



Figure 1. Fluorine nmr spectra for the  $\text{SiF}_3\text{B}_5\text{H}_8$  isomers, as recorded for a mixture by the Varian HA-100 instrument. The side quartets of dots represent the splitting effect of  $^{29}\text{Si}$  ( $J = 307$  or  $308 \pm 3$  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- $\text{SiF}_3\text{B}_5\text{H}_8$  are the second, fourth, and sixth peaks of the  $^{19}\text{F}$ - $^{10}\text{B}$  septet, for which  $J = 26$  cps. For 2- $\text{SiF}_3\text{B}_5\text{H}_8$ , the  $^{10}\text{B}$  effect shows only as a loss of symmetry for the central peaks. The chemical shifts are measured upfield from  $\text{Cl}_3\text{CF}$ .

The proton nmr spectrum of 1- $\text{SiF}_3\text{B}_5\text{H}_8$  has the same appearance as that of 1- $(\text{CF}_3)_2\text{PB}_5\text{H}_8$ :<sup>5</sup> 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  $^{19}\text{F}$  nmr spectra of the two isomers are shown in full detail in Figure 1. The  $^{29}\text{Si}$ - $^{19}\text{F}$  coupling constants are within the range previously observed for Si-F compounds.<sup>6</sup> It is interesting that B-1, with its environment of four basal boron atoms, has far less blurring effect upon the  $^{19}\text{F}$  peaks than is caused by B-2.

The  $^{11}\text{B}$  spectrum of 2- $\text{SiF}_3\text{B}_5\text{H}_8$  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  $\text{SiF}_3$  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.<sup>7</sup>

The 100-Mc proton spectrum of 2- $\text{SiF}_3\text{B}_5\text{H}_8$  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  $167 \pm 10$  cps.

**Infrared Spectra.** The Beckman IR7 instrument with NaCl or CsI optics was used to obtain the accurate frequencies shown below (in  $\text{cm}^{-1}$ ) (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- $\text{HSiF}_2\text{B}_5\text{H}_8$ :** 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

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

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

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

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In the eight-coordinate class of tetrakis-chelate complexes,  $\text{M}(\text{chel})_4$ , it has been shown<sup>1</sup> that for  $N,N$ -dialkyldithiocarbamate 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  $^{13}\text{C}$  and  $^1\text{H}$  nmr spectra from +30 to  $-160^\circ$ . Polytopal form in  $\text{Ti}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_4$ <sup>2</sup> is the dodecahedron, hence there should be inequivalence (A and B sites) of alkyl groups in  $\text{M}(\text{S}_2\text{CNR}_2)_4$  and the presence of stereoisomers in the solution state of  $\text{M}(\text{S}_2\text{CNR}'_2)_4$ .<sup>3,4</sup> The observation that a mix-

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 (3) If the alkyl substituents differ only slightly in steric character, as was the case for the earlier study,<sup>1</sup> 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.<sup>5,6</sup> 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<sup>3</sup> for a  $\text{M}(\text{S}_2\text{CNR}'_2)_4$  complex.

ture of chelate complexes of the type  $Zr[S_2CN(C_2H_5)_2]_x-[S_2CN(C_3H_7)_2]_{4-x}$  with  $x = 1, 2,$  and  $3$  showed single  $CH_3$  and  $CH_2(N-C_2H_5)$  and  $CH_3, CH_2,$  and  $CH_2(N-C_3H_7)$   $^1H$  nmr multiplets suggests that *N*-alkyl substituents are at best sensors only of A and B site environments in the dodecahedron<sup>4</sup> and that their resonances are substantially unaffected by the nature of the neighboring alkyl groups.

It was hoped that substitution of the perfluorophenyl group for one of the *N*-alkyl groups in the dithiocarbamate ligand might provide a greater environmental perturbation and allow detection of stereoisomers in an  $M[S_2CN(R)C_6F_5]_4$  complex. In fact, the  $^{13}C, ^{19}F,$  and  $^1H$  nmr spectra of  $Zr[S_2CN(CH_3)(C_6F_5)]_4$  show no evidence of stereoisomers from  $+30$  to  $-130^\circ$ . The  $CH_3-N$   $^{13}C$  resonance is a singlet to  $-130^\circ$ , and the  $^{13}C$   $C_6F_5$  resonance is a set of four widely spaced multiplets. The  $CH_3-N$  proton resonance at  $30^\circ$  is a triplet which slowly broadens with temperature decrease (half-height widths were 2 and 9 Hz at  $-35$  and  $-150^\circ$ , respectively). Below  $-150^\circ$ , the resonance broadened rapidly due to viscosity effects. The  $^{19}F$  spectrum is complex with separated multiplets for *o*-, *m*-, and *p*-perfluorophenyl resonances. Broadening of the  $^{19}F$  multiplets is discernible below  $0^\circ$  and is severe below  $-60^\circ$ ; the broadening rate is comparable here to that in the proton spectra but seems magnified because of the wide range of spectral transitions for the spins of these fluorine atoms. Broadening, evident in the  $^1H$  spectra of all  $M[S_2CNR_2]_4$  complexes investigated to date, has been ascribed primarily to lower rates of molecular tumbling in these *quasi*-spherical-symmetrical complexes.

It can only be concluded that stereoisomers were not detected in this specific compound. Since the electronic effects of the  $C_6F_5$  and  $CH_3$  groups are substantially different, there may only be a single stereoisomer for  $Zr[S_2CN(CH_3)(C_6F_5)]_4$ . However, this is deemed unlikely for the solution state because the *N*-R groups are well removed from the metal center and the  $S_2CN$  system does not appear<sup>8</sup> to effectively transmit electronic effects. Models do not show any unique steric demands that the  $C_6F_5$  group might exert in either polytopal form ( $D_{2d}$  or  $D_{4d}$ ). Accordingly, the general situation<sup>1</sup> of high stereochemical nonrigidity in eight-coordinate chelates appears to extend to this specific case.

### Experimental Section

**Reagents.** All reagents and solvents were obtained from commercial suppliers and were not further purified.

**Synthesis of  $(C_6F_5)(CH_3)NH$ .** Methylamine (15.5 g, 0.5 mol) was distilled into a stainless steel lined reaction vessel (100 ml) containing hexafluorobenzene (46.5 g, 0.25 mol). The vessel was closed and heated to  $100^\circ$  for 12 hr. The product, a gelatinous mass, was dissolved in ethanol to which was then added a solution of sodium hydroxide (10.0 g, 0.25 mol) in 40 ml of water. After filtration, the amine was separated by distillation at  $44-45^\circ$  ( $\sim 0.1$  mm) in a spinning band column and then redistilled at  $33^\circ$  ( $\sim 0.01$  mm): 60-MHz  $^1H$  nmr [ $(CH_3)_4Si = 0$ ]  $\delta$  2.80 (t, 3,  $J_{HH} = 5.3$  Hz

and  $J_{NH} = 2.4$  Hz) and 3.27 (b, 1).<sup>9</sup>  $^{19}F$  nmr parameters agreed with reported data.<sup>10</sup> *Anal.* Calcd for  $C_7H_4F_5N$ : C, 42.65; H, 2.04; N, 7.11. Found: C, 42.64; H, 2.36; N, 7.12.

**Synthesis of  $(C_6F_5)(n-C_4H_9)NH$ .** Hexafluorobenzene (93.0 g, 0.50 mol) and *n*-butylamine (73.14 g, 1.0 mol) were slurried in 80:20 ethanol-water (100 ml) and refluxed for 12 hr under nitrogen. To the resulting clear yellow solution was added sodium hydroxide (20 g, 0.5 mol) in 20 ml of  $H_2O$ . After stirring for 1 hr at  $25^\circ$ , the volatile liquid product was separated from the solids by vacuum distillation. The pale yellow product was distilled in a spinning band distillation column at  $72.5^\circ$  ( $\sim 0.25$  mm): 60-MHz  $^1H$  nmr  $\delta$  0.6-3.1 (complex); 56.4-MHz  $^{19}F$  nmr<sup>4</sup> ( $CFCl_3 = 0$ )  $\delta$  181.3 (para), 187.9 (meta), and 194.1 (ortho) ( $J_{pm} = \pm 21.5$  and  $J_{op} = \mp 7.0$  Hz).<sup>9</sup> *Anal.* Calcd for  $C_{10}H_{16}NF_5$ : C, 50.21; H, 4.21; N, 5.86. Found: C, 50.47; H, 4.40; N, 6.11.

**Synthesis of  $Zr[S_2CN(CH_3)(C_6F_5)]_4$ .**  $(C_6F_5)(CH_3)NH$  (11.06 g, 0.05 mol) was dissolved in 75 ml of dry, nitrogen-saturated tetrahydrofuran in an oxygen-free drybox. To this solution was added dropwise  $(CH_3)_2NLi$  (2.55 g, 0.05 mol) in 50 ml of tetrahydrofuran. After the addition was complete, stirring was continued for 1 hr. The yellow solution was filtered, and solvent was removed on a Rinco evaporator. Residual yellow solids were dried *in vacuo* at  $25^\circ$  at 0.001 mm. The product,  $LiNC_6F_5(CH_3)$ , was then dissolved in tetrahydrofuran, and the solution was cooled to  $-45^\circ$  in an oxygen- and moisture-free drybox. To this cold solution was added zirconium tetrachloride (0.0125 mol) to give a near-purple solution that was stirred 30 min after the addition had been completed. The solution was filtered and evaporated *in vacuo* to dryness. Residual material was extracted with toluene to separate the product from the lithium chloride. Extracts were filtered and reduced to a yellow oil *in vacuo* at  $25^\circ$  (0.001 mm). This oil, crude  $Zr[(C_6F_5)N(CH_3)]_4$ , was placed in a 100-ml stainless steel reaction vessel with 35 ml of carbon disulfide. After heating the vessel to  $100^\circ$  for 16 hr, the reaction mixture was recovered and filtered. Petroleum ether was added to the filtrate to precipitate yellow solids. These were collected and dissolved in a minimum amount of toluene. Petroleum ether was added until incipient precipitation was evident. After cooling to  $-40^\circ$ , yellow crystals were collected by filtration. Recrystallization was repeated. The crystals were dried *in vacuo* at  $50^\circ$  (0.001 mm): 60-MHz  $^1H$  nmr [ $(CH_3)_4Si = 0$ ]  $\delta$  3.08 (t,  $J_{NH} = 7$  Hz); 22.63-MHz  $^{13}C$  nmr ( $CS_2 = 0$ )  $\delta$  -129.7; 56.4-MHz  $^{19}F$  nmr ( $CFCl_3 = 0$ )  $\delta$  192.9 (meta), 201.6 (para), and 209.0 (ortho) ( $J_{pm} = 23.5$  Hz and  $J_{op} = 1.9$  Hz). *Anal.* Calcd for  $C_{32}H_{12}N_4F_{20}S_8Zr$ : C, 32.57; H, 1.03; N, 4.75; S, 21.74. Found: C, 33.34; H, 1.46; N, 4.59; S, 22.42.

**Attempted Synthesis of  $Zr[S_2CN(C_6F_5)(n-C_4H_9)]_4$ .** The above outlined procedure, based on  $(C_6F_5)(n-C_4H_9)NH$ , was followed, but the final product was a yellow oil which was not successfully purified. The crude oil showed no evidence (nmr) of *N*-ligand substituent inequivalence.

**Nmr Studies.** Proton nmr spectra were obtained with Varian HA-60, HR-220, and HA-100 spectrometers for 25,  $+25$  to  $-50$ , and  $+25$  to  $-160^\circ$  temperature ranges, respectively. Fluorine spectra were obtained with Varian HA-60 and HA-100 spectrometers for 25 and  $+25$  to  $-100^\circ$  spectra, respectively. The  $^{13}C$  spectra ( $^1H$  decoupled) were observed over the range  $+25$  to  $-160^\circ$  with a Bruker HFT-90 with Digilab FTS/NMR-3 accessory (fluorine lock). Data for the amines are based on the pure liquids. For the zirconium complex, toluene-*d*<sub>8</sub> and dichloromethane-chlorotrifluoromethane were the solvents for the 25 to  $-60$  and  $-50$  to  $-160^\circ$  range, respectively.

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**Registry No.**  $(C_6F_5)(CH_3)NH$ , 1201-02-1;  $(C_6F_5)(n-C_4H_9)NH$ , 50311-45-0;  $Zr[S_2CN(CH_3)(C_6F_5)]_4$ , 50276-23-8;  $ZrCl_4$ , 10026-11-6;  $CS_2$ , 75-15-0.

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(5) See ref 6 and 7 for a discussion of change in polytopal form in eight-atom clusters.

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