)	N(1)–P–N(3)	113.1(1)
B–N(2)–P	86.4(2)	N(2)–P–N(3)	109.2(1)
C(5)–N(3)–P	108.3(2)		

atom than in **5c** or **8**—the dihedral angles being 31.6(2)° and 30.7(1)° in **6d** and **6e**, respectively. The greater deviation from coplanarity may be caused in part by stronger repulsions between the exocyclic substituents of the N(1) and C(1) atoms in the six-membered rings as compared to those arising between substituents of the four-membered rings in **5c** and **8**.

Interestingly, the B–N(1) distances in **6d** and **6e** are on the average 0.031(6) Å longer than those in **5c** and **8**. Here, the lengthening may have resulted from the relatively greater crowding of the CF<sub>3</sub> and aryl substituents of the six-membered heterocycles. On the other hand, the B–C(7) distances in **6d** and **6e** appear normal.



**Figure 3.** Perspective drawing of one of the two crystallographically independent molecules of  $(\text{CF}_3)_2\text{B}-\text{NPh}-\text{C}(=\text{NMe}_2)-\text{NPh}$  (**5c**) with 20% probability thermal ellipsoids for the non-hydrogen atoms.



**Figure 4.** Perspective drawing of  $(\text{CF}_3)_2\text{B}-\text{CMe}_2-\text{C}(=\text{NMe}_2)-\text{NPh}$  (**8**) with 20% probability thermal ellipsoids for the non-hydrogen atoms.

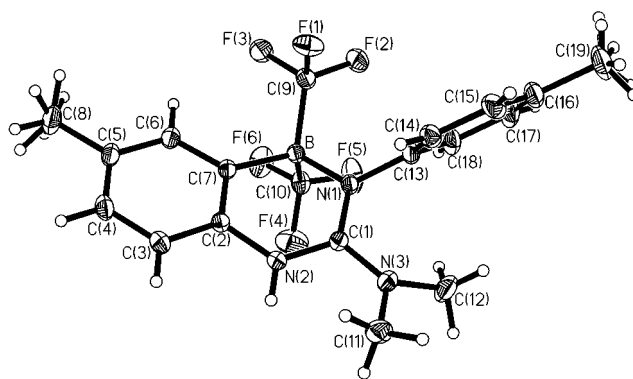
**Table 7. Selected Bond Lengths (Å) and Angles (deg) for  $(\text{CF}_3)_2\text{B}-\text{NPh}-\text{C}(=\text{NMe}_2)-\text{NPh}$  (**5c**)**

B(1)–N(11)	1.553(3)	B(2)–N(21)	1.555(3)
B(1)–C(12)	1.604(3)	B(2)–C(22)	1.603(3)
C(11)–N(11)	1.356(2)	C(21)–N(21)	1.355(2)
C(11)–N(12)	1.315(3)	C(21)–N(22)	1.317(3)
C(13)–N(12)	1.456(3)	C(23)–N(22)	1.454(2)
C(14)–N(11)	1.422(2)	C(24)–N(21)	1.423(2)
N(11)–B(11)–N(11') <sup>a</sup>	83.9(2)	N(21)–B(21)–N(21') <sup>b</sup>	83.7(2)
N(11)–C(11)–N(11')	100.0(2)	N(21)–C(21)–N(21')	99.9(2)
N(11)–C(11)–N(12)	130.0(1)	N(21)–C(21)–N(22)	130.0(1)
B(1)–N(11)–C(11)	88.1(1)	B(2)–N(21)–C(21)	88.2(1)
B(1)–N(11)–C(14)	132.6(2)	B(2)–N(21)–C(24)	133.3(1)
C(11)–N(11)–C(14)	130.6(2)	C(21)–N(21)–C(24)	130.2(2)
C(11)–N(12)–C(13)	121.8(1)	C(21)–N(22)–C(23)	121.5(1)
C(13)–N(12)–C(13')	116.4(3)	C(23)–N(22)–C(23')	117.1(2)

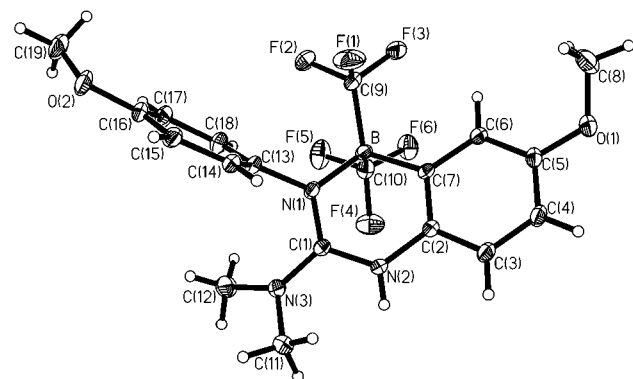
<sup>a</sup>  $x, y, z = -x + 1, y, -z + 1$ . <sup>b</sup>  $x', y', z' = -x + 1, y, -z$ .

## Discussion

To our knowledge no reaction of aminoboranes with *N*-sulfinylsulfonamides and aminoiminophosphines have been described so far. The observed [2 + 2] cycloaddition that **1** undergoes with these reactants underscores, again, its alkene-like behavior. Compounds **2a–e** and **3a–e** are the first examples with BNSN and BNPN four-membered rings where both boron and nitrogen are tetracoordinated. However, related cycloadducts with tricoordinate boron and nitrogen have been obtained with aminoiminophosphines and iminoboranes.<sup>6</sup>



**Figure 5.** Perspective drawing of  $(\text{CF}_3)_2\text{B}-\text{C}=\text{CH}-\text{C}-\text{Me}=\text{CH}-\text{CH}=\text{C}-\text{NH}-\text{C}(=\text{NMe}_2)-\text{N}(4-\text{MeC}_6\text{H}_4)$  (**6d**) with 20% probability thermal ellipsoids for the non-hydrogen atoms—the aryl-bonded methyl groups being disordered.



**Figure 6.** Perspective drawing of  $(\text{CF}_3)_2\text{B}-\text{C}=\text{CH}-\text{CO}-\text{Me}=\text{CH}-\text{CH}=\text{C}-\text{NH}-\text{C}(=\text{NMe}_2)-\text{N}(4-\text{MeOC}_6\text{H}_4)$  (**6e**) with 20% probability thermal ellipsoids for the non-hydrogen atoms.

**Table 8. Selected Bond Lengths (Å) and Angles (deg) for  $(\text{CF}_3)_2\text{B}-\text{CMe}_2-\text{C}(=\text{NMe}_2)-\text{NPh}$  (**8**)**

B–N(1)	1.559(3)	C(1)–C(2)	1.523(3)
B–C(2)	1.662(3)	C(2)–C(5)	1.535(3)
B–C(7)	1.610(3)	C(2)–C(6)	1.534(3)
B–C(8)	1.611(3)	C(3)–N(2)	1.460(3)
C(1)–N(1)	1.331(2)	C(4)–N(2)	1.466(3)
C(1)–N(2)	1.314(3)	C(9)–N(1)	1.433(2)
N(1)–B–C(2)	84.7(1)	B–N(1)–C(1)	93.4(2)
N(1)–C(1)–N(2)	130.0(2)	C(1)–N(1)–C(9)	132.5(2)
N(1)–C(1)–C(2)	98.8(2)	C(1)–N(2)–C(3)	124.3(2)
C(2)–C(1)–N(2)	131.1(2)	C(1)–N(2)–C(4)	121.0(2)
B–C(2)–C(1)	82.8(1)	C(3)–N(2)–C(4)	114.6(2)
B–N(1)–C(1)	133.3(2)		

The reaction of (diethylamino)diphenylborane with bis(*p*-tolyl)carbodiimide has already been described by Lappert et al. in 1966.<sup>7</sup> Thus, a direct comparison of the reactivity of **1** versus that of  $\text{Ph}_2\text{BNet}_2$  is possible. The latter combines according to eq 10 to yield a product, **15**, with an open-chain structure. This has the same framework as does **4'd**, which is a proposed intermediate in the formation of **5d** and **6d**. Apparently, the trifluoromethyl substituents of **4'd** make its

(6) Paetzold, P.; Plotho, C. v.; Niecke E.; Rüger, R. *Chem. Ber.* **1983**, *116*, 1678.

(7) Jefferson, R.; Lappert, M. F.; Prokai, B.; Tilley, B. P. *Soc. A* **1966**, 1584.



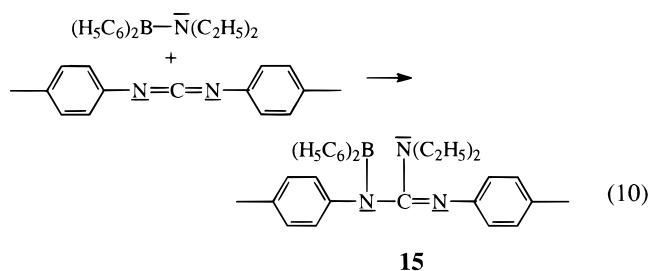
**Table 9. Selected Bond Lengths (Å) and Angles (deg) for (CF<sub>3</sub>)<sub>2</sub>B-C=CH-CMe=CH-CH=C-N-**

H-C(=NMe <sub>2</sub> )-N(4-MeC <sub>6</sub> H <sub>4</sub> ) (6d)			
B-N(1)	1.590(3)	C(1)-N(3)	1.346(3)
B-C(7)	1.610(3)	C(2)-N(2)	1.412(3)
B-C(9)	1.633(3)	C(2)-C(7)	1.392(3)
B-C(10)	1.620(3)	C(11)-N(3)	1.456(3)
C(1)-N(1)	1.340(3)	C(12)-N(3)	1.455(3)
C(1)-N(2)	1.337(3)	C(13)-N(1)	1.449(3)
N(1)-B-C(7)	108.6(2)	B-N(1)-C(13)	123.5(2)
N(1)-C(1)-N(2)	119.9(2)	C(1)-N(1)-C(13)	116.3(2)
N(1)-C(1)-N(3)	122.9(2)	C(1)-N(2)-C(2)	125.5(2)
N(2)-C(1)-N(3)	117.2(2)	C(1)-N(3)-C(11)	121.3(2)
N(2)-C(2)-C(7)	119.4(2)	C(1)-N(3)-C(12)	122.2(2)
B-C(7)-C(2)	117.9(2)	C(11)-N(3)-C(12)	115.6(2)
B-N(1)-C(1)	119.9(2)		

**Table 10. Selected Bond Lengths (Å) and Angles (deg) for (CF<sub>3</sub>)<sub>2</sub>B-C=CH-COME=CH-CH=C-N-**

H-C(=NMe <sub>2</sub> )-N(4-MeOC <sub>6</sub> H <sub>4</sub> ) (6e)			
B-N(1)	1.583(3)	C(1)-N(3)	1.350(3)
B-C(7)	1.612(3)	C(2)-N(2)	1.415(3)
B-C(9)	1.633(3)	C(2)-C(7)	1.382(3)
B-C(10)	1.626(3)	C(11)-N(3)	1.450(3)
C(1)-N(1)	1.344(3)	C(12)-N(3)	1.461(3)
C(1)-N(2)	1.340(3)	C(13)-N(1)	1.449(3)
N(1)-B-C(7)	108.2(2)	B-N(1)-C(13)	123.1(2)
N(1)-C(1)-N(2)	120.0(2)	C(1)-N(1)-C(13)	116.7(2)
N(1)-C(1)-N(3)	122.6(2)	C(1)-N(2)-C(2)	124.9(2)
N(2)-C(1)-N(3)	117.3(2)	C(1)-N(3)-C(11)	121.6(2)
N(2)-C(2)-C(7)	119.5(2)	C(1)-N(3)-C(12)	121.2(2)
B-C(7)-C(2)	118.0(2)	C(11)-N(3)-C(12)	115.9(2)
B-N(1)-C(1)	119.8(2)		

boron much more electrophilic than that of **15**. Thus, **4'd** rearranges either by attack by boron on the nitrogen of the carbodiimide or on the ortho carbon of the phenyl ring. The product distribution mentioned above indicates that the ratio of the two isomers formed depends on the relative nucleophilicity of the phenyl carbon atoms.



Lacking *N*-phenyl groups, compounds **2a–3e** could still possibly rearrange, as indicated in eq 1 to structures analogous to **5c–e** and **8**, but indeed, they show no tendency to do so. The driving force for formation of the rearranged heterocycles would appear to be the shift of the formal positive charge from the quaternary nitrogen to the less electronegative ring carbon atom with concomitant delocalization of the charge by C–N  $\pi$  bonding. The latter is best served by a planar four-membered ring which is coplanar with the valencies of the exocyclic nitrogen atom. Such coplanarity is prohibited by large substituents on the ring nitrogen atom, and compounds like **10** were shown not to rearrange. The corresponding rearrangement of **3a–e** seems unfavorable since it would leave the formal charge on a

nitrogen atom and decrease the coordination number of the NMe<sub>2</sub> group at the expense of the sterically more encumbered NR'<sub>2</sub> entity. Rearrangement of compounds **2a–e** would not only shorten the distance between the nitrogen substituents but also place a formal positive charge on the sulfur atom. Perhaps this positive charge cannot be sufficiently delocalized to the substituents of the sulfur atom by hyperconjugative N–S and O–S  $\pi$  bonding.

## Experimental Section

**X-ray Crystal Structural Determinations.** While crystals of **2a** and **3c** were mounted in glass capillaries under argon, those of **5c**, **6d**, **6e**, and **8** were glued to glass fibers. Cell constants were calculated from the  $2\theta$  angles measured with a Siemens AED1 or Enraf-Nonius CAD4 diffractometer or from the setting angles determined with a Siemens P3 device. While the Siemens AED1 diffractometer used zirconium-filtered Mo K $\alpha$  radiation, the other instruments employed graphite monochromators and Cu K $\alpha$  radiation. Intensity data were determined by  $\theta$ – $2\theta$  scan techniques and corrected for absorption. The structures were solved by direct methods, refined by full-matrix least-squares techniques and displayed using the SHELXL/PC, version 5, program package (Sheldrick, G. M. Siemens Industrial Automation, Inc., Madison, WI), which also provided the scattering factors. The hydrogen atoms of the phenyl and ordered methyl groups were idealized (C–H 0.95 Å), and the torsional orientations of the methyl groups about their X–CH<sub>3</sub> bonds were refined. While the hydrogen atoms were varied isotropically, all other atoms were assigned anisotropic temperature factors. The extinction corrections have the form  $F_c^* = F_c k [1 + 0.001x F_c^2 \lambda^3 / \sin 2\theta]^{-1/4}$ . Crystal data and refinement details are given in Table 4.

**Structure of 2a.** The cell constants were determined from the Bragg angles of 35 reflections between 10.5° and 14.9°. No extinction correction was necessary.

**Structure of 3c.** Unit cell dimensions were determined from the Bragg angles of 25 reflections between 17.2° and 28.6°. No extinction correction was necessary. The absolute structure parameter,<sup>8</sup> –0.05(3), shows that the absolute configuration shown in Figure 2 is correct.

**Structure of 5c.** Cell constants were determined from 40 reflections with  $\theta$  between 30.6° and 34.4° and confirmed by oscillation and Weissenberg photographs made with crystals mounted along *b* and *c*. Of the space groups *C2*, *Cm*, and *C2/m* which are consistent with the systematic absences, *C2* was chosen on the basis of intensity statistics and confirmed by the refinement. Following the conventional refinement with hydrogen atoms, the top 21 peaks in a difference Fourier synthesis (0.46–0.12 e/Å<sup>3</sup>) were found to be related to the atoms of the asymmetric unit by the translation 0 0 1/2. In order to account for this electron density, the crystal was assumed to be composed of molecules in the original positions of occupancy  $\alpha$  and molecules translated by *d*/2 with occupancy 1 –  $\alpha$  and otherwise identical parameters. This empirical twinning model converged rapidly to give  $\alpha = 0.950(1)$ . The absolute structure parameter, 0.1(1), was determined less precisely.

**Structure of 6d.** The unit cell dimensions were determined from 40 reflections with  $\theta$  in the range 30.6–34.4°. The aryl-bonded methyl groups were found to be disordered, and the electron density of the hydrogen atoms was fit to hexagons of six, half-occupancy hydrogen atoms. The other hydrogen atoms are ordered in the crystal—the coordinates of H(N2) being refined.

**Structure of 6e.** Cell constants were determined using 40 reflections with  $\theta$  between 27.4° and 34.2°. All of the hydrogen positions were idealized except for that bonded to N(2), which

was refined. The value of the absolute structure parameter,  $-0.04(13)$ , shows that the correct polarity was assigned to the polar axis.

**Structure of 8.** Cell constants were determined from 48 reflections with  $\theta$  between  $30.1^\circ$  and  $33.4^\circ$ . Since the overall structure is also consistent with that of its precursor, a composite atom model (C/N) was used to test the identity of the C(2) and N(2) atoms. Refinement of this model revealed no significant disorder (2(2)%); therefore, an ordered structure was assumed in the final refinement cycles.

**Preparation of compounds.** **3,3-Bis(trifluoromethyl)-4,4-dimethyl-2-(methylsulfonyl)-1-thia-2-aza-4-azonia-3-boratacyclobutan-1-one (2a)**, **3,3-Bis(trifluoromethyl)-4,4-dimethyl-2-(ethylsulfonyl)-1-thia-2-aza-4-azonia-3-boratacyclobutan-1-one (2b)**, **3,3-Bis(trifluoromethyl)-4,4-dimethyl-2-(isopropylsulfonyl)-1-thia-2-aza-4-azonia-3-boratacyclobutan-1-one (2c)**, **3,3-Bis(trifluoromethyl)-4,4-dimethyl-2-(phenylsulfonyl)-1-thia-2-aza-4-azonia-3-boratacyclobutan-1-one (2d)**, **3,3-Bis(trifluoromethyl)-4,4-dimethyl-2-((4-methylphenyl)sulfonyl)-1-thia-2-aza-4-azonia-3-boratacyclobutan-1-one (2e)**, and **5,5-Bis(trifluoromethyl)-1,1,1-trifluoro-6-methyl-4-thia-3-aza-6-azonia-5-borata-hept-2-en-4-one (9)**. To a stirred solution of 10 mmol of *N*-sulfinyl reagent in 20 mL of  $\text{CH}_2\text{Cl}_2$ , 1.93 g (10 mmol) of  $(\text{CF}_3)_2\text{BNMe}_2$  was added dropwise at  $0^\circ\text{C}$ . The reaction mixture was then allowed to warm to room temperature as stirring was continued for 30 min. The solvent and other volatile byproducts were removed in vacuo at 0.1 mbar/ $20^\circ\text{C}$ . **9** was purified by sublimation at  $25^\circ\text{C}/10^{-2}$  mbar and condensed at  $-25^\circ\text{C}$ , whereas **2a–e** were crystallized from chloroform. **2a**: yield 82%, mp  $96^\circ\text{C}$ . IR ( $\text{cm}^{-1}$ ): 1370 (s,  $\nu_{\text{as}}(\text{SO}_2)$ ), 1153 (s,  $\nu_{\text{s}}(\text{SO}_2)$ ), 1109 (vs,  $\nu(\text{CF}_3)$ ). **2b**: yield 78%, mp  $96^\circ\text{C}$ . IR ( $\text{cm}^{-1}$ ): 1378 (s,  $\nu_{\text{as}}(\text{SO}_2)$ ), 1155 (s,  $\nu_{\text{s}}(\text{SO}_2)$ ), 1103 (vs,  $\nu(\text{CF}_3)$ ). **2c**: yield 80%, mp  $97^\circ\text{C}$ . IR ( $\text{cm}^{-1}$ ): 1366 (s,  $\nu_{\text{as}}(\text{SO}_2)$ ), 1147 (s,  $\nu_{\text{s}}(\text{SO}_2)$ ), 1110 (vs,  $\nu(\text{CF}_3)$ ). **2d**: yield 88%, mp  $102^\circ\text{C}$ . IR ( $\text{cm}^{-1}$ ): 1356 (s,  $\nu_{\text{as}}(\text{SO}_2)$ ), 1161 (s,  $\nu_{\text{s}}(\text{SO}_2)$ ), 1103 (vs,  $\nu(\text{CF}_3)$ ). **2e**: yield 85%, mp  $104^\circ\text{C}$ . IR ( $\text{cm}^{-1}$ ): 1352 (s,  $\nu_{\text{as}}(\text{SO}_2)$ ), 1159 (s,  $\nu_{\text{s}}(\text{SO}_2)$ ), 1109 (vs,  $\nu(\text{CF}_3)$ ). **9**: yield 93%, mp  $<30^\circ\text{C}$ . IR ( $\text{cm}^{-1}$ ): 3272 (w,  $\nu(\text{NH})$ ), 1576 (w,  $\nu(\text{C}=\text{N})$ ), 1107 (vs,  $\nu(\text{CF}_3)$ ).

**4,4-Bis(trifluoromethyl)-2-(bis(trimethylsilyl)amino)-3,3-dimethyl-1-(trimethylsilyl)-1-aza-3-azonia-2-phospha-4-boratacyclobutane (3a)**, **4,4-Bis(trifluoromethyl)-2-(2,2,6,6-tetramethylpiperidyl)-3,3-dimethyl-1-(trimethylsilyl)-1-aza-3-azonia-2-phospha-4-boratacyclobutane (3b)**, **4,4-Bis(trifluoromethyl)-2-(*N*-trimethylsilyl-*N*-*tert*-butylamino)-3,3-dimethyl-1-*tert*-butyl-1-aza-3-azonia-2-phospha-4-boratacyclobutane (3c)**, **4,4-Bis(trifluoromethyl)-2-di(isopropylamino)-3,3-dimethyl-1-*tert*-butyl-1-aza-3-azonia-2-phospha-4-boratacyclobutane (3d)**, and **4,4-Bis(trifluoromethyl)-2-(2,2,6,6-tetramethylpiperidyl)-3,3-dimethyl-1-*tert*-butyl-1-aza-3-azonia-2-phospha-4-boratacyclobutane (3e)**. To a stirred solution of 10 mmol of aminoiminophosphine in 20 mL of pentane, 1.93 g (10 mmol) of  $(\text{CF}_3)_2\text{BNMe}_2$  was added dropwise at  $0^\circ\text{C}$ . The reaction mixture was then allowed to warm to room temperature as stirring was continued for 1 h. The solvent and other volatile byproducts were removed in vacuo at 0.1 mbar/ $20^\circ\text{C}$ , and the residue was crystallized from chloroform. **3a**: yield 91%, mp  $65^\circ\text{C}$ . IR ( $\text{cm}^{-1}$ ): 1110 (vs), 1091 (vs,  $\nu(\text{CF}_3)$ ), 935 (vs,  $\nu(\text{PN/SiN})$ ). **3b**: yield 90%, mp  $70^\circ\text{C}$  (dec). IR ( $\text{cm}^{-1}$ ): 1104 (vs), 1088 (vs,  $\nu(\text{CF}_3)$ ), 955 (s), 941 (s,  $\nu(\text{PN/SiN})$ ). **3c**: yield 85%, mp  $107^\circ\text{C}$ . IR ( $\text{cm}^{-1}$ ): 1113 (vs), 1069 (vs,  $\nu(\text{CF}_3)$ ), 971 (s), 943 (s,  $913\text{ s } \nu(\text{PN/SiN})$ ). **3d**: yield 94%, mp  $127^\circ\text{C}$ . IR ( $\text{cm}^{-1}$ ): 1104 (vs), 1079 (vs,  $\nu(\text{CF}_3)$ ), 954 (vs,  $\nu(\text{PN/SiN})$ ). **3e**: yield 89%, mp  $98^\circ\text{C}$  (dec). IR ( $\text{cm}^{-1}$ ): 1106 (vs), 1069 (vs,  $\nu(\text{CF}_3)$ ), 970 (vs,  $\nu(\text{PN/SiN})$ ).

**2,2-Bis(trifluoromethyl)-4-(dimethyliminio)-1,3-diisopropyl-1,3-diaza-2-boratacyclobutane (5a)**.  $(\text{CF}_3)_2\text{BNMe}_2$  (1.93 g, 10 mmol) and diisopropylcarbodiimide (1.62 g, 10 mmol) were sealed in a small ampoule and kept for 2 weeks at  $60^\circ\text{C}$ . The ampoule was opened, all unreacted material pumped off, and the residue crystallized from chloroform/pentane: yield 89%; mp  $160^\circ\text{C}$ . IR ( $\text{cm}^{-1}$ ): 1624 (s,  $\nu(\text{C}=\text{N})$ ), 1086, 1050 (vs,  $\nu(\text{CF}_3)$ ).

**2,2-Bis(trifluoromethyl)-1,3-dicyclohexyl-4-(dimethyliminio)-1,3-diaza-2-boratacyclobutane (5b)**, **2,2-Bis(trifluoromethyl)-4-(dimethyliminio)-1,3-diphenyl-1,3-diaza-2-boratacyclobutane (5c)**, **1,1-Bis(trifluoromethyl)-2-phenyl-2,4-diaza-3-(dimethyliminio)-1-borata-1,2,3,4-tetrahydronaphthalene (6c)**, **2,2-Bis(trifluoromethyl)-4-(dimethyliminio)-1,3-bis(4-methylphenyl)-1,3-diaza-2-boratacyclobutane (5d)**, **1,1-Bis(trifluoromethyl)-2-(4-methylphenyl)-7-methyl-2,4-diaza-3-(dimethyliminio)-1-borata-1,2,3,4-tetrahydronaphthalene (6d)**, **2,2-Bis(trifluoromethyl)-4-(dimethyliminio)-1,3-bis(4-methoxyphenyl)-1,3-diaza-2-boratacyclobutane (5e)**, and **1,1-Bis(trifluoromethyl)-2-(4-methoxyphenyl)-7-methoxy-2,4-diaza-3-(dimethyliminio)-1-borata-1,2,3,4-tetrahydronaphthalene (6e)**. General procedure: To a stirred solution of 10 mmol of the carbodiimide in 10 mL of pentane, 1.93 g (10 mmol) of  $(\text{CF}_3)_2\text{BNMe}_2$  was added dropwise at  $-78^\circ\text{C}$ . The reaction mixture was then allowed to warm to room temperature as stirring was continued for 3 h. The solvent and other volatile byproducts were removed in vacuo at 0.1 mbar/ $20^\circ\text{C}$ , and **5b**, **5c/6c–5e/6e** were crystallized from chloroform/pentane. Thus, separation of the **5/6** mixture of isomers was achieved only in part. Pure material for spectroscopic and structural investigations of **5c**, **6d**, and **6e** was obtained by manual selection of the differently shaped crystals. **5b**: yield 94%; mp  $195^\circ\text{C}$ . IR ( $\text{cm}^{-1}$ ): 1617 (s,  $\nu(\text{C}=\text{N})$ ), 1096, 1042 (vs,  $\nu(\text{CF}_3)$ ). **5c/6c**: yield 91%; **6c**  $\sim 190^\circ\text{C}$  (dec). IR ( $\text{cm}^{-1}$ ): 1619 (s,  $\nu(\text{C}=\text{N})$ ), 1077, 1051 (vs,  $\nu(\text{CF}_3)$ ). **5d/6d**: yield 86%; **6d**  $\sim 206^\circ\text{C}$  (dec). IR ( $\text{cm}^{-1}$ ): 3425 (s,  $\nu(\text{NH})$ ), 1615 (s,  $\nu(\text{C}=\text{N})$ ), 1087 (vs,  $\nu(\text{CF}_3)$ ). **5e/6e**: yield 65%; **6e**  $\sim 200^\circ\text{C}$  (dec). IR ( $\text{cm}^{-1}$ ): 3431 (s,  $\nu(\text{NH})$ ), 1600 (s,  $\nu(\text{C}=\text{N})$ ), 1080 (vs,  $\nu(\text{CF}_3)$ ).

**2,2-Bis(trifluoromethyl)-3,3-dimethyl-4-(dimethyliminio)-1-phenyl-aza-2-boratacyclobutane (8)**. To a stirred solution of dimethylketene-*N*-phenylimine (1.2 g, 8.3 mmol) in 15 mL of pentane,  $(\text{CF}_3)_2\text{BNMe}_2$  (1.7 g, 8.8 mmol) was added dropwise at  $-78^\circ\text{C}$ . The reaction mixture was then allowed to warm to room temperature as stirring was continued for 1 h. The solvent and other volatile byproducts were removed in vacuo at 0.1 mbar/ $20^\circ\text{C}$ , and **8** was crystallized from ethanol/acetone: yield 78%; mp  $130^\circ\text{C}$  (dec). IR ( $\text{cm}^{-1}$ ): 1643 (vs,  $\nu(\text{C}=\text{N})$ ), 1592, 1492 (s,  $\nu(\text{C}=\text{C})$ ), 1078, 1040 (vs,  $\nu(\text{CF}_3)$ ).

For elemental analyses see Table 3.

**Acknowledgment.** We thank Prof. Dr. C. Krüger of the Max Plank Institut für Kohlenforschung, Mülheim/Ruhr, for measuring the X-ray data on **3c**. Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

**Supporting Information Available:** Tables of atomic coordinates, hydrogen coordinates, anisotropic displacement parameters, and bond lengths and angles for **2a**, **3c'**, **5c**, **6d**, **6e**, and **8** (22 pages). Ordering information is given on any current masthead page.

OM970262I