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Crystal and Molecular Structure of *cis*-4,5-Dichloro-1,1,2,2-tetrafluoro-1,2-disilacyclohexane

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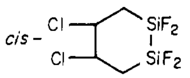
Crystals of the title compound are monoclinic, of space group $P2_1/n$ with $Z = 4$, $a = 6.901$ (4) Å, $b = 10.002$ (8) Å, $c = 13.478$ (4) Å, $\beta = 91.55$ (4)°, and $D_c = 1.837$ g/cm^3. Intensity data were obtained on a single-crystal diffractometer with Cu Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares to $R = 0.069$ for 1101 independent reflections. The enantiomeric pairs of the molecule are related by the n glide symmetry in the crystal. The conformation of the six-membered ring is close to a half-chair; the disilane part of the ring is considerably flattened with the bond length and ring torsional angle of the Si–Si bond being 2.318 (3) Å and 8.9 (4)°, respectively. On the basis of this molecular structure, the energy barrier of the ring inversion process is discussed and compared with those of cyclohexanes.

Introduction

Two products which are isomers of the molecular formula $C_4H_6Cl_2Si_2F_4$ from the cocondensation reaction between difluorosilylene and vinyl chloride are crystalline substances.[2] Largely on the basis of the fluxional behaviors in the ^{19}F NMR spectra of these two compounds, one of them has been identified as the cis isomer of 4,5-dichloro-1,1,2,2-tetrafluoro-1,2-disilacyclohexane (the other isomer is, of course, the trans one). We now report a crystal structure determination of the cis isomer (I), the result of which confirms the original assignment of the molecular structure.



I

Experimental Section

Preparation. Compound I was prepared by a cocondensation reaction between difluorosilylene and vinyl chloride and purified by exhaustive vacuum-line fractionation.[2] The transparent colorless crystals obtained were stable at room temperature in the absence of air and water and sublimable under vacuum. Because of the volatility and reactivity of the compound, D_m was not determined.

Crystallographic Measurement. A single crystal with dimensions 0.4 × 0.3 × 0.1 mm was selected under a dry argon atmosphere and sealed into a Lindemann-glass capillary. The crystal was monoclinic, of space group $P2_1/n$. The cell parameters determined from setting angles of 25 reflections measured on a Nonius CAD-4F automatic diffractometer are $a = 6.901$ (4) Å, $b = 10.002$ (8) Å, $c = 13.478$ (6) Å, and $\beta = 91.55$ (4)°. The density calculated on the basis of four molecules per unit cell is 1.837 g/cm^3.

Three-dimensional intensity data were collected at room temperature with use of θ–2θ scan technique. During the data collection, the intensities of three standard reflections were remeasured periodically and were used to rescale all the data by use of a linear interpolation procedure. The intensities of these standard reflections decreased by about 20% at the end of data collection. Of the total 1937 independent reflections collected with Ni-filtered Cu Kα radiation ($\lambda = 1.54178$ Å, $2\theta \leq 139°$), 1101 were found to have intensities greater than 3 times their estimated standard deviations. Intensity data were then converted to structure factors after Lorentz and polarization corrections were applied in the usual manner. No correction for absorption was applied.

Table I. Fractional Coordinates (× 10^4)

atom	x/a	y/b	z/c
Si(1)	7126 (3)	6606 (2)	2446 (1)
Si(2)	4672 (3)	7896 (2)	3093 (1)
Cl(4)	2231 (3)	9042 (2)	116 (1)
Cl(5)	3412 (4)	5870 (2)	971 (2)
F(22)	5465 (9)	9054 (5)	3782 (4)
F(21)	3258 (7)	7082 (6)	3742 (3)
F(11)	6875 (7)	5060 (5)	2696 (3)
F(12)	9212 (8)	6961 (5)	2882 (3)
C(3)	3229 (11)	8620 (7)	2038 (4)
C(4)	4114 (11)	8572 (7)	1010 (5)
C(5)	5029 (11)	7239 (7)	650 (5)
C(6)	7063 (12)	6952 (8)	1089 (5)
H(11)	3008	9484	2182
H(12)	2095	8176	1999
H(2)	5052	9197	1003
H(3)	5107	7274	−15
H(41)	7817	7658	977
H(42)	7544	6235	776

Table II. Bond Distances and Angles[a]

A. Distances, Å			
Si(1)–Si(2)	2.318 (4)	Si(1)–C(6)	1.861 (9)
Si(2)–C(3)	1.861 (8)	Si(1)–F(11)	1.593 (7)
C(3)–C(4)	1.530 (12)	Si(1)–F(12)	1.581 (7)
C(4)–C(5)	1.558 (12)	Si(2)–F(21)	1.558 (6)
C(5)–C(6)	1.536 (11)	Si(2)–F(22)	1.574 (7)
C(4)–Cl(4)	1.810 (9)	C(5)–Cl(5)	1.826 (9)
B. Angles, Deg			
Si(2)–Si(1)–C(6)	105.6 (3)	F(11)–Si(1)–F(12)	104.0 (4)
C(3)–Si(2)–Si(1)	108.1 (3)	Si(2)–Si(1)–F(11)	112.1 (3)
C(4)–C(3)–Si(2)	117.5 (6)	Si(2)–Si(1)–F(12)	113.7 (3)
C(5)–C(4)–C(3)	118.9 (7)	C(6)–Si(1)–F(11)	112.9 (4)
C(6)–C(5)–C(4)	114.4 (7)	C(6)–Si(1)–F(12)	108.7 (4)
Si(1)–C(6)–C(5)	114.2 (6)	F(21)–Si(2)–F(22)	105.5 (4)
C(3)–C(4)–Cl(4)	107.3 (6)	Si(1)–Si(2)–F(21)	113.3 (3)
C(5)–C(4)–Cl(4)	107.7 (6)	Si(1)–Si(2)–F(22)	112.7 (3)
C(4)–C(5)–Cl(5)	108.2 (5)	C(3)–Si(2)–F(21)	107.6 (4)
C(6)–C(5)–Cl(5)	109.1 (6)	C(3)–Si(2)–F(22)	109.6 (4)

[a] Estimated errors are in parentheses.

Structure Determination. The structure was solved by MULTAN.[3] All nonhydrogen atoms were located from an E map. Full-matrix least-squares refinement with isotropic thermal parameters for these atoms led to an R of 0.127 with $R = \sum||F_o| - |F_c||/\sum|F_o|$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme given by Stout and Jensen.[4] The positions of the hydrogen atoms were then calculated with use of a C–H distnace of 0.9 Å and a tetrahedral angle of 109.5°. The positional and isotropic thermal parameters of the hydrogen atoms were then included in the calculations but not refined. The final refinement with anisotropic thermal parameter for the nonhydrogen atoms led to values of R and R_w of 0.069 and 0.061, respectively, where $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. The atomic

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(1) (a) Institute of Molecular Biology. (b) Department of Chemistry.

(2) Liu, C. S.; Hwang, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 2996.

(3) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(4) Stout, G. H.; Jensen, L. "X-ray Structure Determination"; Macmillan: New York, 1968; 457.

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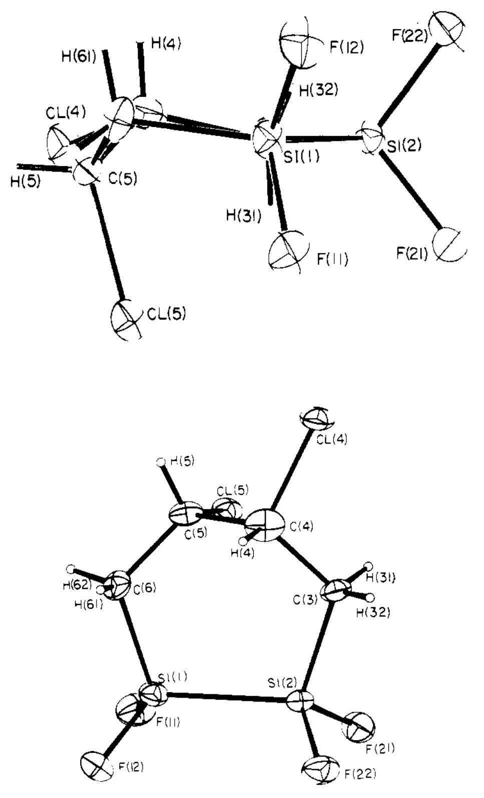

Figure 1. Two perspective views of the molecular structure with the numbering scheme of the atoms.

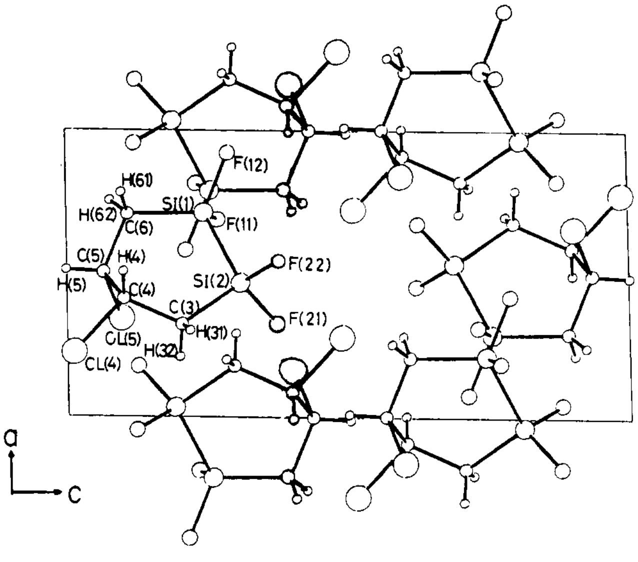

Figure 2. Crystal packing diagram (viewed along the *b* axis).

scattering factors used were all taken from ref 5, with those of Cl and Si corrected for anomalous dispersion.

The final atomic coordinates are given in Table I. Two perspective views of the molecule (and atom numbering scheme) are shown in Figure 1. A crystal packing viewed along the *b* axis is presented in Figure 2. Selected bond distances and angles are listed in Table II. The anisotropic thermal parameters and a table of observed and calculated structure factors are available; see the paragraph at the end of the paper regarding supplementary materials.

Results and Discussion

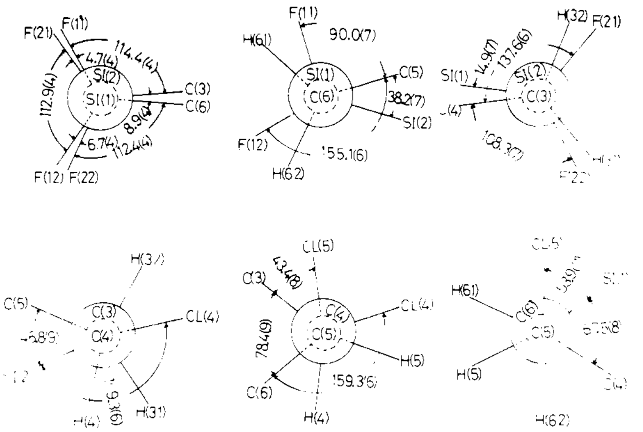

Figure 3. Torsional angles of the ring conformation. Estimated errors are in parentheses. Those angles involving hydrogen atoms are not shown.

Both enantiomers of compound I appear in the crystal as a consequence of the symmetry operations of the centrosymmetric space group $P2_1/n$. The molecule adopts a nearly half-chair conformation with the disilane part of the ring considerably flattened. The Si–Si bond length is 2.318 (3) Å which is comparable to those reported for hexafluorodisilane[6] (2.324 (6) and 2.317 (6) Å). The two Si–C bond lengths (1.861 (7) and 1.861 (6) Å) are identical and are similar to that of 1.867 (20) Å in methylsilane.[7] The C(3)–C(4) and C(5)–C(6) bond lengths (1.530 (9) and 1.536 (10) Å, respectively) approach the normal C(sp^3)–C(sp^3) single-bond length[7] of 1.537 (5) Å. The C(4)–C(5) bond length (1.558 (12) Å) is longer. However, it is close to the value of 1.562 (14) Å reported for hexachloroethane.[8] Therefore, the ring bond lengths are all comparable to their corresponding expected values. Accordingly, the distortion in the conformation of compound I from the chair form is best understood in terms of torsional and bond angles of the ring.

All ring bond angles deviate from the standard tetrahedral value (109.5°) with the carbon bond angles (maximum 118.9 (7)°) showing greater deviation than the silicon ones, indicating the six-membered ring of compound I is rather strained and the bond angles of silicon atom are less deformable than the carbon ones. In *rac*-1,2-diselenane-3,6-dicarboxylic acid which has comparable ring bond distances and adopts a chair conformation,[9] the C–Se–Se bond angles of the ring are 96 (1)°. It appears that one of the causes for compound I to adopt a nearly half-chair conformation rather than a chair one is the inability of silicon atoms to deform the bond angles to a greater extent.

The torsional angles of the ring are shown in Figure 3. The endocyclic torsional angle of the Si–Si bond is 8.9 (4)°. The two chlorine atoms are in staggered positions with a torsional angle (Cl–C(4)–C(5)–Cl) of 78.3 (9)°. The vicinal Cl···Cl nonbonded distances is 3.465 (4) Å. Considering Si(1), Si(2), C(3), and C(6) to form a plane, the out of plane deviations of C(4) and C(5) are 0.172 (3) and −0.576 (3) Å, respectively (Table III). The Cremer–Pople puckering parameters[10] are also given in Table III. The values of Q, θ, and ϕ indicate the conformation of the ring is close to a half-chair and is flattened at the disilane part.

With such a conformation, all four fluorines of compound I are chemically nonequivalent. However, they will average into two distinctive chemical environments if rapid exchange in solution is considered, i.e., $F_1 \rightleftharpoons F_3$ and $F_2 \rightleftharpoons F_4$ are accompanied with the ring inversion.

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(6) (a) Rankin, D. W. H.; Robertson, A. *J. Mol. Struct.* **1975**, *27*, 438. (b) Oberhammer, H. *Ibid.* **1976**, *31*, 237.

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(8) Morino, Y.; Hirota, E. *J. Chem. Phys.* **1958**, *28*, 185.

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Table III. Displacements from Least-Squares Planes and Cremer-Pople Puckering Parameters[a]

A. Least-Squares Planes[b]

Plane I: $4.02x + 8.07y + 1.09z = 8.51$ ($\chi^2 = 2193$)

Si(1)*	−0.047 (3)	Si(2)*	0.078 (3)
C(3)*	−0.033 (3)	C(6)*	0.053 (3)
C(4)	0.172	C(5)	−0.576 (3)

Plane II: $4.31x + 7.71y + 1.48z = 8.54$, ($\chi^2 = 196.7$)

Si(1)*	−0.015 (3)	Si(2)*	0.017 (3)
C(4)*	−0.011 (3)	C(6)*	0.025 (3)
C(3)	−0.204 (3)	C(5)	−0.677 (3)

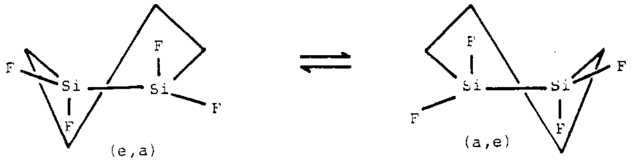
B. Puckering Parameters[c]

conformation I: $q_2 = 0.377$, $q_3 = -0.355$, $\phi_2 = 53.8°$, $Q = 0.541$, $\theta = 135.9°$

conformation II: $q_2 = 0.377$, $q_3 = 0.355$, $\phi_2 = 233.8°$, $Q = 0.541$, $\theta = 44.1°$

[a] Estimated errors are in parentheses. [b] Equations of planes are in the form $lx + my + nz = p$, where x, y, and z are fractional coordinates and p is the distance of the plane from the unit cell origin. [c] Puckering parameters are calculated according to ref 10 with atom numbering as shown in Figure 1. I and II are enantiomeric pairs related by n glide symmetry; only fractional coordinates of I are given in Table I.

The two conformations associated with the ring inversion, (e,a) and (a,e), are indistinguishable. One would therefore



expect equal populations for the two enantiomers in all different chemical environments throughout the exchange; i.e., the equilibrium constant of the conformational pair is equal to unity at all temperatures.

The ^{19}F NMR spectra of I at various temperatures are shown in Figure 4. It is clear that the spectra fit very well the features mentioned above. From the coalescence temperature the barrier for the ring inversion process, $\Delta G^{\ddagger}$, is estimated[11] to be 11.8 (3) kcal/mol. This ring inversion barrier is substantially higher than that of 5.5 kcal/mol reported for a monosilacyclohexane (1,1-dimethylsilacyclohexane).[12]

Ring inversion barriers of a number of six-membered heterocyclic ring systems have been determined by dynamic NMR spectroscopy. In six-membered group 6 pentamethylene heterocycles, the barriers to ring inversion were found to decrease monotonically from tetrahydropyran to tellurane.[13] The barriers appear to correlate well with the torsional properties of the C–X bonds, and angle strain is shown not to be an important contributor to the barrier height.[13] This dependence of barrier to ring inversion on the torsional properties of the C–X bond seems extendable to all six-membered pentamethylene heterocycles.

However, six-membered ring systems containing two adjacent heteroatoms appear not to follow the general conclusion drawn for six-membered group 6 pentamethylene heterocycles; thus 1,2-dithiane[14] has a higher barrier of ring inversion than thiane has, although the increase is small. The ground-state conformations of both thiane and 1,2-dithiane were expected to be chairlike.[15] The higher barrier to ring inversion of 1,2-dithiane, therefore, is likely to be attributable to the inversion pathway taken by the molecule which leads to a higher barrier through the introduction of the X–X bond.

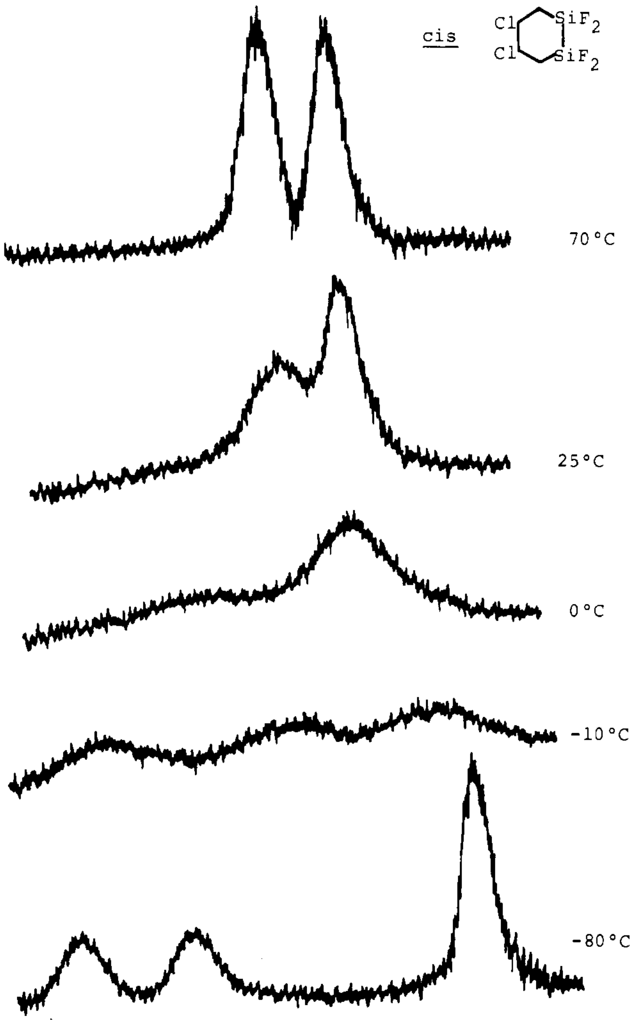


Figure 4. ^{19}F NMR spectra (56.4 MHz) of the molecule at various temperatures.

In analogy, one would expect 1,2-disilacyclohexane to have a higher barrier to ring inversion than monosilacyclohexane. This is indeed the case. The present crystal structure determination has shown that the ground-state conformation of I is close to a half-chair. The part of the ring with chlorine attached is highly puckered. A molecular model of I indicates that the symmetrical boat form is most likely the highest barrier height intermediate involved in the ring inversion process. The introduction of the Si–Si bond inhibits the pseudorotation of the twist-boat intermediate.

Recently, the activation free energy of *cis*-4,5-dimethyl-1,1,2,2-tetrafluoro-1,2-disilacyclohexane has been estimated to be 8.2 kcal/mol,[16] and from the conformational study of other methyl-substituted disilacyclohexanes it is suggested that the $\Delta G^{\ddagger}$ increases with the increase of methyl interaction.[16] The greater increase in inversion barrier of I is, therefore,

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(15) Thiane has an *R* value of 2.61 (see ref 13) which indicates a puckered chair conformation according to the criteria given by Lambert and Keske (Lambert, J. B.; Keske, R. G. *Tetrahedron Lett.* **1967**, *47*, 4755. The crystal structures of 1,2-dithiane-3,6-dicarboxylic acid[9] and 1,4-dithiane (Marsh, R. E. *Acta Crystallogr.* **1955**, *8*, 91) have been determined by X-ray diffraction, both adopt chairlike conformations.

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attributable to the interference of the two chlorine atoms in cis positions. These adjacent Cl atoms not only provide strong steric interaction but also electrostatic repulsion.

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Registry No. I, 70787-84-7.

Supplementary Material Available: Tables of anisotropic thermal parameters of nonhydrogen atoms and structure factor amplitudes for I (6 pages). Ordering information is given on any current masthead page.

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Synthesis, Chemistry, and Low-Temperature Crystal and Molecular Structure of [μ-(η^5-Cyclopentadienyl)beryllio]octahydropentaborane, [μ-(η^5-C_5H_5)Be]B_5H_8

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Reaction of (η^5-C_5H_5)BeCl with KB_5H_8 results in formation of the title compound, which forms crystals in the monoclinic space group $P2_1/c$ with a = 10.266 (8) Å, b = 5.616 (4) Å, c = 16.187 (7) Å, β = 98.50 (5)°, V = 923.0 (5) Å^3, and Z = 4. The low-temperature X-ray structure was solved by direct methods, using anisotropic refinement of positional and temperature factors for nonhydrogen atoms and isotropic refinement for hydrogen atoms, which converged to R_1 = 0.0551 and R_2 = 0.0831 for 1294 independent observed reflections. The structure of [μ-(η^5-C_5H_5)Be]B_5H_8 is like that of B_5H_9, but with a bridge hydrogen replaced by the (η^5-C_5H_5)Be moiety. Selected chemical properties of the title compound are described.

Introduction

Beryllium, in the form of $Be(BH_4)_2$, may be inserted into a borane cluster by reaction with 1-ClB_5H_8 to produce 2-berylla-2-(tetrahydroborato)hexaborane(11),[1] $B_5H_{10}BeBH_4$, which has a six-vertex pentagonal-pyramidal B_5–Be cluster framework.[2] The mechanism of this reaction is complex, and $Be(BH_4)_2$ presents some handling difficulties. Thus other synthetic routes to beryllaborane clusters are desirable. The successful insertion of boron, as $(CH_3)_2BCl$, into a bridging position in pentaborane(9) and subsequent rearrangement to a hexaborane(10) derivative[3] (eq 1) suggested that a similar

$$LiB_5H_8 + (CH_3)_2BCl \rightarrow [\mu\text{-}(CH_3)_2B]B_5H_8 \rightarrow 2,3\text{-}(CH_3)_2B_6H_8 \quad (1)$$

insertion might occur with use of selected beryllium compounds. We present here the results of our initial investigations of such a beryllium-insertion reaction, in which (η^5-C_5H_5)BeCl was used as the insertion reagent.

Results and Discussion

The reaction of (η^5-C_5H_5)BeCl with KB_5H_8 in a pentane slurry at ca. −40 °C produces good yields of [μ-(η^5-C_5H_5)-Be]B_5H_8 according to eq 2. The product is a colorless solid

$$KB_5H_8 + (\eta^5\text{-}C_5H_5)BeCl \rightarrow KCl + [\mu\text{-}(\eta^5\text{-}C_5H_5)Be]B_5H_8 \quad (2)$$

of low volatility that melts at ca. 38 °C. Characterization of the product was accomplished initially via mass and NMR spectroscopy, and the detailed structural parameters were obtained from a single-crystal X-ray study.

The ambient ^{11}B FT NMR spectrum of [μ-(η^5-C_5H_5)-Be]B_5H_8 is appropriate for a μ-substituted B_5H_9 derivative. It consists of three doublets of intensity 2:2:1 at δ −13.4 (J = 161 Hz), −21.8 (J = 141 Hz), and −54.6 (J = 170 Hz), respectively. With ^1H decoupled, ^{11}B(apex)–^{11}B(base) coupling is observed in both sets of basal boron resonances. the most interesting feature of the ^{11}B NMR spectrum is the large upfield shift of the resonances associated with two of the basal borons, suggesting a higher concentration of electron density, while the other chemical shifts are not significantly different from those of B_5H_9. It is interesting to note that the average of the chemical shifts for the two sets of basal boron resonances of [μ-(η^5-C_5H_5)Be]B_5H_8 is the same as that observed for $B_5H_8^-$ salts.[3] The static structure, solubility in hydrocarbons, and volatility, however, confirm the covalency of the B–Be–B bonding. The 270-MHz ^1H FT NMR spectrum contains a sharp singlet at δ 5.4 (C_5H_5), quartets at δ 2.7, 1.8, and 1.1 (B_t–H) for the terminal B–H's, and broad singlets of intensity 1:2 at δ −2.5 and −3.7, respectively, for the bridging hydrogens.

Table I. Interatomic Distances (Å) for [μ-(η^5-C_5H_5)Be]B_5H_8

C(1)–C(2)	1.391 (3)	B(2)–B(5)	1.812 (3)
C(1)–C(5)	1.397 (3)	B(2)–H(2)	1.102 (20)
C(1)–H(6)	0.931 (22)	B(2)–H(5-2)	1.263 (20)
C(2)–C(3)	1.398 (3)	B(1)–B(2)	1.696 (3)
C(2)–H(7)	0.929 (24)	B(1)–B(3)	1.705 (3)
C(5)–H(4)	1.401 (3)	B(1)–B(4)	1.675 (3)
C(5)–H(10)	1.045 (24)	B(1)–B(5)	1.663 (3)
C(4)–C(3)	1.396 (4)	B(1)–H(1)	0.980 (25)
C(4)–H(9)	0.980 (33)	B(3)–B(4)	1.821 (3)
C(3)–H(8)	0.899 (27)	B(3)–H(3)	1.041 (20)
Be(1)–C(1)	1.886 (3)	B(3)–H(3-4)	1.268 (20)
Be(1)–C(2)	1.894 (3)	B(4)–B(5)	1.799 (3)
Be(1)–C(5)	1.892 (3)	B(4)–H(4)	1.039 (20)
Be(1)–C(4)	1.877 (3)	B(4)–H(3-4)	1.251 (22)
Be(1)–C(3)	1.884 (3)	B(4)–H(4-5)	1.242 (21)
Be(1)–B(2)	2.045 (3)	B(5)–H(5)	1.065 (27)
Be(1)–B(3)	2.055 (3)	B(5)–H(4-5)	1.293 (20)
B(2)–B(3)	1.726 (3)	B(5)–H(5-2)	1.310 (21)

The X-ray determined structure of [μ-(η^5-C_5H_5)Be]B_5H_{10} is shown in Figure 1. The internuclear distances and angles are given in Tables I and II, respectively. Some interesting features appeared in the structural data which were not discernible from the NMR data. The shortening of the B(2)–B(3) distance (Table I) suggests a higher concentration of electron density in this region in agreement with the assignment of the higher field resonance in the ^{11}B NMR spectrum to the borons adjacent to beryllium. The tilt of H(4,5) under

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