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Crystal and Molecular Structure of 9-Cyclohexyl-5(7)-(dimethyl sulfide)-*nido*-decaborane(11), $B_{10}H_{11}C_6H_{11}S(CH_3)_2$

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The crystal structure of 9-cyclohexyl-5(7)-(dimethyl sulfide)-*nido*-decaborane(11), $B_{10}H_{11}C_6H_{11}S(CH_3)_2$, has been determined by using single-crystal X-ray diffraction methods. The compound crystallizes in the orthorhombic space group *Pbca* with unit cell dimensions $a = 11.821$ (4) Å, $b = 29.37$ (3) Å, and $c = 9.707$ (4) Å. The observed density of the crystal is 1.0 g cm^{-3}, and for $Z = 8$ molecules/unit cell the calculated density is 1.04 g cm^{-3}. The crystal structure was refined by full-matrix, least-squares calculations to a final R value of 0.058 by using 1200 independent reflections with $I > 3\sigma$. The boron atoms form a *nido*-decaborane framework containing eight terminal hydrogens and three bridging hydrogens at positions B6–B7, B8–B9, and B9–B10. The B–B distances are similar to those in the $B_{10}H_{13}^-$ ion. The dimethyl sufide ligand is attached to the B5 atom with a B–S bond distance of 1.89 (1) Å. The cyclohexyl group is attached to the B9 atom with a B–C bond distance of 1.58 (1) Å. The mean C–C bond distance for the cyclohexyl ring is 1.52 (1) Å, and the mean C–C–C bond angle is 111.6 (4)°.

Introduction

A number of $B_{10}H_{12}^{2-}$ (base) type decaborane derivatives have been prepared[1] and used in the syntheses of various *o*-carboranes.[2] One such *o*-carborane, 1,2-dicarba-*closo*-dodecaborane(12), has been synthesized by reacting bis(dimethyl sulfide)-*arachno*-decaborane(12) with acetylene.[3] The mechanism by which acetylene attaches to the decaborane framework has been studied by reacting bis(dimethyl sulfide)-*arachno*-decaborane(12) with cyclohexene and relating the structural and chemical characteristics of the major product formed to possible reaction intermediates of the mechanism. This is described in the preceding paper.[4] Because the molecular structure of the major product could not be conclusively determined by NMR and IR data, it was decided to perform a single-crystal X-ray structural analysis. The result of this study, reported below, shows the structure of the major product to be that of 9-cyclohexyl-5(7)-(dimethyl sulfide)-*nido*-decaborane(11), $B_{10}H_{11}C_6H_{11}S(CH_3)_2$.

Experimental Section

(a) Preparation and Physical Properties. 9-Cyclohexyl-5(7)-(dimethyl sulfide)-*nido*-decaborane(11), $B_{10}H_{11}C_6H_{11}S(CH_3)_2$, was synthesized and recrystallized following the procedure described in the preceding paper by Tolpin et al.[4] The colorless, needle-shaped crystals were washed with cold hexane and dried in vacuo before use. The density, measured by flotation using distilled water at 21 °C, was very close to 1.0 g cm^{-3}. Physical and spectral data and the chemical analysis have been reported for the compound.[4]

(b) X-ray Data Collection. A transparent, well-formed crystal was mounted on the end of a glass fiber with epoxy cement, placed on an *xyz* goniometer, and optically centered on a Syntex P2$_1$ diffractometer equipped with a molybdenum tube ($\lambda(K\alpha) = 0.71069$ Å) and a graphite monochromator. Preliminary unit cell parameters were obtained from nine centered reflections of the crystal. A short data set was collected, and thirteen reflections of relatively strong intensity were selected to recenter the crystal and to obtain improved unit cell parameters. Systematic absences were found for $0kl$ with $k = 2n + 1$, $h0l$ with $l = 2n + 1$, and $hk0$ with $h = 2n + 1$ indicating the space group *Pbca* (ref 5, space group No. 61). The unit cell parameters are given in Table I as part of a summary of data for this study.

The 6538 reflections, including standards, were measured with the Syntex P2$_1$ diffractometer at 21 °C over a 2θ range of 0–50°. Of the reflections measured, 2972 were unique and 1200 were unique with $I > 3\sigma$. Two standard reflections were measured beginning every 100 reflections to monitor experimental consistency. For both reflections, there was no observable decay. An absorption correction was not applied for the crystal of of size 0.69 × 0.16 × 0.27 mm^3 with an absorption coefficient (μ) of 1.59 cm^{-1} for Mo ($K\alpha$) radiation.

Table I. Summary of Crystal Data for $B_{10}H_{11}C_6H_{11}S(CH_3)_2$

fw	264.5
D_M at 21 °C	1.0 g cm^{-3}
D_x, calcd density	1.04 g cm^{-3}
Z, formula units/unit cell	8
cryst size	0.69 × 0.16 × 0.27 mm^3
a	11.821 (4) Å
b	29.37 (3) Å
c	9.707 (4) Å
V	3370 Å^3
temp of data collection	21 °C
wavelength of Mo Kα radiation	0.710 69 Å
scan range	2.0–2.1°
scan rate	2.02–29.3° min^{-1}
ratio of total bkgd/scan time	0.5
max 2θ	50.0°
no. of reflctns measd	6538
no. of unique reflctns	2972
no. of unique reflctns with $I > 3\sigma$	1200
std and % decay	$2\bar{2}0$ and $13\bar{4}$; no observable decay

(c) Structure Determination. The x, y, and z coordinates for the one sulfur atom were deduced from the three highest peaks of a three-dimensional Patterson map at (0.6718, $^1/_2$, 0), (0, 0.3971, $^1/_2$), and ($^1/_2$, 0, 0.5819), respectively. The phases calculated for the sulfur atom allowed successive location of the positions of all 18 nonhydrogen atoms by iterative least-squares and Fourier calculations. The atoms were easily labeled once the cyclohexyl ligand and the *nido*-decaborane framework were identified. The sulfur atom was assigned an isotropic temperature factor of 2.5 Å^2, the eight carbon and ten boron atoms were assigned isotropic temperature factors of 4.0 Å^2, and all parameters were refined by repetitive cycles of full-matrix least-squares calculations. Using anisotropic thermal parameters for the heavier atoms, successive full-matrix least-squares refinement and difference Fourier calculations revealed the positions of all 28 hydrogen atoms. For the final cycles of full-matrix least-squares refinement calculations, the sulfur, carbon, and boron atoms were refined with anisotropic thermal parameters and the hydrogen atoms were taken to move isotropically. The final unweighted value of $R = \sum||F_o| - |F_c||/\sum|F_o|$ was 0.058 and $R_w = \sum[w(|F_o - F_c|)^2/w|F_o|^2]^{1/2}$ had a value of 0.066, weights being taken as $w = 1/\sigma^2(I)$. The scattering factors for sulfur and carbon were taken from Cromer and Mann,[6] those for hydrogen from Stewart et al.,[7] and those for boron from ref 8. Final positional parameters for $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ are listed in Table II and final

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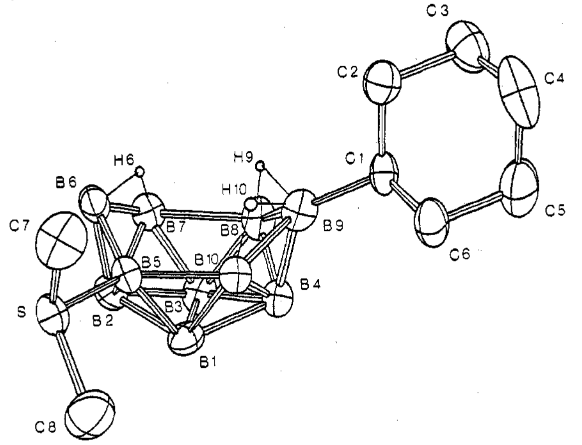

Figure 1. ORTEP drawing of $B_{10}H_{11}C_6H_{11}S(CH_3)_2$. All hydrogen atoms except bridge hydrogens have been omitted.

thermal parameters in Table III. Atomic labels correspond to those in Figure 1. All calculations with the exception of the calculations of the final values of $|F_o|$ and $|F_c|$ were performed by using the program X-RAY 72.[9] The final values of $|F_o|$ and $|F_c|$ were calculated by using the program X-RAY 76.[10]

Discussion

The molecular structure of $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ is shown in Figure 1 and is proved to be 9-cyclohexyl-5(7)-(dimethyl sulfide)-*nido*-decaborane(11), thus providing the unequivocal basis for the interpretation of the NMR spectra reported in the preceding paper.[4] The most important interatomic distances and angles are listed in Tables IV and V. A table listing all B–B–B angles in the decaborane framework is available.[11] The labeling of the heavier atoms and of the three bridge hydrogens is shown in Figure 1. The labels of the remaining hydrogens follow from Table V.

The ten boron atoms form a *nido*-decaborane framework similar to that of decaborane(14) but distorted as a result of the absence of the symmetry that decaborane(14) has. This lack of symmetry in turn is imposed by the odd number of bridge hydrogens on the open face, by the bonding of the cyclohexyl group to B9, and by the bonding of the dimethyl sulfide to B5. In fact, the individual boron–boron distances in the framework are comparable to those in the $B_{10}H_{13}^-$ ion[12] rather than to the distances in $B_{10}H_{14}$,[13] as shown in Table IV, where some of the values for $B_{10}H_{13}^-$ and $B_{10}H_{14}$ are listed for comparison. The similarity of the *nido*-decaborane framework found here to that of $B_{10}H_{13}^-$ is understandable since both have three hydrogen bridges on the open face, viz., between B6 and B7, B8 and B9, and B9 and B10. In the present structure determination these three bridge hydrogens were located unambiguously in the course of the refinement. There are two immediate results of this arrangement of hydrogen bridges: (1) The bond length B5–B6 is 1.64 Å in the present structure and 1.65 Å in $B_{10}H_{13}^-$, with no hydrogen bridge across the bond. In contrast the same bond length in $B_{10}H_{14}$, where the hydrogen bridge is present, is 1.79 Å. (2) There is a difference of 0.19 Å in the bond lengths of B5–B10 (1.84 Å) and B7–B8 (2.03 Å). In the $B_{10}H_{13}^-$ ion this difference is 0.18 Å. In $B_{10}H_{14}$ on the other hand the two bond lengths are identical (1.99 Å) as dictated by the symmetry of the molecule. If one accepts the calculated atomic charges presented in Figure 6 of the preceding paper[4] to be at least approximately correct, then this difference in bond length can be understood from the values and signs of these charges: B5 (charge −0.17) and B10 (charge +0.15) would attract each other, resulting in a relatively short bond, while B7 (charge +0.23) and B8 (charge +0.27) repel each other, resulting in a relatively long bond.

Table II. Atomic Coordinates for $B_{10}H_{11}C_6H_{11}S(CH_3)_2$[a]

atom	*x*	*y*	*z*
S	0.4170 (1)	0.5521 (1)	0.0208 (2)
C1	0.2968 (5)	0.7052 (2)	0.6085 (6)
C2	0.3517 (6)	0.7403 (2)	0.7048 (6)
C3	0.3105 (8)	0.7885 (2)	0.6719 (8)
C4	0.1831 (9)	0.7916 (2)	0.6736 (8)
C5	0.1289 (6)	0.7575 (2)	0.5766 (7)
C6	0.1679 (6)	0.7090 (2)	0.6085 (7)
C7	0.2992 (6)	0.5786 (2)	0.1049 (7)
C8	0.5336 (6)	0.5828 (3)	0.0952 (8)
B1	0.5151 (6)	0.5904 (2)	0.7442 (8)
B2	0.4560 (6)	0.5371 (2)	0.7007 (7)
B3	0.4850 (6)	0.5774 (2)	0.5690 (7)
B4	0.4790 (6)	0.6358 (2)	0.6267 (7)
B5	0.3991 (6)	0.5710 (2)	0.8357 (6)
B6	0.3115 (6)	0.5395 (2)	0.7459 (8)
B7	0.3547 (6)	0.5472 (2)	0.5705 (7)
B8	0.3765 (6)	0.6130 (2)	0.5114 (7)
B9	0.3422 (6)	0.6556 (2)	0.6383 (7)
B10	0.4073 (6)	0.6318 (2)	0.7920 (6)
H1	0.600 (4)	0.596 (1)	0.788 (5)
H2	0.508 (4)	0.508 (1)	0.712 (5)
H3	0.551 (4)	0.569 (1)	0.494 (5)
H4	0.546 (5)	0.661 (2)	0.597 (6)
H5	0.252 (5)	0.514 (1)	0.778 (5)
H6	0.277 (4)	0.558 (2)	0.645 (5)
H7	0.320 (4)	0.526 (2)	0.482 (6)
H8	0.372 (5)	0.626 (2)	0.399 (7)
H9	0.286 (4)	0.626 (2)	0.577 (5)
H10	0.312 (5)	0.640 (2)	0.753 (7)
H11	0.420 (3)	0.656 (1)	0.872 (4)
H12	0.328 (4)	0.712 (1)	0.519 (5)
H13	0.331 (4)	0.736 (2)	0.796 (5)
H14	0.445 (6)	0.734 (2)	0.707 (8)
H15	0.338 (4)	0.799 (2)	0.579 (6)
H16	0.355 (5)	0.807 (2)	0.737 (6)
H17	0.154 (6)	0.789 (2)	0.767 (8)
H18	0.159 (5)	0.818 (2)	0.657 (6)
H19	0.150 (4)	0.766 (2)	0.484 (6)
H20	0.042 (4)	0.761 (2)	0.584 (6)
H21	0.139 (5)	0.701 (2)	0.696 (6)
H22	0.134 (5)	0.687 (2)	0.538 (7)
H23	0.229 (5)	0.564 (2)	0.066 (6)
H24	0.303 (5)	0.573 (2)	0.196 (7)
H25	0.301 (5)	0.614 (2)	0.084 (6)
H26	0.529 (6)	0.621 (2)	0.078 (8)
H27	0.532 (6)	0.582 (2)	0.175 (8)
H28	0.599 (7)	0.576 (3)	0.055 (9)

[a] Standard deviations in parentheses.

In addition to the three bridging hydrogen atoms there are eight terminal hydrogen atoms in the framework, viz., on B1–4, B6–8, and B10. The mean value of the B–H bond length for terminal hydrogens is 1.10 (3) Å; for bridging hydrogens it is 1.25 (5) Å. Within the standard deviations the bridging hydrogen atoms are located equidistantly between the boron atom pair, and the mean B–H–B angle is 94 (2)°.

The *cyclohexyl group* is attached to B9 with a B–C bond length of 1.58 (1) Å, which can be compared with 1.56 Å in compounds such as $(CH_3)_3B$, $(CH_3)_2BF$, and CH_3BF_2.[14] The cyclohexyl ring has the chair conformation with mean car-

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Table III. Thermal Parameters for $B_{10}H_{11}C_6H_{11}S(CH_3)_2$[a]

(a) Anisotropic Temperature Factors

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	5.6 (1)	3.8 (1)	3.4 (1)	0.6 (1)	−0.2 (1)	0.6 (1)
C1	5.6 (4)	3.0 (3)	3.0 (3)	0.0 (3)	0.5 (3)	0.4 (3)
C2	7.8 (5)	3.4 (4)	4.2 (4)	−0.2 (3)	−1.1 (4)	−0.2 (3)
C3	10.2 (7)	3.9 (4)	6.2 (5)	−1.1 (5)	−1.7 (5)	−0.1 (4)
C4	14.1 (9)	4.4 (4)	5.6 (5)	3.5 (5)	1.4 (6)	0.9 (4)
C5	7.2 (5)	5.6 (4)	5.3 (4)	1.5 (4)	0.9 (4)	1.7 (4)
C6	4.7 (4)	4.8 (4)	5.9 (5)	−0.2 (3)	0.4 (4)	1.8 (3)
C7	7.4 (5)	6.6 (5)	4.4 (4)	−0.6 (4)	1.6 (4)	−0.9 (4)
C8	6.8 (5)	9.9 (6)	5.5 (5)	−2.6 (5)	−1.9 (4)	1.5 (5)
B1	3.1 (4)	4.3 (4)	4.5 (4)	−0.0 (3)	0.3 (4)	−0.1 (4)
B2	4.5 (4)	3.8 (4)	4.0 (4)	1.2 (3)	−0.1 (3)	−0.1 (3)
B3	4.3 (4)	3.8 (4)	4.2 (4)	0.0 (3)	1.5 (4)	−0.4 (3)
B4	4.3 (4)	3.2 (4)	3.8 (4)	−0.0 (3)	0.5 (4)	0.0 (3)
B5	4.5 (5)	2.8 (3)	3.2 (3)	0.7 (3)	0.1 (3)	0.3 (3)
B6	4.5 (4)	2.8 (3)	4.3 (4)	0.2 (3)	−0.7 (4)	0.4 (3)
B7	5.3 (5)	3.3 (3)	4.0 (4)	0.7 (3)	0.3 (3)	−0.9 (3)
B8	6.3 (5)	4.1 (4)	3.6 (4)	−0.3 (3)	0.2 (4)	−0.6 (3)
B9	5.6 (5)	3.9 (4)	2.6 (4)	−1.0 (4)	−0.2 (4)	−0.2 (3)
B10	4.2 (4)	3.3 (3)	3.2 (3)	0.1 (3)	0.3 (4)	−0.4 (3)

(b) Isotropic Temperature Factors (Å²)

atom	U	atom	U	atom	U	atom	U
H1	3.5 (1.4)	H8	8.2 (2.3)	H15	4.4 (1.7)	H22	7.5 (2.1)
H2	2.8 (1.3)	H9	4.6 (1.6)	H16	5.2 (1.7)	H23	8.1 (2.1)
H3	3.9 (1.4)	H10	7.0 (2.0)	H17	9.1 (2.3)	H24	7.9 (2.2)
H4	5.8 (1.7)	H11	1.3 (1.0)	H18	5.5 (1.9)	H25	6.3 (1.8)
H5	3.7 (1.5)	H12	2.8 (1.3)	H19	5.4 (1.6)	H26	13.8 (2.6)
H6	4.2 (1.4)	H13	3.5 (1.5)	H20	5.3 (1.8)	H27	6.0 (2.7)
H7	4.5 (1.6)	H14	11.5 (2.8)	H21	6.0 (2.0)	H28	10.8 (3.1)

[a] The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. U_{ij} and U values have been multiplied by 10^2. Standard deviations are in parentheses.

Table IV. Boron-Boron Interatomic Distances (Å)

	$B_{10}H_{11}C_6H_{11}S(CH_3)_2$	$B_{10}H_{13}^-$ [a]	$B_{10}H_{14}$ [b]
B1-B2	1.77 (1)		1.79
B1-B3	1.78 (1)		1.78
B1-B4	1.80 (1)		1.78
B1-B5	1.73 (1)		1.75
B1-B10	1.82 (1)		1.75
B2-B3	1.78 (1)		1.78
B2-B5	1.78 (1)		1.79
B2-B6	1.77 (1)		1.73
B2-B7	1.77 (1)		1.79
B3-B4	1.81 (1)		1.79
B3-B7	1.78 (1)		1.75
B3-B8	1.75 (1)		1.75
B4-B8	1.78 (1)		1.79
B4-B9	1.72 (1)		1.73
B4-B10	1.82 (1)		1.79
B5-B6	1.64 (1)	1.65	1.79
B5-B10	1.84 (1)	1.86	1.99
B6-B7	1.79 (1)		1.78
B7-B8	2.03 (1)	2.04	1.99
B8-B9	1.80 (1)		1.79
B9-B10	1.82 (1)		1.78

[a] Reference 12. [b] Reference 13.

Table V. Selected Interatomic Distances (Å) and Angles (Deg) of $B_{10}H_{11}C_6H_{11}S(CH_3)_2$

(a) Interatomic Distances (Å)

S-C7	1.791 (7)	C7-H23	1.01 (6)
S-C8	1.797 (8)	C7-H24	0.90 (6)
S-B5	1.892 (6)	C7-H25	1.05 (5)
C1-C2	1.54 (1)	C8-H26	1.14 (7)
C1-C6	1.53 (1)	C8-H27	0.77 (7)
C1-B9	1.58 (1)	C8-H28	0.89 (8)
C1-H12	0.96 (5)	B1-H1	1.10 (5)
C2-C3	1.53 (1)	B2-H2	1.06 (5)
C2-H13	0.93 (5)	B3-H3	1.09 (5)
C2-H14	1.12 (7)	B4-H4	1.12 (5)
C3-C4	1.51 (1)	B6-H5	1.07 (5)
C3-H15	1.00 (5)	B6-H6	1.19 (5)
C3-H16	0.98 (6)	B7-H6	1.21 (5)
C4-C5	1.52 (1)	B7-H7	1.14 (5)
C4-H17	0.98 (7)	B8-H8	1.16 (7)
C4-H18	0.84 (5)	B8-H9	1.30 (5)
C5-C6	1.53 (1)	B9-H9	1.24 (5)
C5-H19	0.97 (6)	B9-H10	1.26 (7)
C5-H20	1.03 (5)	B10-H10	1.21 (6)
C6-H21	0.94 (6)	B10-H11	1.07 (4)
C6-H22	1.03 (6)		

(b) Interatomic Angles (Deg)

C7-S-C8	101.3 (3)	C2-C3-C4	111.9 (6)
B5-S-C7	102.6 (3)	C3-C4-C5	112.0 (6)
B5-S-C8	108.7 (3)	C4-C5-C6	111.3 (6)
S-B5-B1	119.7 (5)	C5-C6-C1	111.7 (5)
S-B5-B2	119.5 (4)	C1-B9-B4	128.3 (5)
S-B5-B6	114.2 (4)	C1-B9-B8	126.3 (5)
S-B5-B10	119.9 (4)	C1-B9-B10	130.4 (5)
B9-C1-C2	111.4 (5)	B6-H6-B7	96 (3)
B9-C1-C6	114.1 (5)	B8-H9-B9	90 (3)
C6-C1-C2	111.8 (5)	B9-H10-B10	95 (4)
C1-C2-C3	111.1 (5)		

bon–carbon distance of 1.52 (1) Å and mean C–C–C angle of 111.6 (4)°. These values are in excellent agreement with those found for free cyclohexane,[15] viz., 1.523 Å and 111.34°.

Since the compound was prepared by the reaction of $B_{10}H_{12}[S(CH_3)_2]_2$ and cyclohexene and since there clearly is no double bond in the cyclohexyl ring after formation of the product, it follows that the reaction is indeed a hydroboration which occurs by addition of the BH at position 9 across the double bond of the cyclohexene, once the dimethyl sulfide in the 9-position is removed. The reaction is in complete analogy to the hydroboration of alkenes and alkynes by *nido*-6-SB_9H_{11}.[16]

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The geometry of the *dimethyl sulfide group*, bonded to B5, is entirely normal. The bond lengths B–S = 1.89 (1) Å and S–C(mean) = 1.79 (1) Å and the angle C–S–C = 101.3 (3)° are within three standard deviations of the values of 1.92 (1) Å, 1.82 Å, and 102.4 (14)° found in $B_{10}H_{12}[S(CH_3)_2]_2$.[17] The unusual feature of the dimethyl sulfide group is of course that, while it was originally attached to B6, it has "migrated" to B5 during the course of the reaction. In view of the arguments discussed in the previous paper it is likely that this "migration" occurs after the hydroboration has taken place (Scheme I, ref 4). It is clearly accompanied by a complicated rearrangement of the hydrogen atoms in the boron cage. The starting substance bis(dimethyl sulfide)-*arachno*-decaborane(12) has terminal hydrogens on each boron atom and two hydrogen bridges, viz., across B5–B10 and B7–B8.[17] One of a number of possible pathways from this starting molecule to the end product is the following: the dimethyl sulfide group at B9 leaves, and the hydrogen atoms in the bridges B7–B8 and B5–B10 move to form bridges across B8–B9 and B9–B10, thus generating the same configuration that undergoes hydroboration in $6\text{-}SB_9H_{11}$.[16] The hydroboration takes place with the cyclohexyl group attaching to B9, and a reactive intermediate now exists which has a dimethyl sulfide attached to B6. When a dimethyl sulfide molecule in the solution approaches this intermediate toward B5 (or B7), the $(CH_3)_2S$ at B6 leaves, the terminal hydrogen atom of B5 moves to B6, the hydrogen atom on B6 forms the B6–B7 bridge, and the approaching $(CH_3)_2S$ attaches at B5. It would require extended Hückel calculations of several possible intermediate molecular configurations to decide which particular pathway is the most likely one on a theoretical basis.

It is worth noting that the individual molecules in the structure presented here have a molecular asymmetry; i.e., they can occur in a Δ or in a Λ configuration.[18] In this structure the unit cell contains four Δ and four Λ molecules. It is difficult to explain why the structure prefers that arrangement to one which would contain all Δ or all Λ molecules, since this depends on intermolecular interactions in the two possible cases. A survey of hydrogen–hydrogen contacts in the present structure reveals one very short distance of 2.18 Å between H3 of one molecule and H23 of its neighbor. There are no further short contacts less than 2.45 Å, and there are fourteen neighboring H–H contacts between 2.45 and 2.67 Å.

Registry No. 9-Cyclohexyl-5(7)-(dimethyl sulfide)-*nido*-decacarborane(11), 72765-44-7.

Supplementary Material Available: Tables of the observed and calculated structure factors and of the B–B–B angles in the boron framework (13 pages). Ordering information is given on any current masthead page.

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Copper–Amine–Carbonyl Chemistry. Solution and Solid-State Studies of the Copper(I)–Ethylenediamine–Carbon Monoxide System: Synthesis and X-ray Structures of Mononuclear and Binuclear Copper(I)–Carbonyl Complexes

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Copper(I) iodide in methanol absorbs carbon monoxide at room temperature and atmospheric pressure in the presence of ethylenediamine, en, giving colorless solutions. Depending on the Cu^I/en molar ratio and the anion present, the following thermally stable copper(I) carbonyls have been isolated as white crystals: $[Cu(en)_2(CO)]I$ (I) [ν_{CO}(Nujol) 2060 cm^{-1}]; $[Cu_2(en)_3(CO)_2]I_2$ (II) [ν_{CO}(Nujol) 2062 cm^{-1}]; $[Cu_2(en)_3(CO)_2](PPh_4)_2$ (III) [ν_{CO}(Nujol) 2078 cm^{-1}]. The structure of III consists of discrete dimeric cations $[Cu_2(en)_3(CO)_2]^{2+}$ and BPh_4^- anions. The two centrosymmetric copper atoms are surrounded in a pseudotetrahedral geometry by a set of three nitrogen atoms, provided by one chelating and one bridging en, and a carbon monoxide molecule. The bond distances associated with the Cu–C–O units are Cu–C = 1.73 (1) and 1.75 (1) Å and C–O = 1.17 (2) and 1.16 (2) Å. The addition of $NaBPh_4$ to a methanolic solution of Cu(en)COCl (IV) gives at −20 °C white crystals of $[Cu(en)(CO)PhBPh_3]$ (V) [ν_{CO}(Nujol) 2117 cm^{-1}]. The ion-pair nature of V was established by an X-ray analysis. Copper(I) interacts with both a carbon monoxide molecule and one of the C═C bonds of the BPh_4^- anion, in a pseudo-trigonal-pyramidal geometry completed by an ethylenediamine molecule. The Cu–C and C–O bond distances are 1.806 (6) and 1.110 (7) Å, respectively. Crystallographic details for III are as follows: space group $P2_1/n$ (monoclinic), a = 13.769 (2) Å, b = 19.184 (3) Å, c = 9.833 (2) Å, β = 90.99 (2)°, V = 2596.9 $Å^3$, Z = 2. The final R factor was 4.7% for 3088 observed reflections. Crystallographic details for V are as follows: space group $P2_1/c$ (monoclinic), a = 10.301 (1) Å, b = 12.234 (1) Å, c = 18.390 (2) Å, β = 91.11 (1)°, V = 2317.1 $Å^3$, Z = 4. The final R factor was 4.9% for 3150 observed reflections.

Introduction

The chemistry of the copper(I)–nitrogen ligand complexes is practically restricted to the compounds containing copper(I) coordinated to unsaturated nitrogen ligands.[1] The stabilization of the (+1) oxidation state for copper should be ascribed to the nature of these nitrogens, while the amino groups stabilize the (+2) oxidation state and promote facile disproportionation of Cu(I).[2] Besides this, the extreme lability of these complexes is the reason for the paucity of structural, reactivity, and mechanistic information on copper(I)–nitrogen ligand chemistry. It must be noticed, however, that, when the (+1) oxidation state is stabilized by unsaturated nitrogen ligands, the metal center is not further available for coordinating π-acid

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