the erythro adduct.[16] An increase in the depth of this minimum *qualitatively* correlated with a decrease in the ratio of observed adducts. If allylic 1,3 interactions were the most important controlling factor, one would have predicted that conformer **v** was the source of the erythro products. Apparently stabilization through σ donation (and minimization of $A_{1,2}$ interactions in the electron-poor radical) compensates for the destabilizing dipole–dipole and allylic 1,3 effects present in conformer **iv**.

One of our most interesting results involved the experimental observation that pentafluorophenyl system **1f** delivered only about half of the selectivity of phenyl system **1h**. Quantitatively this result could not have been predicted by our calculations although qualitatively there is a profound difference between the two cases. Pentafluoro compound **1f** shows an equivalent energy of conformers located between 210° and 260°, which is suggestive of other controlling factors such as through-space interactions or changes in the σ donating ability of R^2, aspects that we are currently studying. We are also performing a theoretical evaluation of the transition states involved in the reaction, and ESR studies are presently being conducted in order to confirm experimentally the conformational preferences indicated by our calculations.

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Supplementary Material Available: A listing of experimental procedures and spectral data (^{1}H NMR, ^{13}C NMR, IR, MS, and/or HRMS) for compounds **1–3** as well as calculation data (12 pages). Ordering information is given on any current masthead page.

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(16) GAUSSIAN 90 calculations were also performed on the radical derived from **1d**. Ab initio SCF at UHF/6-31G*//3-21G was used; Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Guassian Inc., Pittsburgh, PA, 1990. Rotamer i was again identified as being the most stable rotamer. It is interesting to note that MNDO did not reproduce these effects, instead generating a rotamer in which the ester was twisted out of plane with respect to the radical carbon.

Synthesis and Structural Characterization of a Hybrid Triazene–Thiaborane Cluster: (μ_2(4,*exo*-9)-1-SiMe$_3$-3-H-N$_3$)-*arachno*-6-SB$_9$H$_{10}$

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Azide compounds have proven to be valuable building blocks for the synthesis of boron nitrogen compounds. Early investigations focused on the reaction of azides with compounds containing classically bonded borons,[2,3] but recently azide reactions have also been employed for the synthesis of polyhedral azaborane clusters.[4,5] For example, the reaction of HN_3 with $B_{10}H_{12}(SMe_2)_2$ was found to yield *nido*-$NB_{10}H_{13}$ by way of an azido(μ-amino)decaborane intermediate.[4a]

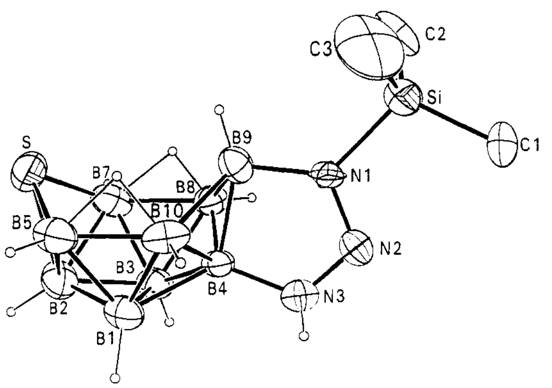

Figure 1. ORTEP drawing of the molecular structure of (μ_2(4,*exo*-9)-1-SiMe$_3$-3-H-N$_3$)-*arachno*-6-SB$_9$H$_{10}$. (The hydrogen atoms on the trimethylsilyl group are not shown.) Selected bond lengths (Å) and angles (deg): S–B5, 1.874 (11); S–B7, 1.921 (10); B4–B9, 1.698 (10); B7–B8, 1.815 (12); B5–B10, 1.849 (14); B8–B9, 1.921 (13); B9–B10, 1.917 (11); B4–N3, 1.486 (10); B9–N1, 1.515 (10); N2–N3, 1.283 (7); N1–N2, 1.292 (8); B9–B4–N3, 97.2 (5); B4–N3–N2, 118.2 (6); N1–N2–N3, 110.7 (5); N2–N1–B9, 115.0 (5); N1–B9–B4, 98.8 (6).

These previous results suggested that other classes of polyhedral boranes, and in particular the polyhedral thiaboranes, might also be susceptible to similar insertion reactions to yield previously unknown hybrid (μ-amino)thiaboranes or thiaazaboranes. We report here that *nido*-6-SB$_9$H$_{11}$ reacts readily with an organic derivative of hydrazoic acid, trimethylsilyl azide, to give the first example[6] of a new class of hybrid fused-ring cluster triazene–thiaborane compounds, (μ_2(4,*exo*-9)-1-SiMe$_3$-3-H-N$_3$)-*arachno*-6-SB$_9$H$_{10}$ (**1**).

$$\textit{nido}\text{-6-SB}_9\text{H}_{11} + \text{Me}_3\text{SiN}_3 \rightarrow (\mu_2(4,\textit{exo}\text{-9})\text{-1-SiMe}_3\text{-3-H-N}_3)\text{-}\textit{arachno}\text{-6-SB}_9\text{H}_{10} \quad \mathbf{1}$$

In a typical reaction, 5.36 g of *arachno*-Me$_4$N$^+$SB$_9$H$_{12}^-$ (25 mmol), 3.15 g of I$_2$ (12.5 mmol), and 50 mL of toluene were used to generate *nido*-6-SB$_9$H$_{11}$ as described previously.[7] The solution was filtered into a second flask, and an excess of trimethylsilyl azide (3.6 g, 31 mmol) was added dropwise at room temperature. This solution was then heated at reflux for approximately 3 h. The solvent was removed and the remaining oily residue dissolved in ether, filtered, and recrystallized. Sublimation at 80 °C/10^{-3} Torr, and recrystallization afforded 2.7 g (10.5 mmol) of **1**[8] as a white powder in 42% nonoptimized yield.

In contrast to free triazenes,[9] **1** exhibits both thermal and photolytic stability. For example, no nitrogen was evolved nor any decomposition observed upon xylene reflux for 3 days or upon photolysis in toluene solution for 3 h.

The structure of (μ_2(4,*exo*-9)-1-SiMe$_3$-3-H-N$_3$)-*arachno*-6-SB$_9$H$_{10}$, as determined by a single-crystal X-ray study, is shown in the ORTEP drawing in Figure 1.[10] The cage framework is

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(8) Spectroscopic data: IR (KBr pellet) 3370 (s), 2960 (w), 2910 (w), 2550 (s), 2530 (s), 1460 (w), 1345 (m), 1255 (m), 1000 (m), 850 (s), 840 (s); ^{11}B-NMR (64.2 MHz, in CDCl$_3$) (ppm, Hz) 7.4 (s, B4), –6.0 (d, B5,7, J_{BH} 149), –8.3 (d, B9, J_{BH} 136), –19.9 (d, B2, J_{BH} 183), –38.7 (d, B8–10, J_{BH} 136), –40.3 (d, B1–3, J_{BH} 143). Two-dimensional ^{11}B–^{11}B-COSY-NMR established the following connectivities: B1,3–B2, –B4, –B5,7, –B8,10; B4–B9, –B8,10; B9–B8,10; ^{1}H-NMR (200 MHz, CDCl$_3$) (ppm) 10.36 (1 H, NH), 0.48 (9 H, SiMe$_3$), –1.7 (2 H, μH); exact mass calcd for $^{12}C_3{}^1H_{20}{}^{11}B_9{}^{14}N_3{}^{32}S^{28}Si$ 257.1985, found 257.2018; mp 116 °C. Anal. Calcd C, 14.09; H, 7.89; N, 16.44. Found: C, 13.49; H, 7.80; N, 15.56.

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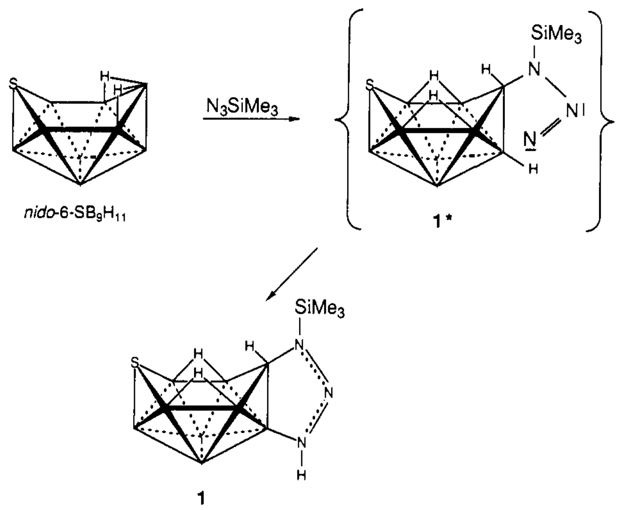

Figure 2. Proposed reaction sequence leading to the formation of (μ_2-(4,*exo*-9)-1-SiMe$_3$-3-H-N$_3$)-*arachno*-6-SB$_9$H$_{10}$ **1** from *nido*-6-SB$_9$H$_{11}$.

consistent with those observed for other 10-vertex, 26-skeletal-electron systems such as *exo*-9-Et$_3$N-*arachno*-6-SB$_9$H$_{11}$,[11] thus indicating that the triazene group is functioning as a two-skeletal-electron donor to the cage. The triazene bridges the B4 and B9 atoms, forming a planar exopolyhedral five-membered ring composed of the three azide nitrogens and the two cage boron atoms. The B4-N3 distance, 1.486 (10) Å, is slightly shorter than the B9-N1 distance, 1.515 (10) Å. Both distances are significantly shorter than the N-B9 distance observed[11b] in *exo*-9-Et$_3$N-*arachno*-6-SB$_9$H$_{11}$ (1.600 (4) Å) and fall between the ranges normally observed for boron-nitrogen single (1.57-1.60 Å) and double (1.30-1.43 Å) bonds.[2] The distances and angles for the triazene unit (N1-N2, 1.292 (8) Å; N2-N3, 1.283 (7) Å; N1-N2-N3, 110.7°) are similar to those observed in 1,3-diphenyltriazene (1.32 Å, 1.27 Å, 115°).[12] Surprisingly, the B4-B9 distance (1.698 (10) Å) is only slightly shorter than in *exo*-9-Et$_3$N-*arachno*-6-SB$_9$H$_{11}$, suggesting that the electron delocalization evident in the triazene nitrogen-nitrogen and boron-nitrogen distances does not extend to the cage borons. The remaining intracage distances and angles are similar to those in *exo*-9-Et$_3$N-*arachno*-6-SB$_9$H$_{11}$.[11b]

Because of its strong Lewis acid properties, *nido*-6-SB$_9$H$_{11}$ is unique among the larger polyhedral boranes. For example, the compound readily forms adducts[11] at the B9 boron with many bases, such as in *exo*-9-Et$_3$N-*arachno*-6-SB$_9$H$_{11}$, and hydroborates olefins and acetylenes by a process that is proposed to involve an initial electrophilic attack on the unsaturated organic by the thiaborane.[13] The formation of **1**, therefore, most likely arises via the reaction sequence outlined in Figure 2. The trimethylsilyl azide is strongly polarized, with the α-nitrogen having a partial negative and the γ-nitrogen a partial positive charge. Therefore, an initial electrophilic attack of the thiaborane would be directed at the α-nitrogen to yield the indicated base-adduct intermediate (**1***) in which the azide is bonded to the exo position of the B9 boron, as in *exo*-9-Et$_3$N-*arachno*-6-SB$_9$H$_{11}$. Subsequent insertion (hydroboration) of the γ-nitrogen of the azide into the B4-H bond would then result in ring closure, yielding the structure observed for **1**.

Preliminary studies of the reactions of benzyl azide with *nido*-6-SB$_9$H$_{11}$ also indicate the formation of the benzyl analogue of **1**. In addition, the data obtained for minor products produced in both the trimethylsilyl azide and benzyl azide reactions are consistent with the formation of new azathiaborane clusters. The observed stability of **1** suggests that it is not the precursor to these insertion products, and that they may have resulted via an intermediate analogous to **1***, in which the azide is bound to the *endo*-B9 position. We are presently exploring the characterization of these products and the expansion of these azide reactions to the generation of new classes of aza-cage/ring complexes.

Acknowledgment. We thank the Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, and the Deutsche Forschungsgemeinschaft, DFG, for the support of this research.

Supplementary Material Available: Tables of positional parameters, anisotropic temperature factors, bond distances, bond angles, and least-squares planes for **1** (12 pages); listing of observed and calculated structure factors for **1** (10 pages). Ordering information is given on any current masthead page.

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[10] Single crystals of **1** were grown at 50 °C over several days in a glass tube in vacuo. Structural data: space group $P2_1/c$, $a = 11.027$ (1) Å, $b = 11.431$ (2) Å, $c = 12.819$ (3) Å, $\beta = 105.12$ (1)°, $V = 1559.9$ (9) Å^3, $Z = 4$, and $d_{\text{calcd}} = 1.080$ g/cm^3. The structure was solved by direct methods (MULTAN 11/82). Refinement was by full-matrix least-squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically. Positions of cage hydrogens were refined (thermal parameters were fixed at 6.0 Å^2); all other hydrogen atoms were included as a constant contribution to the structure factors and were not refined. Refinement converged to $R_1 = 0.076$ and $R_2 = 0.080$.

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Singlet-Triplet Separations Measured by Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy. Applications to the Molybdenum-Molybdenum Quadruple Bond and to Edge-Sharing Bioctahedral Complexes

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Generally speaking, the separation in energy of a low-lying triplet state from a diamagnetic ground state has been estimated (often with great accuracy, as for copper(II) acetate) by measurements of the magnetic susceptibility of the solid compound over a broad temperature range (typically 5-300 K).[1-3] We report here an alternative way to obtain such data that is more convenient, sensitive, and widely applicable for samples in the solid state and solution.[4] We also report results for two important classes of compounds (shown in Figure 1) and important conclusions to be drawn therefrom, such as the δ-electron contribution to the barrier to rotation about the Mo-Mo quadruple bond.

The ^{31}P solution-state NMR spectra of compounds of the types M$_2$Cl$_4$(L-L)$_2$ and M$_2$Cl$_6$(L-L)$_2$, where L-L is a bidentate phosphine ligand, are characterized by variations in the chemical shifts of the phosphorus atoms with temperature. On the basis of a negligible dipolar contribution, the temperature dependence of the ^{31}P chemical shift can be used to calculate the hyperfine coupling constant (A), the diamagnetic chemical shift (δ_{dia}) for

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