hydrolyzed to [*t*-Bu(py)Co(DH)$_2$(H$_2$O)]NO$_3$ which is poorly soluble in CH$_2$Cl$_2$. The filtrate from above was allowed to evaporate to dryness and spectral characterization showed the residue to be primarily *t*-Bu(py)Co(DH)$_2$NO$_2$ with some *t*-Bu(py)Co(DH)$_2$NO$_3$.

***t*-Bu(py)Co(DH)$_2$NO$_3$ by Direct Preparation.** To a solution of *t*-Bu(py)Co(DH)$_2$Cl[6] (3.0 g, 0.0067 mol) in methanol (75 ml), silver nitrate (1.28 g, 0.0075 mol) was added. The suspension was warmed and stirred for 2 hr and let stand overnight. After filtration, water (75 ml) was added to the filtrate in an open beaker. After 2 days the solution had evaporated (to ~30 ml) and the crystals which had formed were collected and washed with water (5 ml) and diethyl ether (90 ml). The product [*t*-Bu(py)Co(DH)$_2$(H$_2$O)]NO$_3$ (2.15 g, 60% yield) was dehydrated (110° *in vacuo*) to give *t*-Bu(py)Co(DH)$_2$NO$_3$ quantitatively. *Anal.* Calcd for C$_{17}$CoH$_{27}$N$_6$O$_7$: C, 42.0; H, 5.6; Co, 12.2. Found: C, 42.4; H, 5.4; Co, 11.9.

Acknowledgment. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. Cobaloxime nitrosyl, 36509-25-8; (*t*-Bu(py))Co(DH)$_2$NO$_3$, 50276-21-6.

Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90007

Trifluorosilylpentaboranes

Anton B. Burg

Received September 17, 1973

The prospect of making (fluorinated silyl)pentaboranes was encouraged by the results of an attack by SiF$_2$ upon B$_5$H$_9$ in a cocondensation process performed by Dr. David Solan in these laboratories. His crude product was separated from resinous nonvolatiles, and the unstable volatiles were allowed to decompose until it became possible to isolate 0.013 mmol of a slightly volatile liquid (vapor tension near 1 mm at 0°) having infrared and ^{11}B nmr spectra suggesting 1-HSiF$_2$B$_5$H$_8$.

Accordingly, a direct synthesis of SiF$_3$B$_5$H$_8$ was attempted, using LiB$_5$H$_8$ with excess SiF$_4$ in ether at −78° or lower. The volatile product was almost exclusively 2-SiF$_3$B$_5$H$_8$, convertible by a difficult catalysis to its isomer 1-SiF$_3$B$_5$H$_8$.

Syntheses. An ether solution of LiB$_5$H$_8$ was made from B$_5$H$_9$ and LiC$_2$H$_5$,[1] rather than LiC$_4$H$_9$,[2] because the evolved ethane could be isolated easily, as a measure of the formation of LiB$_5$H$_8$. The reaction occurred in a vertical 350 mm long tube (25 mm wide), attached to the high-vacuum manifold. For complete conversion to LiB$_5$H$_8$, 12 hr at −78° usually sufficed, but sometimes temperatures as high as −40° were allowed. Small excesses of B$_5$H$_9$ seemed not to harm the subsequent process.

The ether solution of LiB$_5$H$_8$ was covered by a layer of fresh ether (distilled in slowly at −78°); then SiF$_4$ in 3:1 ratio to LiB$_5$H$_8$ was forced into this ether layer (at −78° or as low as −120°), from above. The reaction was started by sudden mixing of the layers at −78° or lower, using a magnetic plunger as a stirrer. The mixture was allowed to stand for 12 hr at −78°, and then all volatiles were drawn off *in vacuo* during slow warming, finally to 60°.

This procedure led to yields of 2-SiF$_3$B$_5$H$_8$ representing as much as 45% of the LiB$_5$H$_8$. For example, 3.280 mmol of LiB$_5$H$_8$ and 9.717 mmol of SiF$_4$ produced 1.497 mmol of 2-SiF$_3$B$_5$H$_8$, with consumption of 3.94 mmol of SiF$_4$, some of which, of course, would have gone to form Li$_2$SiF$_6$. The question of formation of SiF$_2$(B$_5$H$_8$)$_2$ was not decided; the nonvolatile resinous product could have included its successor. The yield of 1-SiF$_3$B$_5$H$_8$ may have been close to 1%; it was completely separable from 2-SiF$_3$B$_5$H$_8$ by slow high-vacuum fractional condensation at −40°.

For larger samples of 1-SiF$_3$B$_5$H$_8$, catalytic isomerization of 2-SiF$_3$B$_5$H$_8$ can be accomplished by contact with resins made from pentaborane, such as the nonvolatile yellow residue from the SiF$_3$B$_5$H$_8$ synthesis, but the process is sharply limited by inactivation of the catalyst—an effect varying widely among different samples of such resins. Also, the loss of SiF$_3$B$_5$H$_8$ material often exceeds the amount converted. The conversion is accompanied by formation of small amounts of highly volatile products, including SiF$_4$ and HSiF$_3$, easily detected by their infrared spectra. On account of the uncertainty about catalyst potency, the question of reversibility of the isomerization has not been decided. Both isomers seem stable for months at 25°.

Hexamethylenetetramine has served as an effective catalyst for isomerizing halogenated pentaboranes[3] or 2-(CH$_3$)$_3$SiB$_5$H$_8$,[4] but it had only a limited effect upon crude 2-SiF$_3$B$_5$H$_8$, and even then apparently only through resin formation. With pure samples of either 1-SiF$_3$B$_5$H$_8$ or 2-SiF$_3$B$_5$H$_8$ (12 hr at 60°) it failed to cause any detectable isomerization.

The most successful procedure for the LiB$_5$H$_8$-SiF$_4$ reaction was repeated with HSiF$_3$ and with PF$_3$, yielding neither HSiF$_2$B$_5$H$_8$ nor PF$_2$B$_5$H$_8$, but only yellow resins. If the desired compounds actually were formed at low temperatures (but perhaps base catalyzed to resins on warming), they might be isolated by some special method, such as low-temperature solution chromatography.

Physical Properties. The melting range of a nearly pure sample of 2-SiF$_3$B$_5$H$_8$ (for which the ^{19}F nmr spectrum showed 0.3% presence of 1-SiF$_3$B$_5$H$_8$) was −11.5 to −10.8°, whereas well-purified 1-SiF$_3$B$_5$H$_8$ (isomer not detectable) melted in the range 7.7–8.1°. The equilibrium vapor pressure of solid 1-SiF$_3$B$_5$H$_8$ at 0° is 1.04 mm, or for the liquid, 6.35 mm at 24.5°; a rough estimate of the normal boiling point would be 140°. The 99.7% pure sample of 2-SiF$_3$B$_5$H$_8$ showed vapor pressure values of 5.02 mm at 0°, 22.18 mm at 22.5°, 31.40 mm at 31.1°, 50.02 mm at 40.35°, and 78.58 mm at 50.0°, determining the equation $\log P = 6.6605 + 1.75 \log T - 0.005T - 2367/T$ (bp 113.3°; Trouton constant 21.7 eu; calculated values: 5.03, 22.13, 31.48, 50.05, 78.50 mm). The vapor-phase molecular weight measurements gave 147.5 for 1-SiF$_3$B$_5$H$_8$ and 148.8 for 2-SiF$_3$B$_5$H$_8$ (calculated for both 147.2).

Nmr Spectra. The ^{11}B spectra of 1-SiF$_3$B$_5$H$_8$ and the presumed 1-HSiF$_2$B$_5$H$_8$ are nearly identical: a broad but clean doublet at 30.4 or 30.8 ppm upfield of methyl borate (J = 169 cps for both) and a broad singlet at 80.1 ppm, one-fourth as intense. This B-1 singlet is considerably farther upfield than B-1 for other known B$_5$H$_9$ derivatives, possibly because the fluorine lone-pair electrons exert a π-type electronic induction across the Si 3d orbitals, toward the B-1 atom.

---

(1) A. B. Burg, *Inorg. Chem.*, **12**, 3017 (1973).

(2) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **89**, 3375 (1967).

(3) A. B. Burg, *J. Amer. Chem. Soc.*, **90**, 1407 (1968).

(4) D. F. Gaines and T. V. Iorns, *Inorg. Chem.*, **10**, 1094 (1971).

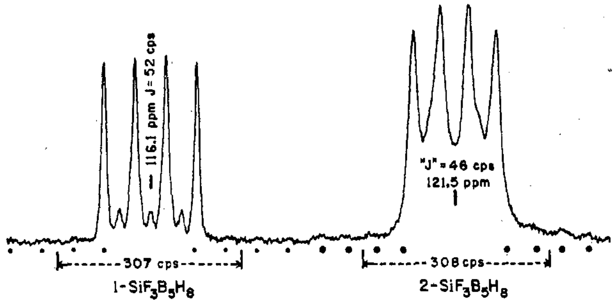

Figure 1. Fluorine nmr spectra for the SiF$_3$B$_5$H$_8$ isomers, as recorded for a mixture by the Varian HA-100 instrument. The side quartets of dots represent the splitting effect of ^{29}Si (J = 307 or 308 ± 3 cps). The outermost three peaks of each of these quartets (here barely recognizable above the noise level) were well recorded in other runs at higher radiofrequency power, with the central quartets (kept on scale by lower amplification) also recorded for comparison. The three small peaks within the pattern for 1-SiF$_3$B$_5$H$_8$ are the second, fourth, and sixth peaks of the ^{19}F–^{10}B septet, for which J = 26 cps. For 2-SiF$_3$B$_5$H$_8$, the ^{10}B effect shows only as a loss of symmetry for the central peaks. The chemical shifts are measured upfield from Cl$_3$CF.

The proton nmr spectrum of 1-SiF$_3$B$_5$H$_8$ has the same appearance as that of 1-(CF$_3$)$_2$PB$_5$H$_8$:[5] the quartet is centered at 2.53 ppm downfield of TMS (J = 169 cps) and the large singlet maximizes at 2.20 ppm upfield of TMS.

The ^{19}F nmr spectra of the two isomers are shown in full detail in Figure 1. The ^{29}Si–^{19}F coupling constants are within the range previously observed for Si-F compounds.[6] It is interesting that B-1, with its environment of four basal boron atoms, has far less blurring effect upon the ^{19}F peaks than is caused by B-2.

The ^{11}B spectrum of 2-SiF$_3$B$_5$H$_8$ at 32.1 Mc showed B-1 as a clear doublet at 69.4 ppm from methyl borate (J = 178 cps) and B-2 as a clean singlet at 41.4 ppm. The 3,5 doublet at 28.8 ppm (J = 173 cps) obscured the upfield branch of the B-4 doublet, centered near 23 ppm (J uncertain). Apparently the SiF$_3$ group at the B-2 position has an electron-withdrawing effect upon the B-4 atom, in contrast to the electron-donor action of F-2 upon the B-4 atom.[7]

The 100-Mc proton spectrum of 2-SiF$_3$B$_5$H$_8$ also could not be fully resolved, but the record is clear enough for the major 3,5-BH quartet centered at 2.46 ppm downfield of TMS (J = 176 cps). For the asymmetric B-H-B bridge peak, maximizing at 2.06 ppm upfield of TMS, one may assume superposition of two kinds of bridging protons, along with some coverage of the most upfield B-H terminal peaks for the B-1 and B-4 protons. The quartets for these seem to be centered at 0.87 and 0.16 ppm downfield of TMS, with J values 167 ± 10 cps.

Infrared Spectra. The Beckman IR7 instrument with NaCl or CsI optics was used to obtain the accurate frequencies shown below (in cm^{-1}) (with relative intensities in parentheses) for three compounds in the vapor phase at pressures from 3 to 10 mm, in 10-cm cells with KBr windows.

For the Supposed 1-HSiF$_2$B$_5$H$_8$: 2621 (7.3), 2142 (1.5), 1862 (2.2), 1817 (1.0), broad absorption 1520–1330, with peaks at 1502 (2) and 1414 (3.3), complex 1115 (1.3), complex 1065 (3.7), 957 (20), 947 (21), 864 (16), 846 (12), uncertain 767 (0.8), 706 (1.6), 683 (2.3), uncertain 670 (3), 515 (2.3), R 477 (6), Q 473 (8), P 468 (6).

For 1-SiF$_3$B$_5$H$_8$: 2620 (13), broad 1864 (1.6) and 1813 (1.1), range 1525–1325, with peaks at 1498 (2.4), 1460 (3.1), and 1410 (3.0), 1209 (1.2), 1205 (1.3), R 1069 (3.2), Q 1065 (5.2), P 1062 (3.8), uncertain 1033 (1.0), 943 (48), R 868 (24), Q 862 (29), P 858 (25), 766 (2.0), 763 sh (1.7), complex 683 (2.7), range 625–515 with flat maximum 605–585 (0.4), R 474 (14), Q 470 (21), P 466 (15).

For 2-SiF$_3$B$_5$H$_8$: 2621 sh (10), 2616 (11), broad 1846 (0.5), uncertain 1780 (0.15), range 1600–1240 with peaks at 1535 (0.2), 1495 (0.4), 1455 (0.5), 1406 (3.8), 1315 (0.3), and 1268 (0.25), 1164 (0.05), 1113 (1.2), 1061 (1.7), uncertain 1020 (0.08), 957 (27), 926 (10), R 877 (10.6), Q 873 (10.6), P 869 (9.0), complex 823 (9.2), 776 (0.40), uncertain 702 (0.37), R 684 (1.50), Q 680 (1.52), P 677 (1.44), complex 611 (0.9), broad 575 (0.36), 509 (0.44), 506 (0.44), R 456 (7.8), Q 452 (9.0), P 488 (8.3), 344 (2.0).

It is obvious that the supposed 1-HSiF$_2$B$_5$H$_8$ is different from 1-SiF$_3$B$_5$H$_8$, although showing many similarities to both of the SiF$_3$B$_5$H$_8$ isomers. The peak at 2142 cm^{-1} is assignable to Si-H stretching, and the absence of a second peak argues against the presence of an SiH$_2$ group. Most of the other assignments for these compounds are either obvious or uncertain, as is true for the infrared spectra of most other B$_5$H$_9$ derivatives.

Acknowledgment. This research was supported in part by Grant No. GP-17472 from the National Science Foundation.

Registry No. 2-SiF$_3$B$_5$H$_8$, 50442-27-8; 1-SiF$_3$B$_5$H$_8$, 50442-28-9; LiB$_5$H$_8$, 34370-18-8; SiF$_4$, 7783-61-1; 1-HSiF$_2$B$_5$H$_8$, 50442-29-0.

---

[5] A. B. Burg and H. Heinen, *Inorg. Chem.*, 7, 1023 (1968).

[6] R. B. Johannesen, F. E. Brinckman, and T. D. Coyle, *J. Phys. Chem.*, 72, 662 (1968).

[7] A. B. Burg, *J. Amer. Chem. Soc.*, 90, 1407 (1968).

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14850

Solution State, Nuclear Magnetic Resonance Spectral Features for Zr[S$_2$CN(CH$_3$)(C$_6$F$_5$)]$_4$

E. L. Muetterties

Received October 23, 1973

In the eight-coordinate class of tetrakis-chelate complexes, M(chel)$_4$, it has been shown[1] that for *N,N*-dialkyldithiocarbamato complexes of Ti, Zr, and Nb(IV) there is no evidence of nonequivalence in the alkyl groups (symmetrical chelates) or of stereoisomers (unsymmetrical chelates) based on ^{13}C and ^{1}H nmr spectra from +30 to −160°. Polytopal form in Ti[S$_2$CN(C$_2$H$_5$)$_2$]$_4$[2] is the dodecahedron, hence there should be inequivalence (A and B sites) of alkyl groups in M(S$_2$CNR$_2$)$_4$ and the presence of stereoisomers in the solution state of M(S$_2$CNRR')$_4$.[3,4] The observation that a mix-

---

[1] E. L. Muetterties, *Inorg. Chem.*, 12, 1963 (1973).

[2] M. Colapietro, A. Vaciago, D. C. Bradley, M. B. Hursthouse, and I. F. Rendall, *Chem. Commun.*, 743 (1970).

[3] If the alkyl substituents differ only slightly in steric character, as was the case for the earlier study,[1] it is eminently reasonable to expect stereoisomers to be present for the solution state.

[4] This assumes no change in polytopal form in going from the solid to solution states.[5,6] If the square antiprismatic form were to prevail in the solution state, then there would be strict R group equivalence in the ligand if and only if the D_4 isomer were the only square antiprismatic form present. Irrespective of polytopal form, stereoisomers are expected[3] for a M(S$_2$CNRR')$_4$ complex.