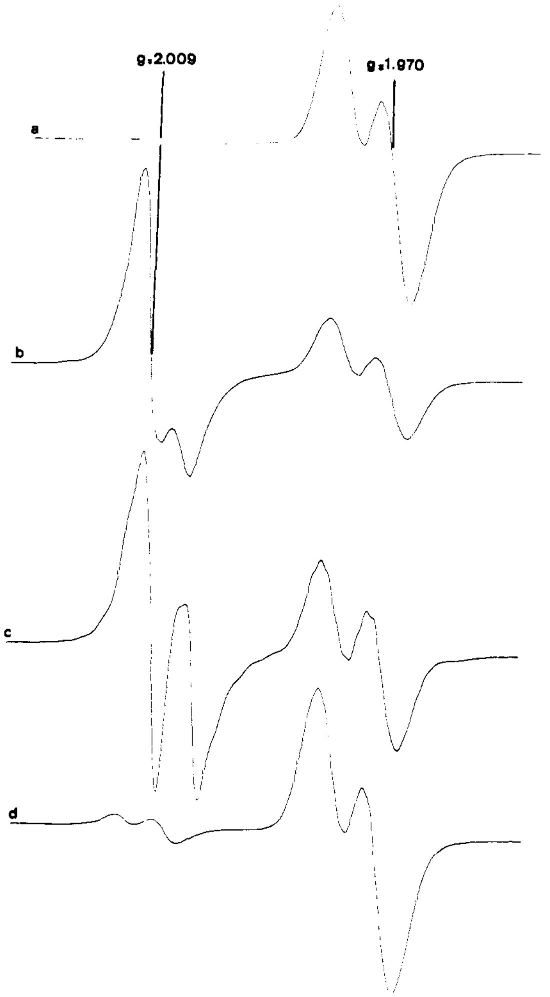

**Figure 3.** EPR spectra of Ti(F)(TPP) ~1% in Ti(O)(TPP) host crystals: (a) under argon at 20 °C; (b) under dioxygen at 20 °C (the new signal at $g = 2.009$ corresponds to the dioxygen adduct $Ti(O_2)(F)(TPP)$, **5**); (c) under dioxygen at −196 °C; (d) after evacuation overnight at 20 °C. Conditions of EPR spectroscopy: microwave frequency, 9.1 GHz; microwave power, 20 mW; modulation amplitude, 0.16 G; magnetic field sweep rate, 50 $G/min^{-1}$; time constant, 0.25 s; instrument gain, 250 (a, b, d), 200 (c).

compounds **3** and **4**. The high stability of $Ti(O_2)(TPP)$ and the preference of **1** for six coordination probably are strong driving forces for reaction 3. Reasoning that combined immobilization and dilution of the dioxygen binding sites of **1** might afford the desired kinetic stabilization of **5**, we grew crystals from a $CH_2Cl_2$ solution containing Ti(O)(TPP),[14] **6**, and Ti(F)(TPP) in an ~100:1 ratio. EPR examination of the ground crystals under Ar at room temperature shows that **1** is indeed present in low concentration in the lattice of the diamagnetic, probably isostructural **6** (Figure 3a). Upon admission of $O_2$, a new two-line signal grows at lower field ($g = 2.009$), while the resonance of **1** decreases in intensity (Figure 3b). Evacuation of the sample for a few hours restores the signal of **1** almost quantitatively (Figure 3d). Eight such oxygenation-deoxygenation cycles have been performed without any noticeable alteration in the EPR signal of **1**. The fact that the new paramagnetic species obtained under $O_2$ appears at the expense of **1**, and the observation that **1** is recovered upon evacuation of the sample, led to the safe conclusion that the new species is **5**, a dioxygen adduct of **1**. It would seem reasonable to assign to this dioxygen adduct the superoxo titanium(IV) formalism. At 77 K, however, the EPR signal of **5** reveals additional hyperfine structure, presumably from the porphyrin nitrogen nuclei (Figure 3c). Moreover, oxygenation of **1** with a $^{17}O-^{18}O$ mixture enriched to 25.29% $^{17}O$ results only in a small broadening of the EPR signal of **5** at 77 K. These observations indicate a substantial spin density on the porphyrin and only a small spin density on the dioxygen ligand,[15] and they suggest a significant contribution of a peroxo-porphyrin cation radical-titanium(IV) resonance form to the electronic configuration of **5**. Efforts are underway at this time to elucidate further the nature of the dioxygen adduct **5**.

The reactions of Ti(III) complexes with dioxygen have been studied for several years.[16] However, we believe this is the first demonstration that a mononuclear peroxo Ti(IV) complex can be prepared using $O_2$ and low-valent Ti rather than the more obvious $H_2O_2$ and Ti(IV) route. Moreover, this is the first report of a Ti(III) complex which gives a reversible dioxygen adduct. Finally, we note that the existence of two distinct mononuclear dioxygen complexes of a synthetic metalloporphyrin formally differing by one electron is unprecedented, and that it is conceptually reminiscent of cytochrome P-450 oxygenation and subsequent reduction.

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## Detection of Thiobenzoylphenylmethylene by Electron Spin Resonance Spectroscopy

*Sir:*

Ketocarbenes have been implicated in a large variety of reactions involving the thermal and photochemical decom-

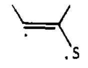
**Table I.** Zero-Field Parameters of Triplet Species

| assigned struct | $D$, cm$^{-1}$ | $E$, cm$^{-1}$ | ref |
|---|---|---|---|
| **1** | 0.3815 | 0.0489 | 6 |
| **2** t-a[a] | 0.617 | 0.053 | 7 |
| t-b | 0.616 | 0.053 | 7 |
| c-a | 0.663 | 0.030 | 7 |
| c-b | 0.661 | 0.031 | 7 |
| **3** | 0.0318 | 0.00105 ± 0.00015 | this work |
| **6a** | 0.1069 | 0.0058 | 17 |
| **6b** | 0.1110 | 0.0069 | 17 |
| **6c** | 0.1217 | 0.0066 | 17 |

[a] a and b denote carbomethoxycarbene and carboethoxycarbene, respectively, t and c denote the two rotameric structures.

position-rearrangement sequence of $\alpha$-diazo ketones, $\alpha$-diazo esters, photolyses of ketenes, oxidation of acetylenes,[1-3] etc., but reports on the direct observation of these elusive intermediates are sparse. According to ab initio type molecular orbital calculations,[4] the parent compound, formylmethylene, has a singlet ground state while semiempirical-type calculations[5] seem to favor a triplet ground state. A decade ago Trozzolo and Fahrenholtz[6] succeeded in stabilizing benzoylphenylmethylene (**1**) from the low-temperature photolysis of azibenzil in organic glasses and identified its triplet ground state by ESR spectroscopy. More recently, Hutton and Roth[7] observed the triplet state spectra of carbalkoxymethylenes (**2**), which indicated the presence of rotameric structures. The ESR spectra of all these carbenes feature large zero-field splitting parameters (Table I).

Thioketocarbenes have also been implicated as reactive intermediates in numerous reactions[8] but thus far have eluded direct detection. Krauss and co-workers[9] investigated the photolysis of some 1,2,3-thiadiazoles (potential precursors of thioketocarbenes) by ESR spectroscopy, but they were able to observe only the characteristic sulfur pattern which they attributed to the thioketocarbene 1,3-biradical



and concluded that the dipole interaction between the two spins is very weak.

We wish to report here the first ESR spectrum of a thioketocarbene, namely, that of thiobenzoylphenylmethylene (**3**), from the 77 K photolysis of 4,5-diphenyl-1,2,3-thiadiazole (**4**) powder with Pyrex-filtered light, and to show that the appearance of the sulfur pattern is the result of secondary photolytic decompositions.

On irradiation the sample turned brown and gave the ESR spectrum shown in Figure 1. The triplet signal is assigned to the randomly oriented triplet ground state of **3**, and the sulfur pattern, to some doublet sulfur radical.[10] In the early stages of the photolysis, only those absorptions attributable to **3** were visible, but on extended photolysis the sulfur pattern intensity increased rapidly, clearly indicating that its carrier is formed in the secondary photolysis of either **3** or some other species present. In fact, substituted thiirenes, which also may be present, are known to extrude sulfur with formation of acetylene, as well as rearrange to thioketenes, upon photolysis.[11] The secondary origin of the sulfur pattern was further confirmed by experiments using Vycor-filtered light, in which case the sulfur pattern intensity markedly increased. Both the triplet and doublet spectra were stable for hours at 77 K, but the former faded irreversibly in a few minutes at 100 K. The decay follows good first-order kinetics (Figure 2), which led to a linear Arrhenius plot (Figure 3), giving an activation energy of 5.4 kcal/mol and an $A$ factor of $1.2 \times 10^9$ s$^{-1}$ in the temperature range 77–105.5 K. Upon warming to room temperature, all ESR signals disappeared and the color of the sample changed to violet. The IR spectrum in Nujol featured a distinctive absorption at 1728 cm$^{-1}$ which is characteristic for thioketenes[12] and is assigned to diphenylthioketene (**5**) probably formed in part by the Wolff rearrangement of **3**. Thus, the following reactions seem to take place:[13]

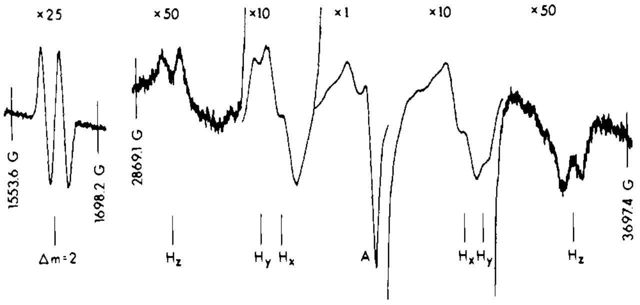


**Figure 1.** ESR spectrum of the $\Delta m = 1$ ($H_x$, $H_y$, $H_z$) and $\Delta m = 2$ transitions of the triplet thiobenzoylphenylmethylene and the doublet sulfur radical exhibiting the sulfur pattern (A) generated in the photolysis of 4,5-diphenyl-1,2,3-thiadiazole at 77 K (klystron frequency 9.168 GHz).

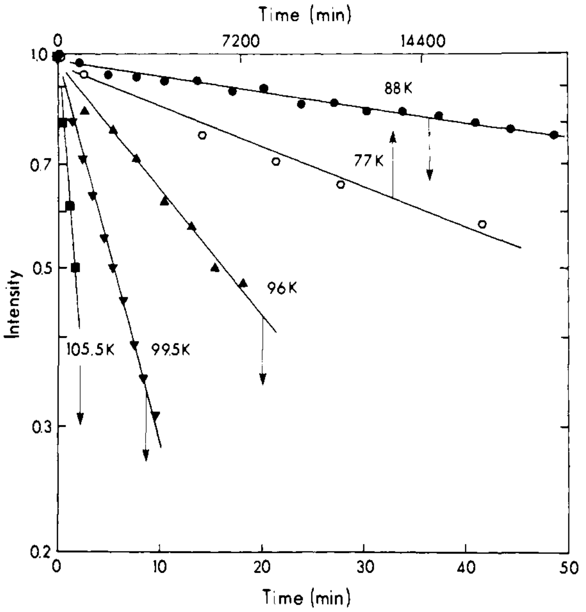
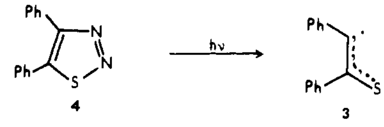


**Figure 2.** Signal intensity of the $\Delta m = 2$ transition of thiobenzoylphenylmethylene vs. time.



$$3(S_1) \xrightarrow[\text{crossing}]{\text{intersystem}} 3(T_0)$$

$$3(T_0) + h\nu \rightarrow \text{doublet radical}$$

$$3(T_0) \xrightarrow{\Delta} \underset{\mathbf{5}}{Ph_2C{=}C{=}S}\ (S_0) \text{ or products}$$

Although the triplet spectrum has been assigned to $3(T_0)$, thermally populated $3(T_1)$ as carrier cannot a priori be discounted on the basis of the present data. However, the known chemistry of 4,5-diphenyl-1,2,3-thiadiazole is best rationalized in terms of a ground-state triplet thioketocarbene intermediate.[14]

The values of the zero-field parameters for $3(T_0)$ derived[15] from the spectrum are listed in Table I along with those re-

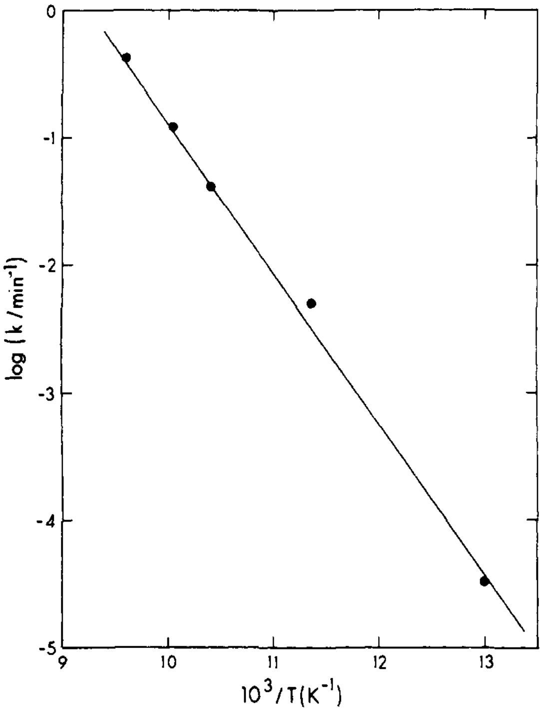
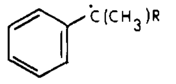


**Figure 3.** Arrhenius plot of the first-order rate constant for thiobenzoylphenylmethylene decay.

ported for similar species. The outside lines of the spectrum featuring a hyperfine structure are due to the $Z$ component of the $\Delta m = 1$ transition, and the inside lines are composed of the superimposed $X$ and $Y$ components having a hyperfine structure. The $\Delta m = 2$ transition is also clearly recognizable. The hyperfine splittings (hfs) observed were between 20 and 29 G for the $\Delta m = 1$ and 31 G for the $\Delta m = 2$ transitions. This rather isotropic hfs is probably due to a proton on one of the phenyl rings lying in close proximity to one of the half-filled orbitals.

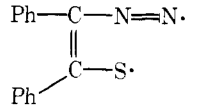
From the value of $D$, the magnetic dipole interaction between the two spins seems to be weak. This implies that one of them is largely localized in the $\sigma$ orbital of the carbene carbon and the other is highly populated in the $\pi$ orbital of sulfur. The average separation of the spins is computed to be 4.3 Å, in terms of a point-dipole approximation, somewhat longer than the distance between the corresponding atoms. This may be interpreted as follows. If the principal axes of $3(T_0)$ are close to those of triplet ketocarbenes,[7] the sulfur atom lies almost on the $Z$ axis. Therefore, the high $\pi$ spin density on sulfur contributes negatively and the $\pi$ spin density on the carbene carbon positively to $D$, offsetting each other. Consequently, the C-C and C-S bond distances may be close to the double and single bond values, respectively, as computed from ab initio type MO calculations for the parent compound, thioformylmethylene.[16] A similar situation appears to prevail for the intermediates



**6a**, R = CN
**b**, R = $COCH_3$
**c**, R = $OCH_3$

formed in the photolysis of 3$H$-indazoles.[17]

The choice for alternative structures as the carrier of the triplet spectrum is quite limited. One may envisage a nitrogen-containing diradical such as



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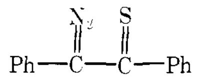
having small $D$ and $E$ values, as a possible candidate. However, the ground state of this species would be the diazo thioketone


$$\mathrm{Ph-\overset{N_2}{\overset{\|}{C}}-\overset{S}{\overset{\|}{C}}-Ph}$$

and the reason why this should be a triplet is not at all apparent. Moreover, the spectrum of a nitrogen radical should show a hyperfine splitting caused by the terminal nitrogen, $I = 1$, which is not observed, and, furthermore, the doublet splitting present is more consistent with a proton interaction. Finally, the observed relative high photostability of the carrier even at $\lambda \geq 210$ nm appears to favor **3** over **7**.

The assignment of the triplet spectrum to **3** is also in full accord with the results of earlier MO computations[16] on thioformylmethylene and other possible isomers of $C_2H_2S$ (thioketene, thiirene, ethynyl and vinylidene thiols, and thiiranylidene) according to which only the thioketocarbene structure is predicted to have a triplet ground state and that this triplet is the lowest lying one in the entire triplet energy manifold.

4,5-Diphenyl-1,2,3-thiadiazole (**4**) was prepared according to Hurd and Mori,[18] and the ESR spectra were recorded with a Bruker ER-420 system spectrometer equipped with 100-kHz modulation in which the magnetic field was controlled by a Varian Fielddial V-FR 2503 and monitored by an Alpha digital NMR gaussmeter, Model 3093. The microwave frequency was determined with a Hewlett-Packard Model X532B frequency meter.

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## Insertion of Beryllium into a Boron–Boron Bond. The Synthesis of $\mu$-[$\eta^5$-Cyclopentadienylberylla]octahydropentaborate, $\mu\text{-}[\eta^5\text{-}(C_5H_5)Be]B_5H_8$

*Sir:*

We report here the synthesis and structural characterization of $\mu\text{-}[\eta^5\text{-}(C_5H_5)Be]B_5H_8$, which is an unusually good example of the very different bonding of the $\eta^5\text{-}(C_5H_5)Be$ moiety to different borane groupings. In the recently reported $2\text{-}[\eta^5\text{-}(C_5H_5)]\text{-}2\text{-}BeB_5H_{10}$[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 $\eta^5\text{-}(C_5H_5)Be$ moiety resides in a nonvertex bridging position ($\mu$) between two adjacent basal boron atoms in a square-pyramidal framework. Other known $\mu\text{-}(X_nM)B_5H_8$ compounds, such as $\mu\text{-}[Cl(PPh_3)Cd]B_5H_8$[2] and $\mu\text{-}[(PPh_3)_2Cu]B_5H_8$[3,4] have not been shown to form the corresponding $2\text{-}(X_n)\text{-}2\text{-}MB_5H_{10}$ analogues, nor has the direct conversion of $\mu\text{-}[\eta^5\text{-}(C_5H_5)Be]B_5H_8$ to $2\text{-}[\eta^5\text{-}(C_5H_5)]\text{-}2\text{-}BeB_5H_{10}$ 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 $\mu\text{-}[\eta^5\text{-}(C_5H_5)Be]B_5H_8$, 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 $\mu\text{-}[\eta^5\text{-}(C_5H_5)Be]B_5H_8$ 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 $\mu\text{-}[\eta^5\text{-}(C_5H_5)Be]B_5H_8$ consists of three doublets of intensity 2:2:1 at $\delta$ −13.4 ($J$ = 161 Hz), −21.8 ($J$ = 141 Hz) and −54.6 ($J$ = 170 Hz), respectively.[7] ${}^{11}B_{(apex)}\text{-}{}^{11}B_{(base)}$ coupling is observed in both sets of basal boron resonances. The spectrum is appropriate for a $\mu$-substituted $B_5H_9$ derivative, but the chemical shift between the basal boron resonances is quite large. The 270-MHz ${}^{1}H$ FT NMR spectrum contains a sharp singlet at $\delta$ 5.4 ($C_5H_5$); quartets at $\delta$ 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.

A single crystal of $\mu\text{-}[\eta^5\text{-}(C_5H_5)Be]B_5H_8$ 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; $\beta$ = 98.50 (5)°; $Z$ = 4. There were 1709 reflections collected at −100 °C using Mo K$\alpha$ 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.

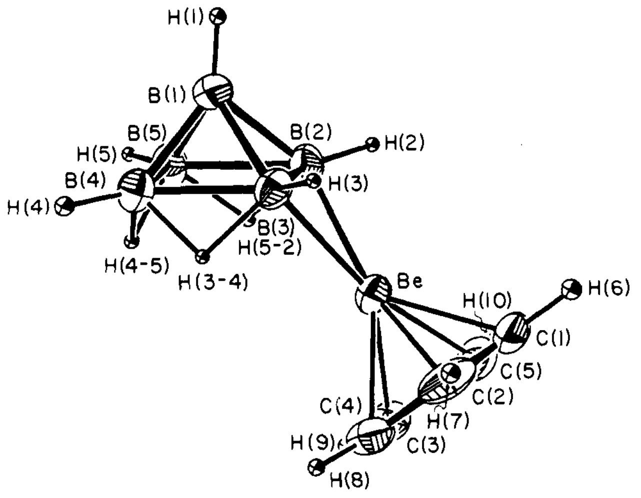

**Figure 1.** An ORTEP drawing of the structure of $\mu\text{-}[\eta^5\text{-}(C_5H_5)Be]B_5H_8$. The atoms are represented as 40% elipsoids with the H atom temperature factors reduced by a factor of 10.

**Table I.** Selected Crystallographic Data for $\mu\text{-}[\eta^5\text{-}(C_5H_5)Be]B_5H_8$

| group | distance, Å |
|---|---|
| $B_a\text{-}B_b{}^c$ | 1.663 (3)–1.705 (3) |
| Be | |
| $B_b\text{-}B_b$ | 1.726 (3)–1.821 (3) |
| $B\text{-}H_{(terminal)}$ | 0.98 (3)–1.10 (2) |
| $B\text{-}H_{(bridge)}$ | 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) |

| $\mu^a$ | 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).

$C_5H_5BeB_5H_8$ 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

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