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Received January 9, 1979

Insertion of Beryllium into a Boron–Boron Bond. The Synthesis of μ-[η^5-Cyclopentadienylberylla]octahydropentaborate, μ-[η^5-$(C_5H_5)Be]B_5H_8$

Sir:

We report here the synthesis and structural characterization of μ-[η^5-$(C_5H_5)Be]B_5H_8$, which is an unusually good example of the very different bonding of the η^5-$(C_5H_5)Be$ moiety to different borane groupings. In the recently reported 2-[η^5-(C_5H_5)]-2-BeB_5H_{10}[1] the Be appears to be incorporated as a vertex in a six-atom nido framework that is structurally and electronically similar to that of the pentagonal pyramidal B_6H_{10} molecule. In the title compound, however, the same η^5-$(C_5H_5)Be$ moiety resides in a nonvertex bridging position (μ) between two adjacent basal boron atoms in a square-pyramidal framework. Other known μ-$(X_nM)B_5H_8$ compounds, such as μ-$[Cl(PPh_3)Cd]B_5H_8$[2] and μ-$[(PPh_3)_2Cu]B_5H_8$[3,4] have not been shown to form the corresponding 2-(X_n)-2-MB_5H_{10} analogues, nor has the direct conversion of μ-[η^5-$(C_5H_5)Be]B_5H_8$ to 2-[η^5-(C_5H_5)]-2-BeB_5H_{10} been demonstrated as yet.

The reaction of a stirred pentane slurry of 10 mmol of KB_5H_8[5] with excess C_5H_5BeCl,[6] while the reaction mixture warms from −40 °C to ambient, produces high yields of μ-[η^5-$(C_5H_5)Be]B_5H_8$, which is purified by high-vacuum trap-to-trap fractionation. The compound is a colorless solid of low volatility (vp $\ll$ 1 Torr at ambient) which melts at ca. 38 °C. It is stable at room temperature in the solid state and in nonbasic solvents such as C_6H_6 or CH_2Cl_2. It decomposes rapidly in the presence of O_2 or H_2O. In C_6H_6 solution, thermal decomposition occurs slowly at 80 °C and rapidly at 140 °C.

The mass spectrum of μ-[η^5-$(C_5H_5)Be]B_5H_8$ is as expected, exhibiting a mass cutoff at *m/e* 137 corresponding to ${}^{12}C_5{}^{11}B_5{}^{9}Be_1{}^{1}H_{13}$ (calcd 137.16052, obsd 137.1600).

The room-temperature 86.7-MHz ^{11}B FT NMR spectrum of μ-[η^5-$(C_5H_5)Be]B_5H_8$ 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.[7] ${}^{11}B_{(apex)}$–${}^{11}B_{(base)}$ coupling is observed in both sets of basal boron resonances. The spectrum is appropriate for a μ-substituted B_5H_9 derivative, but the chemical shift between the basal boron resonances is quite large. 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, 1.1 for the terminal B–H's; and broad singlets of intensity 1:2 at −2.5 and −3.7, respectively, for the bridging hydrogens.

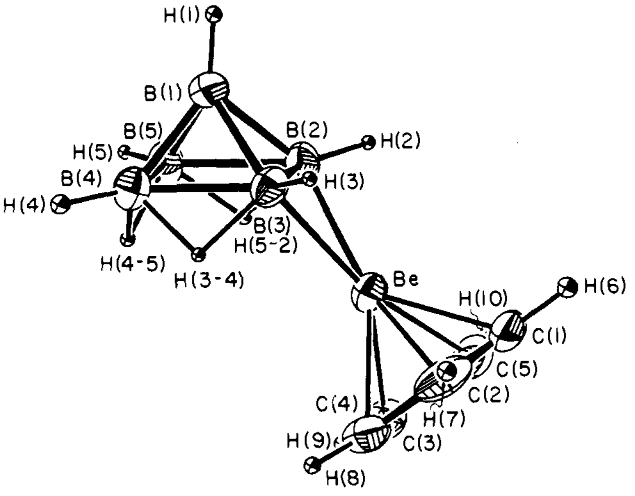

Figure 1. An ORTEP drawing of the structure of μ-[η^5-$(C_5H_5)Be]B_5H_8$. The atoms are represented as 40% elipsoids with the H atom temperature factors reduced by a factor of 10.

Table I. Selected Crystallographic Data for μ-[η^5-$(C_5H_5)Be]B_5H_8$

group	distance, Å
B_a–B_b[c]	1.663 (3)–1.705 (3)
Be	
B_b–B_b	1.726 (3)–1.821 (3)
B–$H_{(terminal)}$	0.98 (3)–1.10 (2)
B–$H_{(bridge)}$	1.24 (2)–1.31 (2)
B–Be	2.050 (3) (av)
Be–C	1.877 (3)–1.894 (3)
C–C	1.391 (3)–1.401 (3)
C–H	0.90 (3)–1.05 (3)
intermolecular	3.670 (4) (minimum)

μ[a]	dihedral ∠, deg[b]	∠ from basal plane, deg
Be	33.82	56.18
H(3,4)	25.92	64.08
H(2,5)	27.27	62.73
H(4,5)	21.35	68.65

[a] Bridging substituent. [b] The angles between the perpendicular to the plane of the four basal boron atoms and the vector from the center of each basal edge to its bridging group. [c] B_a = apex boron, B(1); B_b = basal borons, B(2)–B(4).

A single crystal of μ-[η^5-$(C_5H_5)Be]B_5H_8$ was grown in a Pyrex capillary on a Syntex $P\bar{1}$ autodiffractometer. The crystal contained a monoclinic unit cell: space group $P2_1/c$; a = 10.266 (8), b = 5.616 (4), and c = 16.187 (7) Å; β = 98.50 (5)°; Z = 4. There were 1709 reflections collected at −100 °C using Mo Kα radiation. Data reduction yielded 1294 independent observed reflections. The positions and temperature factors of all nonhydrogen atoms were anisotropically refined. The hydrogen atom temperature factors were isotropically refined. Final values of R_1 = 5.51 and R_2 = 8.31 were obtained. The molecular structure (Figure 1) confirms the substitution of $C_5H_5Be^+$ in a bridging position on $B_5H_8^-$ as indicated by NMR data. The B(2)–B(3) bond is shorter than the rest of the basal B–B distances (Table I). H(1) is tilted 5° from the pyramid perpendicular toward the Be. The C_5H_5Be moiety is tilted up as a unit toward H(1). H(4,5) is tilted further under the base of the B_5 framework than H(3,4) or H(2,5). The $C_5H_5^-$ is nearly planar with local fivefold symmetry except that the C–H's are all tilted slightly inward toward the Be. These distortions cannot be explained by crystal-packing phenomena as the intermolecular distances are much too large. The Be–B(2,3) distance of 2.050 (3) Å is about 10% longer than the sum of the covalent radii (B = 0.85–0.90 Å, Be = 0.91Å), which is in the normal range for substituents in bridging positions on B_5H_9. The Be–C_5H_5 distance is comparable to that observed in C_5H_5BeX[6] compounds.

$C_5H_5BeB_5H_8$ reacts with Brønsted acids to produce B_5H_9, and with B_2H_6, upon heating, to produce $B_{10}H_{14}$ and traces of other boranes. Its reactions with halogens are complex, but

0002-7863/79/1501-3979$01.00/0

the major product with bromine, for example, is 1-BrB_5H_8. The derivative chemistry of $C_5H_5BeB_5H_8$ will be discussed more extensively later.

Acknowledgment. We thank the National Science Foundation for partial partial support of this work.

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Received February 1, 1979

NMR Evidence for C_3 Ground-State Conformations and Multiple Site Exchange Processes in Systems of the Type t-Bu_3MX

Sir:

The chemical consequences of intramolecular crowding in molecules of the type t-Bu_3MX have attracted considerable interest. Members in this class of stereochemically correspondent[1] molecules are found, by computational methods (EFF[2-5] and CNDO/2[6]) and gas-phase electron diffraction,[7,8] to possess ground states in which the *tert*-butyl groups are twisted in the same sense and to the same extent, resulting in structures with C_3 symmetry. The methyls on each of the three homotopic *tert*-butyl groups are thus rendered symmetry nonequivalent (diastereotopic). However, although there has been much interest in hindered rotation in these systems, the expected three methyl resonances have hitherto eluded observation under conditions of slow rotation in the variable-temperature NMR spectra.[4,5,9-11] We now report the first such observation in two systems, $[t\text{-}Bu_3PCH_3]^+I^-$ (**1**) and t-Bu_3CH (**2**), and present experimental evidence,the first of its kind for a system of the type t-Bu_3MX, that **1** undergoes two independent site exchange processes.

The 25.2-MHz $^{13}C\{^1H\}$ NMR spectrum of **1**[12] in 5:1 $CHF_2Cl/CHFCl_2$ at −144 °C displays three *tert*-butyl methyl singlets of equal intensity at δ_{Me_4Si} 25.7, 28.8, and 31.2 ppm. With an increase in temperature, the two downfield signals coalesce, and at −109 °C the *tert*-butyl methyl region of the spectrum consists of two sharp singlets in a 2:1 ratio, δ_{Me_4Si} 30.3 and 26.1 ppm, respectively. The calculated barrier ($\Delta G^{\ddagger}_{-138}$)[13] for this process is 6.3 ± 0.8 kcal/mol.[15] With a further increase in temperature, the two remaining singlets coalesce, and at −48 °C the spectrum consists of a singlet for the *tert*-butyl methyl carbons, δ_{Me_4Si} 29.4 ppm, and doublets for the *P*-methyl and quaternary carbons, δ_{Me_4Si} 1.8 ($^1J_{CP}$ = 45 Hz) and 38.5 ppm ($^1J_{CP}$ = 32 Hz), respectively. The calculated barrier ($\Delta G^{\ddagger}_{-72}$)[13] for this second process is 9.5 ± 0.5 kcal/mol.[17,18]

The processes responsible for the two coalescence phenomena may be described in terms of the mechanisms elaborated for analogous permutational rearrangements in the stereochemically correspondent t-Bu_3SiH (**3**).[4] Accordingly, the lower energy process, which results in coalescence of two of the three methyl signals, corresponds to an *SSS* mechanism in which each of the *tert*-butyl groups undergoes net conrotation through a staggered (*S*) conformation. The three *tert*-butyl groups librate about an all-staggered C_{3v} structure, and this process thus results in enantiomerization. In the higher energy *ESS* process, one of the *tert*-butyl groups rotates through an eclipsed (*E*) conformation, whereas the other two rotate in the opposite direction through *S* conformations. This pathway, or an alternative topomerization, renders all three *tert*-butyl methyl sites equivalent.[19]

The three diasterotopic methyls in the *tert*-butyl groups of **2** were also found to be observably anisochronous at the slow exchange limit: the 25.2-MHz $^{13}C\{^1H\}$ NMR spectrum of **2**[20] in CF_2Cl_2 at −127 °C exhibits three methyl singlets at δ_{Me_4Si} 26.3, 38.6, and 39.3 ppm. This observation provides the first evidence that the C_3 conformation observed in the gas phase[8] and calculated by a wide variety of force fields[3] also corresponds to the ground state in solution. At −34 °C the methyl carbons exhibit only one singlet at δ_{Me_4Si} 35.1 ppm; singlets for the quaternary and methine carbons appear at δ_{Me_4Si} 39.1 and 65.2 ppm, respectively. Preliminary dynamic NMR studies indicate that the barrier for internal rotation lies between 7 and 9 kcal/mol.[21]

Acknowledgments. We thank the National Science Foundation (CHE77-07665) for support of this work, Mary W. Baum for technical assistance, and Linda D. Iroff for helpful discussions.

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(13) Activation parameters were obtained by a least-squares fit to the Eyring equation of the rate data obtained by line-shape analysis using the Saunders program.[14]
(14) The computer program used was adapted from one developed by M. Saunders (see Saunders, M. In "Magnetic Resonance in Biological Systems"; Ehrenberg, A.; Malmström, B. G.; Vänngård, T., Eds.; Pergamon: New York, 1967; p 85).
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(18) An analogous coalescence phenomenon for the same process was observed in the variable-temperature 100-MHz $^1H\{^{31}P\}$ NMR spectrum of **1**. The *tert*-butyl methyl singlet, δ_{Me_4Si} 1.51 ppm at −50 °C in 5:1 $CHClF_2/CHCl_2F$, is split into two singlets in a 2:1 ratio, δ_{Me_4Si} 1.38 and 1.56 ppm, respectively, at −113 °C.
(19) *EFF* calculations on **1** are precluded by the lack of proper parametrization for tetravalent phosphorus. It is noteworthy, however, that *EFF* calculations predict *three* rearrangement processes for t-Bu_3SiCH_3, which is sterically similar and stereochemically correspondent to **1**. The lower energy process (*SSS*), which averages two of the three methyl sites, requires 6.0 kcal/mol.

0002-7863/79/1501-3980$01.00/0