A [1,3]-metallotropic rearrangement involving a pendular movement of the Ph_3P–Pt groups between vicinal nitrogen atoms has been proposed to account for these observations (see Scheme I of ref 10). The Pt dimer, **5b**, exhibits similar fluxional behavior, At −71 °C the ^{31}P NMR spectrum of **5b** exhibits two equally intense signals at +73.8 and +40.2 ppm for the inequivalent Et_2P groups in addition to the signal for the two equivalent Ph_3P ligands at +12.9 ppm [$^1J(^{31}P-^{195}Pt) = 4140$ Hz]. The large value of $^1J(^{195}Pt-^{31}P)$ (ca. 4200 Hz) for the dimers **5a**,**b** compared with the values of ca. 2850 Hz observed for this interaction in the monomers **2a**–**c** is presumably a reflection of the weak trans influence of nitrogen in the dimers compared to sulfur in the monomers.[30–32]

When the temperature of the solution of **5b** is raised, the two signals for Et_2P groups broaden and collapse. However, an accurate coalescence temperature could not be obtained because **5b** cocrystallizes with another product, but it appears to be higher than that of **5a** consistent with stronger Pt–N bonding in **5b** compared to that in **5a**.[28] The ^{31}P NMR spectrum of the other product at −60 °C in CH_2Cl_2 exhibits four equally intense resonances at 62.8, 53.2, 51.6, and 20.9 ppm, which we attribute to *Et_2P* groups, and two singlets at 13.8 and 12.9 ppm with $^1J(^{31}P-^{195}Pt) = 3655$ and 4240 Hz, respectively, which we assigne to *Ph_3P* groups. Thus, the composition of the other product appears to be similar to that of the dimers **5a**,**b**, but it contains four inequivalent heterocyclic phosphorus atoms and two inequivalent, platinum-bound Ph_3P ligands. This product is also fluxional, and further studies are in progress in an attempt to isolate and structurally characterize it.

As indicated in Table II, the ^{31}P NMR spectra of the Pd dimers **6a**, **7a**, and **7b** at room temperature consist of a 1:1 doublet for the PR_2 groups and a 1:2:1 triplet for the PPh_2R' ligands with relative intensities of 2:1. The four-bond $^{31}P-^{31}P$ couplings, which are not observed for the Pt dimers, are in the range 9–15 Hz. In contrast to the Pt dimers, the resonances for the inequivalent PR_2 groups in the Pd dimers could not be resolved into the expected two components even at −90 °C. Thus, it appears that the energy barrier for the 1,3-shift is significantly lower when Pt is replaced by Pd in these dimers.

Conclusion. Zerovalent Pt or Pd complexes react readily with 1,5-diphosphadithiatetrazocines via insertion into the transannular S–S linkage to give mononuclear complexes of the type $M(PPh_2R')_2(1,5\text{-}R_4P_2N_4S_2)$ (M = Pt, Pd; R = Ph, Et, Me; R′ = Ph, Me) for which an η^2-S,S′ bonding mode has been established. These monomers readily lose one PR_3 molecule to give the dimers $[M(PPh_3)(1,5\text{-}R_4P_2N_4S_2)]_2$ in which the heterocyclic ligand exhibits an η^2-S,N-μ,η^1-S′ interaction with the metal centers. Both the Pt and Pd dimers undergo a facile fluxional process that probably involves a [1,3]-metallotropic rearrangement.

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Supplementary Material Available: Listings of crystal data and details of the structure determination, anisotropic thermal parameters, bond distances, bond angles, and torsion angles for non-hydrogen atoms (9 pages); a listing of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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Experimental and Ab-Initio Stability Correlations among Isomeric Methyl Derivatives of *closo*- and *nido*-Monocarbahexaboranes

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The relative stabilities of the various isomeric methyl derivatives of *closo*-1-CB_5H_7 and *nido*-2-CB_5H_9, determined by both experimental and calculational (MP2/6-31G*//3-21G) methods, are compared. Calculational results indicate a 1.5 kcal/mol lowering of the activation energy for bridging hydrogen tautomerization of CB_5H_7 when the terminal hydrogen attached to the cage carbon is replaced by a methyl group; this is in excellent agreement with experimental observations. The calculated equilibrium ratio of 2-CH_3-*closo*-1-CB_5H_6/4-CH_3-*closo*-1-CB_5H_6 is compared to both past and recent experimental results. The relative stabilities of the four CH_3-*nido*-2-CB_5H_8 isomers are correlated to synthetic reaction results as well as with isomer interconversion observations at elevated temperatures; kinetic vs equilibrium conclusions are reached.

Introduction

The structures of *closo*-1-CB_5H_7[1–3] and *nido*-2-CB_5H_9[4] systems have been determined and found to be consistent with those previously proposed from the analyses of NMR data.[5–15] The (near) octahedral structure of *closo*-1-CB_5H_7 has also been examined by various calculational methods, PRDDO,[16] MNDO,[17] AM1 calculations,[18] and ab-initio (with full geometry optimization at the STO-3G level using the Gaussian-80 code)[19] MO calcu-

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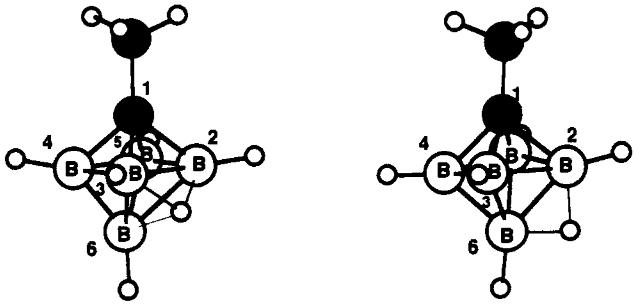

Figure 1. Left: "Stable" structure of the nearly octahedral 1-CH_3-*closo*-1-CB_5H_6 with a bridging hydrogen on a B(2,3,6) face. Right: "Transition-state" structure of 1-CH_3-*closo*-1-CB_5H_6 with a bridging hydrogen along a B(2,6) edge. The two depicted structures are constructed directly from the optimized 3-21G coordinates.

lations, and acceptable agreement is found between these and the experimentally obtained structural results.

The temperature-dependent ^{11}B NMR spectrum[11] of *closo*-1-CB_5H_7 strongly suggests an intramolecular bridging-hydrogen tautomerism at elevated temperatures, the energy barrier for which has been determined to be 14 ± 0.5 kcal/mol.[12] The movement of a bridging hydrogen from an equatorial BB edge, or BBB face, to another such equivalent position (there are a total of four such degenerate positions in the parent compound) very much suggests a routing of the bridging hydrogen across a B(6)–B_{eq} (an equatorial boron (B_{eq}) is defined here as any of the positions 2, 3, 4, or 5) edge. The transition-state structure for this process in the parent *closo*-1-CB_5H_7, and its C-methyl derivative, is reasonably assumed to be that shown in Figure 1,[12,16,20] and the calculated energy barrier for hydrogen tautomerism of this type in the parent *closo*-1-CB_5H_7 is, variously, 19.6 kcal/mol (by the PRDDO method)[16] and 14.8 kcal/mol (ab initio at the MP2/6-31G*//3-21G+ZPE level).[20] The latter value agrees exceptionally well with the experimental result of 14 ± 0.5 kcal/mol.[12] We find that the barrier to bridging hydrogen tautomerism is lowered by 2 ± 0.5 kcal/mol when the cage carbon of *closo*-1-CB_5H_7 is methyl substituted. We wished to test the ability of MO calculations carried out at the MP2/6-31G*//3-21G+ZPE(3-21G) level to postpredict this energy barrier change.

In a study[21] that examined the temperature dependence of the ^{11}B NMR spectrum of a *B*-methyl-*closo*-1-CB_5H_6 mixture there was a suggestion that the equilibrium 2-CH_3-1-CB_5H_6/4-CH_3-1-CB_5H_6 ratio is in the vicinity of ca. 25:75 at room temperature. In the present study, ab-initio calculations suggest the relative stabilities of these *B*-methyl isomers of *closo*-1-CB_5H_7, and these calculated stabilities are compared with those recently, as well as previously, obtained from experimental studies.

The initial report of methyl derivatives of *nido*-2-CB_5H_9 resulted from an analysis of a side product mixture that was isolated in the course of studying the synthesis of *nido*-2,3-$C_2B_4H_8$ from acetylene and pentaborane(9).[6] The 2-, 3-, and 4-CH_3-*nido*-2-CB_5H_8 isomers were identified, but no mention was made of the ratio of isomers that were formed. A viable mechanistic route to these isomers from the reaction of acetylene and pentaborane was supported in a study[22] involving a plausible intermediate,[6] 2-ethenyl-*nido*-B_5H_8; flash thermolysis (355 °C) of the latter compound gave 2-CH_3-*nido*-2-CB_5H_8 (15%), 3-CH_3-*nido*-2-CB_5H_8 (23%), and 4-CH_3-*nido*-2-CB_5H_8 (13%).[22] We have repeated the earlier synthesis of a CH_3-*nido*-2-CB_5H_8 isomer mixture from acetylene/pentaborane under the scrutiny of modern NMR instrumentation in order to better assess the yield of all products in this reaction. Furthermore, we have subjected individual CH_3-*nido*-2-CB_5H_8 isomers to the thermal conditions necessary for their formation, in attempts to determine possible isomer interconversion routes. These results are compared to equilibrium predictions by calculational means.

Experimental Methods and Data

Materials. The parent *closo*-1-CB_5H_7,[23] parent *nido*-2-CB_5H_9,[23] *B*-CH_3-*closo*-2-CB_5H_6,[21] and *B*-CH_3-*nido*-2-CB_5H_8[6] compounds were prepared according to literature procedures.

Nuclear Magnetic Resonance. Boron-11 spectra were recorded on both a Bruker AM-400 instrument at CSULA and a Bruker WM-500 instrument at California Institute of Technology. The ^{11}B chemical shift assignments to individual nuclei of *nido*-2-CB_5H_9, and the pertinent *B*-CH_3-*nido*-2-CB_5H_8 isomers, were previously established,[6,7,10,12] although certain closely spaced resonances were not always completely resolved. The 32.1-MHz ^{11}B NMR spectrum of *closo*-1-CB_5H_7 has been reported,[11,12,23] but no unambiguous evidence was presented for the definitive assignments of the B(2,3) and B(4,5) resonances. The following 128-MHz ^{11}B NMR spectrometric data, and revised assignments, are now presented for *closo*-1-CB_5H_7: Three ^{11}BH doublets are found in an area ratio of 1:2:2, $\delta = +5.17$ (J_{BH} = 170 Hz) for B(6), $\delta = -7.21$ (J_{BH} = 173 Hz) for B(4,5), and $\delta = -16.51$ (J_{BH} = 185 Hz) for B(2,3); the half-width of each individual member of each (doublet) peak is 130, 115, and 85 Hz, respectively, for the three types of resonances. Proton decoupling of these three boron resonances produces three singlets (without the application of resolution enhancement techniques) in the expected ratio of 1:2:2, and each singlet has about the same half-width observed above for the respective undecoupled resonance members. Application of resolution enhancement techniques to the proton-decoupled ^{11}B spectrum shows evidence of a multiplet structure (1:2:3:4:3:2:1 septet, J = ca. 25 Hz) for the lowest field (area 1) resonance assigned to B(6), the half-width of the overall multiplet is ca. 100 Hz; also, there is faint visual evidence of a multiplet structure for the peak at $\delta = -7.21$, J = ca. 25 Hz, and the half-width of the overall multiplet is ca. 100 Hz; for the resonance at $\delta = -16.51$ there is some indication of a doublet structure at the top of the resonance, with an overall half-width of ca. 35 Hz measured for the entire resonance (note: a 1:1:1:1 quartet structure with some degree of quadrupole relaxation may well appear as an ill-defined doublet with the two inner members further apart than the outer adjacent members).[24,25] Very similar results are found for the ^{11}B NMR spectra of *closo*-1-CB_5H_7 taken at 160.464 MHz. Application of [^{11}B–^{11}B 2D]-COSY spectroscopy on a sample of *closo*-1-CB_5H_7 was performed using a procedure described elsewhere.[26] Strong cross peaks were found between the resonances at $\delta = +5.17$ and $\delta = -7.21$; weaker cross peaks were found between the resonances at $\delta = -7.21$ and $\delta = -16.51$; no cross peaks were observed between the resonances at $\delta = +5.17$ and $\delta = -16.51$.

^{11}B NMR Measurements at 128 MHz for the Equilibrated 2- and 4-CH_3-*closo*-1-CB_5H_6 Mixture at Room Temperature. 2-CH_3-1-CB_5H_6. A 1:1 doublet at $\delta = +3.19$ (area 1), assigned to B(6)–H, J(B–H) = 168 Hz, collapses to a somewhat broad singlet, which, upon the application of resolution enhancement, becomes a well-defined 1:2:3:4:3:2:1 septet, $J(B_6,B_{4,5})$ = 24.5 Hz; a singlet at $\delta = -5.27$ assigned to B(2)–CH_3 exhibits only slight evidence of resolution (upon application of proton decoupling and resolution enhancement techniques) into a partially quadrupole-relaxed quartet[24,25] with the two inner members barely, but distinctly, visible; the half-width of the entire resonance is ca. 55 Hz; a 1:1 doublet at δ −8.2, J(BH) = ca. 170 Hz, is observed for B(5) which shows no fine structure upon proton decoupling (the original decoupled resonance has a half-width of ca. 120 Hz; upon the application of resolution enhancement techniques this resonance narrows to ca. 80 Hz). At $\delta = -15.2$ a 1:1 doublet, J(BH) = ca. 170–180 Hz, is assigned to B(4), which becomes a broad singlet (half-width ca. 100 Hz) when proton decoupled and shows no evidence of fine structure even upon the application of resolution enhancement techniques. A 1:1 doublet at $\delta = -17.6$, J(BH) = ca. 185–190 Hz, is assigned to B(3), which shows, with the application of proton decoupling and resonance enhancement techniques, evidence of a (partially) quadrupole-relaxed[24,25] 1:1:1:1 quartet with greater spacing between the inner adjacent members than for the outer adjacent members; the half-width of the entire resonance is ca. 60 Hz.

4-CH_3-1-CB_5H_6. A singlet at $\delta = +1.72$ in the ^{11}B NMR spectrum is assigned to B(4)–CH_3 with only a hint of multiplicity for the resonance when proton decoupled and resolution enhanced (the half-width is ca. 85 Hz); a 1:1 doublet at $\delta = -7.2$, J = ca. 170 Hz, is assigned to B(5); when the latter resonance is proton decoupled, and even when subjected to resolution enhancement techniques, the half-width never becomes nar-

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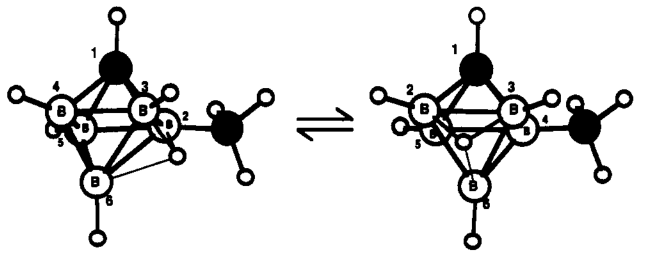

Figure 2. Vibrationally stable structures (at the 3-21G level) of two *B*-methyl derivatives of *closo*-1-CB_5H_7, 2-CH_3-*closo*-1-CB_5H_6, and 4-CH_3-*closo*-1-CB_5H_6. Interconversion is accomplished by simply moving the bridging hydrogen from one B_3 face to another adjacent face. The depicted structures are constructed directly from the optimized 3-21G coordinates. The cage numbering is consistent with the pattern of giving lower numbers to borons bonded to the bridging hydrogen.

rower than ca. 100 Hz, and there is no evidence of fine structure; a 1:1 doublet at $\delta = -18.4$, J(BH) = ca. 180 Hz, is assigned to B(3), which becomes a singlet (half-width ca. 75 Hz) when proton decoupled and shows no evidence of fine structure upon the application of resolution enhancement techniques; a 1:1 doublet at $\delta = -24.1$, J(BH) = 186 Hz, is assigned to B(2) (half-width ca. 65 Hz when proton decoupled) and shows no evidence of fine structure even upon the application of resolution enhancement techniques. The B(6) resonance appears to be hidden underneath the envelope at $\delta = +3.19$ assigned to B(6) of 2-CH_3-1-CB_5H_6 in the equilibrium mixture, and resolution enhancement of this area of the proton-decoupled ^{11}B spectrum does show evidence of a multiplet on the shoulder of the downfield side of the central peak. The relative ratio of the 2- and 4-CH_3-*closo*-1-CB_5H_6 isomers (Figure 2) in the mixture, as determined by the proton-decoupled ^{11}B NMR spectra, is 2.8:1, respectively, at 25 °C.

A proton NMR spectrum of the 2- and 4-CH_3-*closo*-1-CB_5H_6 equilibrium mixture was also examined but was not overly informative; it showed a rather broad bridging hydrogen resonance at $\delta = -3.7$ ppm and a number of broad overlapping H_t–B resonances between 1 and 3 ppm. Two somewhat broad resonances at $\delta = 0.61$ and 0.45 are partially overlapped, but it can be assessed that they are present in the relative area ratio of ca. 3:1, respectively; in light of the present ^{11}B NMR interpretation (vide infra) they are assigned to the methyl groups of 2- and 4-CH_3-*closo*-1-CB_5H_6, respectively.

A very small amount 6-CH_3-*closo*-1-CB_5H_6 appears to be present in the equilibrated mixture of 2- and 4-CH_3-closo-1-CB_5H_6. Only the lowest field resonance can be distinctly observed and is consistent with the data previously reported for this compound.[21,27] Proton-decoupled boron-11 NMR with resolution enhancement, at 25 °C, for 6-CH_3-*closo*-1-CB_5H_6 shows a 1:2:3:4:3:2:1 septet, $J(B_6,B_{4,5}) = 23.7$ Hz, at $\delta = +18.65$ for B(6)–CH_3. Resolution enhancement of this boron resonance, when proton coupled, showed a much more complex multiplet structure. The other resonances of 6-CH_3-*closo*-1-CB_5H_6 are obviously hidden under the much stronger resonances belonging to 2- and 4-CH_3-*closo*-1-CB_5H_6.

Carborane Product Distribution from the Reaction of Acetylene and Pentaborane(9). Two samples were prepared: sample *a* contained B_5H_9 (0.28 mmol, Callery Chemical Co.) and acetylene (1.28 mmol, Matheson) sealed into a 3-mm NMR tube which was previously equipped at one end with a 1.5-mL glass expansion bulb; sample *b* contained B_5H_9 (1.03 mmol) and acetylene (8.10 mmol) sealed into a 100-mL flask. Both were heated simultaneously at 215 °C over a 3-day period followed by 220 °C for 1 day and finally at 225 °C for 3 days. By monitoring of the NMR tube from sample *a*, it was assessed that the first heating period converted only a small portion of the B_5H_9 to products whereas, after the final heating, approximately 85% of the B_5H_9 had disappeared. Some yellow-brown solid material coated the interior of both containers. The volatile portion of sample *b* was then vacuum transferred to a 3-mm NMR tube for analysis. The ^{11}B NMR spectrum of the volatile product mixture from sample *b* indicated that close to 98% of all boron resonances were present as indentifiable cage polyborane substances. The relative quantities (expressed in percentages) found for the cage products, including the starting material, were as follows: B_5H_9 (15.3), *nido*-2,3-$C_2B_4H_8$ (70.8), 3-CH_3-*nido*-2-CB_5H_8 (9.4), 4-CH_3-*nido*-2-CB_5H_8 (2.4), 2-CH_3-nido-2-CB_5H_8 (1.9), 1-CH_3-*nido*-2-CB_5H_8 (0.2). It is pertinent to cite that the ratio of 3-CH_3-*nido*-2-CB_5H_8/4-CH_3-*nido*-2-CB_5H_8 was 3.9:1 at the end of the last heating period and that this ratio was 0.84 at the end of the 215 °C/3-day initial heating period and was 1.6 at the end of the 220 °C/1-day heating period. The ^{11}B NMR chemical shift data for the methyl derivatives of *nido*-2-CB_5H_9 are cited elsewhere in this article; the chemical shifts of additional pertinent materials are as follows: for B_5H_9, $\delta = -52.98$, $J(^{11}B^1H) = 174$ Hz, for B(1), $\delta = -13.19$, $J(^{11}B^1H) = 162$ Hz, for B(2,3,4,5); for *nido*-2,3-$C_2B_4H_8$, $\delta = -52.9$, $J(^{11}B^1H) = 178$ Hz, for B(1), $\delta = -1.30$, $J(^{11}B^1H) = 158$ Hz, $J(^{11}B^1H_\mu) = 47$ Hz, for B(4,6); $\delta = -0.25$, $J(^{11}B^1H)$ = ca. 150 Hz, $J(^{11}B^1H_\mu)$ = ca. 20 Hz, for B(3).

Interconversion Attempts between 3-CH_3-*nido*-2-CB_5H_8 and 4-CH_3-*nido*-2-CB_5H_8. A sample (ca. 0.15 mmol) of 4-CH_3-*nido*-2-CB_5H_8 (93.5% pure, containing 5.3% of the 3-CH_3 isomer and slightly over 1% of unidentified impurities) was heated in a 2-mm capillary NMR tube at 150 °C for 2 h; the NMR spectrum of the sample showed no change over that spectrum recorded of the original mixture. Heating the sample at 175 °C for 1.5 h gave a ratio of 4-CH_3-*nido*-2-CB_5H_8 to 3-CH_3-*nido*-2-CB_5H_8 of 8.32:1.00. Further heating changed this ratio to 3.8:1.0 (after 190 °C for 1 h), 2.54:1.00 (200 °C for 1 h), 1.25:1.00 (220 °C for 1 h), ca. 1.0:1.0 (an additional 2 h at 220 °C), and ca. 0.5:1.0 (an additional 5 h at 220 °C). Beginning at 200 °C the sample began to show signs of decomposition with the formation of a very small quantity of yellow-brown solids on the interior walls.

A sample (ca. 0.1 mmol) of a mixture of 2-CH_3-*nido*-2-CB_5H_8 (53.1%), 3-CH_3-*nido*-2-CB_5H_8 (41.8%), 4-CH_3-*nido*-2-CB_5H_8 (2.5%), and difficult-to-remove impurities (2.6%) was heated in a 2-mm capillary NMR tube at 150 °C for 2 h; the ^{11}B NMR spectrum of the sample did not change significantly from that of the original mixture, i.e. the ratio of *B*-CH_3-*nido*-2-CB_5H_8 isomers was 1.27:1.00:0.06 for *B* = 2, 3, and 4, respectively. After heating of the sample at 175 °C for 1.5 h, the ratio of *B*-CH_3-*nido*-2-CB_5H_8 isomers was measured to be 1.18:1.00:0.09 for *B* = 2, 3, and 4, respectively. Subsequently, after the sample was heated at 200 °C for 1 h, a ratio of 1.31:1.00:0.12, respectively, was found. At 200 °C the sample began to show signs of decomposition with the formation of a small quantity of yellow-brown solids on the interior walls. After heating of the sample at 220 °C for 1 h, the ratio of *B*-CH_3-*nido*-2-CB_5H_8 isomers was 1.47:1.00:0.2; an additional 1 h at 220 °C gave a ratio of 1.74:1.00:0.25; after an additional 5 h at this temperature the ratio was now 2.24:1.00:0.3, respectively.

^{11}B NMR Measurements for All Methyl Derivatives of *nido*-CB_5H_9. 2-CH_3-*nido*-2-CB_5H_8: $\delta = -49.22$, $J(^{11}B^1H) = 165$ Hz, for B(1); $\delta = -4.54$, $J(^{11}B^1H) = 157$ Hz, $J(^{11}B^1H_\mu) = 42$ Hz, for B(4,5); $\delta = +15.39$, $J(^{11}B^1H) = 159$ Hz, $J(^{11}B^1H_\mu) = 41$ Hz, for B(3,6).

3-CH_3-*nido*-2-CB_5H_8: $\delta = -50.15$, $J(^{11}B^1H) = 164$ Hz, for B(1); $\delta = -6.51$, $J(^{11}B^1H) = 159$ Hz, $J(^{11}B^1H_\mu) = 40$ Hz, for B(4 or 5); $\delta = -4.61$, $J(^{11}B^1H) = 158$ Hz, $J(^{11}B^1H_\mu) = 40$ Hz, for B(5 or 4); $\delta = +16.61$, $J(^{11}B^1H) = 164$ Hz, $J(^{11}B^1H_\mu) = 40$ Hz, for B(6); $\delta = +26.42$, $J(^{11}B^1H_\mu) = 36$ Hz, for B(6).

4-CH_3-*nido*-2-CB_5H_8: $\delta = -50.88$, $J(^{11}B^1H) = 159$ Hz, for B(1); $\delta = -3.70$, $J(^{11}B^1H) = 153$ Hz, $J(^{11}B^1H_\mu) = 32$–37 Hz (ill-defined multiplet), for B(5); $\delta = +9.65$, $J(^{11}B^1H_\mu) = 27$ Hz (ill-defined multiplet), for B(4); $\delta = +14.83$, $J(^{11}B^1H) = 160$ Hz, $J(^{11}B^1H_\mu) = 43$ Hz, for B(3 or 6); $\delta = +15.40$, $J(^{11}B^1H) = 161$ Hz, $J(^{11}B^1H_\mu) = 39$ Hz, for B(6 or 3).

1-CH_3-*nido*-2-CB_5H_8: $\delta = -42.4$, for B(1); $\delta = -4.5$, $J(^{11}B^1H)$ = ca. 160 Hz for B(4,5); $\delta = +18.49$, $J(^{11}B^1H) = 160$ Hz, $J(^{11}B^1H_\mu) = 39$ Hz, for B(3,6).

Calculational Methods. All calculations were carried out using the Gaussian 90 codes[28] for the 3-21G optimizations, as well as for the MP2/6-31G*//3-21G single point calculations, and using the Gaussian 88 codes[29] for the 6-31G optimizations and the MP2/6-31G*//6-31G single point calculations. Vibrational frequencies were determined at the 3-21G for all molecules, as well as at the 6-31G level for certain compounds; stationary points in the geometry optimizations are assessed as true minima when no imaginary frequencies are found. Stationary points are saddle points (transition state) when an imaginary frequency is found. Zero-point energy corrections are also derived from the vibrational frequency determinations. It was found that rotation of the methyl group in both the ground- and transition-state structures does not appear to produce significant changes in calculational stability; such rotational changes are considerably less than 0.1 kcal/mol. The energies reported here (Tables I–III) for each methyl isomer are for the methyl conformer

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Table I. Energies of *closo*-1-CB_5H_7 and Its 1-Methyl Derivative

molecule	MP2/6-31G*//3-21G[a]	ZPE (NF)[b]	ΔMP2/6-31G*//3-21G+ZPE[c]
1-CB_5H_7	−165.88258	60.86 (0)	0
1-CB_5H_7 (ts)	−165.85718	59.75 (2)	14.8[d]
1-CH_3-1-CB_5H_6	−205.05298	79.34 (0)	0
1-CH_3-1-CB_5H_6 (ts)	−205.03029	78.34 (2)	13.2
molecule	MP2/6-31G*//6-31G	ZPE (NF)	ΔMP2/6-31G*//6-31G+ZPE
1-CB_5H_7	−165.88247	60.64 (0)	0
1-CB_5H_7 (ts)	−165.85751	59.54 (2)	14.6
1-CH_3-1-CB_5H_6	−205.05289	79.17 (0)	0
1-CH_3-1-CB_5H_6 (ts)	−205.03042	78.18 (2)	13.1

[a] Total energies in hartrees (1 hartree = 627.51 kcal/mol). [b] Zero-point energies in kcal/mol (the number of negative frequencies are given in parentheses) using the 3-21G basis set for the top half of the table and the 6-31G basis set for the bottom half of the table. [c] Energies (kcal/mol) of "transition-state" species relative to related ground-state structures; see row just above. [d] The same value was obtained earlier by McKee.[20]

with the lowest calculated energy. The Gaussian calculations were carried out in, variously, Multiflow-Trace and Elxsi minisupercomputers as well as on a Cray Y-MP8/864 supercomputer. The depicted structures, see figures within, are constructed directly from the optimized coordinates using Molecular Editor on a Mac-IIci.

Results and Discussion

In the present study, two experimentally obtained thermodynamic results for some methyl derivatives of *closo*-1-CB_5H_7 are subjected to MO calculational comparisons. One is the effect of a cage-carbon methyl group on the lowering the barrier of bridging hydrogen tautomerism, and the other is the 2-CH_3-*closo*-1-CB_5H_6/4-CH_3-*closo*-1-CB_5H_6 equilibrium ratio. To better understand these results it is considered best to initially discuss certain structural aspects of the *closo*-1-CB_5H_7 system and its pertinent derivatives. In the vibrationally stable 3-21G-optimized structure of 1-CH_3-closo-1-CB_5H_6, four (equatorial) boron atoms attached to the cage carbon atom are essentially planar (Figure 1); if an imaginary line is drawn from the cage carbon atom to a position perpendicular to the plane of the four equatorial borons, the line would nearly split the geometric center of this isosceles trapezoid of boron atoms (within 0.06 Å, with the carbon slightly displaced toward the bridging hydrogen side of the molecule). In contrast, the unique boron opposite the cage carbon atom is displaced about 0.38 Å from the imaginary line perpendicular to the four equatorial borons and running through the center of the cage carbon atom. This unique boron is displaced in a direction away from the bridging hydrogen. The same is found for the parent *closo*-1-CB_5H_7. It leads to the impression that the bridging hydrogen is helping to distort the cage octahedral geometry by opening up the B(2)B(3)B(6) trigonal face. The bridging hydrogen is close to 125° out of the $B_{2,3,4,5}$ plane directed toward B(6) in both the parent *closo*-1-CB_5H_7 and its *C*-methyl derivative. Because it is apparently easier for the bridging hydrogen to slide around a B_{eq}–B(6) edge (to another BBB trigonal face position) when the cage carbon is methyl substituted,[12] it is not entirely surprising that the H_b–B(6) distance in the ground-state configuration is certainly not found to be longer, but appears to be very slightly shorter, in the 1-methyl derivative than in the parent system. The 3-21G fully optimized geometries indicate that the H_b–B(6) distance in CB_5H_7 is 1.846 Å, as compared to 1.837 Å in the *C*-methyl derivative. Also, the B(2)–H_b distance is about the same or slightly longer in the *C*-methyl derivative (1.355 Å) than in the parent compound (1.353 Å). In the transition-state structures, B(2)–H_b is 1.298 Å in the methyl derivative, which is marginally longer than the 1.292 Å in the parent CB_5H_7; B(6)–H_b is nearly the same in each but perhaps insignificantly shorter in the *C*-methyl derivative at 1.295 Å, cf. 1.297 Å in CB_5H_7. It would be interesting to carry out the MO calculations at much higher levels to see if this trend holds up. Unfortunately, this was not possible with the resources at hand. But at the 3-21G level it does appear that the bridging hydrogen in the 1-methyl derivative is beginning its tautomeric journey in a ground-state position that is probably more geometrically favorable for passage over the edge-bridging "transition state" than is that for the parent *closo*-1-CB_5H_7; i.e., in the ground-state structure the bridging hydrogen of the *C*-methyl derivative begins in a position that is slightly closer to a midway position between B(6) and B(2,3) than in the parent cluster.

We confirmed that the calculated energy barrier for hydrogen tautomerism of this type in the parent CB_5H_7 is 14.8 kcal/mol (ab initio at the MP2/6-31G*//3-21G+ZPE(3-21G) level).[20]

Table II. Energies and Predicted Equilibrium Percentages of the Methyl Derivatives of *closo*-1-CB_5H_7

molecule	MP2/6-31G*//3-21G[a]	δ(ZPE) (NF)[b]	ΔMP2/6-31G*//3-21G+ZPE[c]	*W*[d]	equil % (*T* = 25 °C)[d]
1-CH_3-1-CB_5H_6	−205.05298	0 (0)	4.937	1	0.006
2-CH_3-1-CB_5H_6	−205.06161	0.478 (0)	0	2	51.9
4-CH_3-1-CB_5H_6	−205.06100	0.567 (0)	0.474	2	23.2
6-CH_3-1-CB_5H_6	−205.06187	0.666 (0)	0.028	1	24.8

[a] Total energies in hartrees (1 hartree = 627.51 kcal/mol). [b] Zero-point energies in kcal/mol (the number of negative frequencies are given in parentheses) using the 3-21G basis set. [c] Relative energies (kcal/mol). [d] See ref 36 for definition of the symmetry-permutation factor, *W*, and for the method of incorporating *W* in the calculation of equilibrium-percent quantities.

Table III. Energies and Predicted Equilibrium Percentages of the Methyl Derivatives of *nido*-2-CB_5H_9

molecule	MP2/6-31G*//3-21G[a]	δ(ZPE) (NF)[b]	ΔMP2/6-31G*//3-21G+ZPE[c]	*W*[d]	equil % (*T* = 220 °C)[d]
1-CH_3-2-CB_5H_8	−206.23891	0.161 (0)	1.670	1	5.6
2-CH_3-2-CB_5H_8	−206.23174	0 (0)	6.007	1	0.07
3-CH_3-2-CB_5H_8	−206.24163	0.200 (0)	0	2	61.8
4-CH_3-2-CB_5H_8	−206.24083	0.330 (0)	0.632	2	32.5
molecule	MP2/6-31G*//6-31G	δ(ZPE) (NF)	ΔMP2/6-31G*//6-31G+ZPE	*W*[d]	equil % (*T* = 220 °C)[d]
1-CH_3-2-CB_5H_8	−206.23879	0.064 (0)	1.685	1	5.8
2-CH_3-2-CB_5H_8	−206.23168	0 (0)	6.083	1	0.07
3-CH_3-2-CB_5H_8	−206.24155	0.112 (0)	0	2	64.7
4-CH_3-2-CB_5H_8	−206.24068	0.337 (0)	0.771	2	29.4

[a] Total energies in hartrees (1 hartree = 627.51 kcal/mol). [b] Zero-point energies in kcal/mol (the number of negative frequencies are given in parentheses) using the 3-21G basis set for the top half of the table and the 6-31G basis set for the bottom half of the table. [c] Relative energies (kcal/mol). [d] See ref 36 for definition of the symmetry-permutation factor, *W*, and for the method of incorporating *W* in the calculation of equilibrium-percent quantities.

Furthermore, we find that the corresponding set of calculations at that level for 1-CH_3-*closo*-1-CB_5H_6 gives a barrier of 13.2 kcal/mol. When the calculations are carried out at the MP2/6-31G*//6-31G+ZPE(6-31G) level the tautomeric barriers are 14.6 and 13.1 kcal/mol, respectively, for the parent *closo*-1-CB_5H_7 and its *C*-methyl derivative. The difference in these barriers between the two compounds is on the order of 1.5–1.6 kcal/mol. This agrees very well with the 2.0 ± 0.5 kcal/mol difference obtained from NMR variable-temperature data (see ref 12 and also the data in this study).

Equilibration between the 2-CH_3-*closo*-1-CB_5H_6 and the 4-CH_3-*closo*-1-CB_5H_6 Isomers. In a study[21] that examined the ^{11}B NMR temperature dependence of a *B*-methyl derivative of *closo*-1-CB_5H_7 there was a suggestion that the equilibrium 2-CH_3-*closo*-1-CB_5H_6/4-CH_3-*closo*-1-CB_5H_6 ratio at room temperature is in the vicinity of ca. 25:75 (i.e. 1:3); this was arrived at by assuming that the smaller ^{11}B NMR singlet at $\delta = +1.4$ (see ref 21) is assigned to the B(2)–CH_3 resonance of the 2-CH_3-*closo*-1-CB_5H_6 isomer and that the larger singlet at $\delta = -4.8$ belongs to the B(4)–CH_3 resonance of the 4-CH_3-*closo*-1-CB_5H_6 isomer. These assignments are in keeping with the generally accepted observation that downfield shifts of 5–15 ppm are found when the hydrogen of any cage B-H_t group is substituted by an alkyl group.[30-32] Obviously, the absolute *B*-methyl assignments are correct only if the parent *closo*-1-CB_5H_7 resonances are correctly assigned. Therefore, the previous assignments[21] are plausible only if the high-field B–H doublet in the parent *closo*-1-CB_5H_7 at $\delta = -19.0$[12] belongs to B(4,5), and the B–H doublet at $\delta = -9.8$ to B(2,3). Both the doublet (area 1) at $\delta = +2.7$[12] (now more accurately measured to be $\delta = +5.17$ and unequivocally assigned to B_6) and the doublet (area 2) at $\delta = -9.8$ (now $\delta = -7.21$) are broader than the doublet at $\delta = -19.0$ (now $\delta = -16.51$). It was previously assumed that the bridging hydrogen broadened all of the attached borons (i.e. B(2,3,6)), and thus the previous assignments of the two area (2) peaks appeared settled, i.e. the broader peak at $\delta = -7.21$ assigned to B(2,3) and the sharper higher field resonance to B(4,5). On the basis of the results of the present study it is highly likely that this previous assumption, and the accompanying assignments, are incorrect. It now appears that a significant portion of peak broadening of the two lower field resonances at $\delta = +5.12$ and -7.21 can be attributed to ^{11}B–^{11}B coupling. Upon application of proton decoupling to the ^{11}B NMR spectrum the expected three singlets in an area ratio of 1:2:2 (low field to high field, respectively) are observed; furthermore, the two lowest field singlet peaks are about twice as broad as the highest field singlet. With the application of resolution enhancement techniques, the two lowest field peaks show evidence of multiplet structures, attributable to ^{11}B–^{11}B coupling. The highest field (considerably narrower) peak shows no evidence of multiplicity. It has been noted[31,33] that ^{11}B–^{11}B coupling is considerably weaker between bonded borons sharing bridging hydrogen than between bonded borons that do not have a bridging hydrogen; therefore, the broader $\delta = -7.21$ resonance (area 2) is assigned to B(4,5) (which is broad owing to coupling to B(6)) and the narrower $\delta = -16.51$ resonance (area 2) assigned to B(2,3). Accordingly, the magnitude of ^{11}B–^{11}B coupling is deduced as B(4)–B(6) > B(5)–B(2) ≫ B(2)–B(6). This is entirely consistent with both the experimental and calculated B–B bond distance patterns as well, which suiggests the order B(4)–B(6) < B(5)–B(2) ≪ B(2)–B(6).[1-3,16-20,34] It is also in accordance with a [^{11}B–^{11}B 2D]-COSY experiment on a sample of *closo*-1-CB_5H_7; strong cross peaks were found between the resonance at $\delta = +5.17$ and $\delta = -7.21$; weaker cross peaks were found between the resonances at $\delta = -7.21$ and $\delta = -16.51$; no cross peaks were observed between the resonances at $\delta = +5.17$ and $\delta = -16.51$.

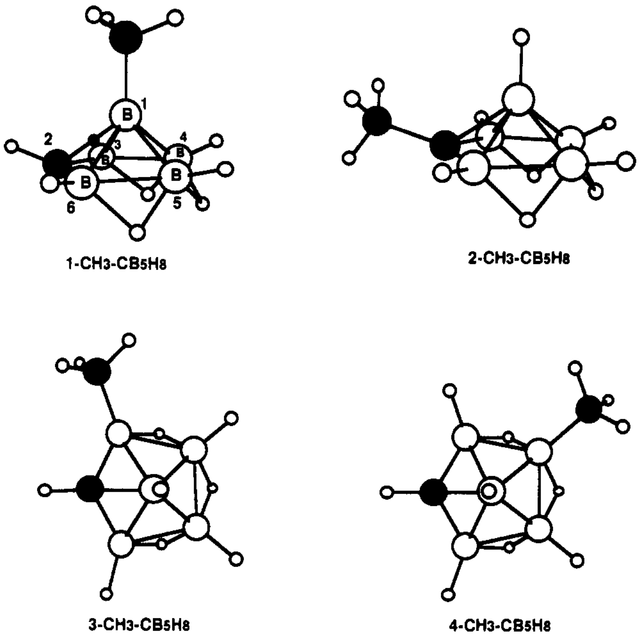

Figure 3. "Stable" structures of the four methyl derivatives of the pentagonal pyramidal *nido*-2-CB_5H_9. The depicted structures are constructed directly from the optimized 3-21G coordinates.

If the chemical shift patterns for the *B*-methyl derivatives of *closo*-1-CB_5H_7 parallel the parent system, as is observed in many other cage boron systems,[31,32,35] the the singlet at $\delta = +1.4$[21] (more accurately measured in the present study to be $\delta = +1.72$) for the 2-CH_3-*closo*-1-CB_5H_6/4-CH_3-*closo*-1-CB_5H_6 mixture belongs to B(4) of 4-CH_3-*closo*-1-CB_5H_6; the higher field singlet at $\delta = -4.8$[21] (more accurately measured to be $\delta = -5.27$) belongs to B(2) of 2-CH_3-*closo*-1-CB_5H_6. Thus, the 2-CH_3-*closo*-1-CB_5H_6/4-CH_3-*closo*-1-CB_5H_6 equilibrium ratio at room temperature is not 1:3[21] but rather closer to 3:1, respectively. A more exact value of 2.8:1.0 for this ratio is evident on remeasurement of the ^{11}B NMR spectrum of the equilibrium mixture at 128 MHz (25 °C).

Calculations at the MP2/6-31G*//3-21G+ZPE(3-21G) level for both the 2-CH_3-*closo*-1-CB_5H_6 and 4-CH_3-*closo*-1-CB_5H_6 isomers show an energy difference of 0.47 kcal/mol in favor of the 2-methyl isomer (Table II), which translates to an equilibrium 2-CH_3-*closo*-1-CB_5H_6/4-CH_3-*closo*-1-CB_5H_6 ratio of 2.2:1 at 25 °C. This is in reasonably good agreement with the 2.8:1 ratio determined from NMR data.

***nido*-2-CB_5H_9 Methyl Derivatives.** Of the four possible methyl derivatives of *nido*-2-CB_5H_9 (Figure 3) the 2-, 3-, and 4-methyl isomers appear to be more prevalent than the 1-methyl isomer, whether produced from the reaction of acetylene and pentaborane(9)[6] or from the rearrangement of vinylpentaborane;[22] moreover, the quantity of the 3-CH_3-*nido*-2-CB_5H_8 isomer generally exceeds that of the other isomers. In the present work we have determined more exactly the relative amounts of the various isomers obtained from the acetylene/pentaborane(9) reaction and find that between 200 and 225 °C the reaction progresses (with

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a manyfold excess of acetylene initially present) to produce a product ratio of 7.5:1.0:0.24:0.19:0.02 of *nido*-2,3-$C_2B_4H_8$, 3-CH_3-*nido*-2-CB_5H_8, 4-CH_3-*nido*-2-CB_5H_8, 2-CH_3-*nido* 2-CB_5H_8, and 1-CH_3-*nido*-2-CB_5H_8, respectively. This assessment is made after heating the sample at 225 °C and after ca. 15% of the initial quantity of pentaborane is still remaining. It is pertinent to note that the 3-CH_3-*nido*-2-CB_5H_8/4-CH_3-*nido*-2-CB_5H_8 ratio is 3.9 at the end of the last heating period. This ratio is 0.84 at the end of an earlier 215 °C heating period and a value of 1.6 at the end of a 220 °C intermediate heating period. (A very small amount of yellow-brown solid material is also produced during the reaction, and it is difficult to know whether or not some of this is a result of some product decomposition; see elsewhere in this paper). In a related study (see Introduction), flash thermolysis (355 °C) of 2-ethenyl-*nido*-B_5H_8 gives 2-CH_3-*nido*-2-CB_5H_8 (15%), 3-CH_3-*nido*-2-CB_5H_8 (23%), and 4-CH_3-*nido*-2-CB_5H_8 (13%).[22] Again, the 3-CH_3-*nido*-2-CB_5H_8 isomer predominates.

In this regard it is of some interest to note that MP2/6-31G*//3-21G+ZPE(3-21G) calculations (Table III) on all of the CH_3-*nido*-2-CB_5H_8 isomers indicate that the order of stabilities to be 3-CH_3-*nido*-2-CB_5H_8 > 4-CH_3-*nido*-2-CB_5H_8 > 1-CH_3-*nido*-2-CB_5H_8 > 2-CH_3-*nido*-2-CB_5H_8. In additional experiments carried out in the present study we discovered that 4-CH_3-*nido*-2-CB_5H_8 will slowly convert to 3-CH_3-*nido*-2-CB_5H_8 under the thermal conditions of its formation. Also, it appears that the 3-CH_3-*nido*-2-CB_5H_8 isomer can convert to 4-CH_3-*nido*-2-CB_5H_8 under the same conditions, but because slow *B*-CH_3-*nido*-2-CB_5H_8 decomposition is occuring simultaneously, it is not possible to achieve true equilibrium quantities. But by examination of the results from both rearrangement reactions, it seems suggestive that the equilibrium ratio at the rearrangement temperature of 225 °C is somewhere between 2:1 and 3.3:1.0 for the 3-CH_3-*nido*-2-CB_5H_8/4-CH_3-*nido*-2-CB_5H_8 ratio. The ratio suggested by MP2/6-31G*//3-21G+ZPE(3-21G) results is 1.9:1. When the calculations are carried out at the MP2/6-31G*//6-31-G+ZPE(6-31G) level, the ratio climbs slightly to 2.2:1. Everything considered, the agreement between the experimentally obtained and calculational approaches is rather good. There is no experimental evidence to suggest that either 1- or 2-CH_3-*nido*-2-CB_5H_8 enter into the equilibrium mixture pot. It does appear, though, that the 2-CH_3-*nido*-2-CB_5H_8 isomer, once produced, is more thermally stable toward further reaction than the *B*-CH_3-*nido*-2-CB_5H_8 isomers.

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A Topological Method for the Enumeration of Bridging Modes and Connectivity Patterns of the Clusters $M_mQ_nL_l$ with Four-Coordinate Metal Sites and $Q_{\mu_{2,3,4}}$ Bridging Atoms

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For the extensive family of metal clusters $M_mQ_nL_l$ containing four-coordinate metal (M) sites, n_a bridging atoms Q_{μ_a} (a = 2–4), and unidentate terminal ligands (L), a topological procedure for isomer enumeration using a matrix method has been developed. The method calculates all possible bridging modalities $[n_2,n_3,n_4]$ for a given formula, which are utilized to generate atom connectivity matrices that uniquely define structures. Because of the very large number of possible structures for $m \geq 4$, other constraints may be applied in order to afford sets of the more probable structures. The structures of 14 Fe_mQ_n clusters (Q = S, Se) taken as a data base indicate certain structural features of frequent occurrence which define these constraints: M_2Q_2 rhomb-only structures, uniterminal ligation, and rational stereochemistry (usually tetrahedral) at the M sites. The method is outlined and is tested and applied, under the various constraints, to clusters of assorted nuclearities. Bridging modalities are calculated for known and unknown structures with nuclearities m = 2–9 ($l \neq 0$) and for certain cyclic clusters (l = 0) of nuclearities m = 18 and 20. The constraints may be altered to include M sites of higher coordination number. The method rationalizes known structures, provides an organizational framework for all structures within its purview, and offers a basis for predicting potentially accessible new clusters. Among the latter are uncharacterized protein-bound iron–sulfur clusters and the cofactors of nitrogenase.

Introduction

An extensive family of metal clusters exists in which the constituent metal atoms are four-coordinate and are bridged by chalcogenide atoms to generate a core unit, M_mQ_n. The best known and most highly developed group within this family is composed of iron–sulfur or –selenium clusters, many of which have been studied extensively in this laboratory.[1-13] These clusters, which span the nuclearity range 2–20, present a diversity of geometric motifs that illustrate important structural principles.

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