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Synthesis and characterization of μ,μ′-M$(B_5H_8)_2$ (M = Cd, Hg and Zn): a reassignment of the NMR spectra for 2,3-μ-metalloderivatives of pentaborane(9)

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Dedicated to Professor Sheldon G. Shore in celebration of his 70th birthday and a career of major contributions to inorganic chemistry.

Abstract

The series of compounds μ,μ′-M$(B_5H_8)_2$, where M = Cd (**I**), Zn (**II**), or Hg (**III**), has been prepared from the reaction between $K(B_5H_8)$ and the metal chloride in THF at low temperatures. The species were characterized by multinuclear NMR spectroscopy, elemental analysis and mass spectrometry. The NMR spectral assignments were confirmed using $^{11}B\{^1H\}$ selective decoupling experiments and heteronuclear $^{11}B-^1H$ chemical shift correlation spectroscopy. The results appeared to be in conflict with the earlier assignment of the ^{11}B-NMR spectra for 2,3-μ-metalloderivatives of pentaborane(9) which appear in the literature. For systems with an electrophilic group replacing a bridging H atom in B_5H_9, the B atoms most shifted in the ^{11}B-NMR spectrum, which appear at the lower field, were assigned to the ones closest to the metal group. Our results for **I**–**III** suggested that the assignment was reversed, that is the higher field resonance is the one closest to the metal group. Thus, we reexamined the spectra of a series of related compounds including 2,3-μ-$SnPPh_3(B_5H_8)$, μ,μ′-$SnPh_2(B_5H_8)$, μ,1′-$SnPh_2(B_5H_8)$, other Sn species and 2,3-μ-Cu(dppe)B_5H_8. In all cases our assignments were in accord with those for **I**–**III** and we suggest that this is general for all such B_5H_9 derivatives. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nido-pyramidal boranes and carboranes such as B_5H_9, B_6H_{10} and $C_2B_4H_8$ contain bridging hydrogen atoms that are acidic and which may be removed with strong bases. This was demonstrated independently by the research groups of Onak [1a], Gaines [1b] and Shore [1c] in 1967. The resulting anions were shown to be susceptible to electrophilic attack by Lewis acids in studies, reported soon after initial discovery by the three groups, in which the original bridging hydrogen is replaced by the Lewis acid [2]. For B_5H_9, the Lewis acids used range from simple species such as a proton [1b,c] and borane(3) [3] through more complex main group [2a,4] species and transition metal moieties [5]. The main group units thus introduced into the cluster contain elements from p-block Groups 2 [6], 13 [7], 14 [8], and 15 [9]. The first pentaborane(9) derivative with a metal group in a bridging position was prepared by Brice and Shore [10] and characterized fully [11]. Now, examples of bridged substituted metalloboranes based on pentaborane(9) are known for nickel [12,13], palladium [13,14], platinum [13,14], copper [10,11,15,16], silver [15], gold [15,17], beryllium [6], zinc [6], cadmium [18], silicon [8a–f,19], germanium [8b,c], tin [8b,8g,20] and lead [8b]. The generic structure of these species is given in Fig. 1. Pentaboranes(9) bridged by mercury [21] are also known and we had prepared some related $SnPPh_2$-bridged pentaboranes(9) [22]. Herein we extend this latter work to some Zn and Cd bridged derivatives and also clarify some aspects of the ^{11}B-NMR spectra for the 2,3-μ-metallopentaboranes [23].

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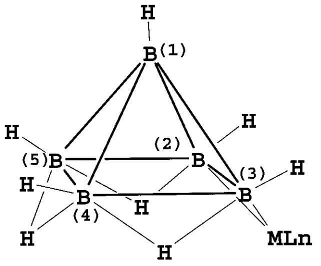

Fig. 1. Generic structure for 2,3-μ-(MLn)B_5H_8 species.

2. Experimental

2.1. General

Reactions were carried using a vacuum line, Schlenk tubes and an inert atmosphere box employing standard methods [24]. All solvents were reagent grade and were dried and distilled prior to use and stored in Pyrex vessels with Teflon stopcocks. B_5H_9 was obtained from laboratory stock, and distilled on the vacuum line before use. Anhydrous $ZnCl_2$ and $CdCl_2$ were dried from $ZnCl_2$ or $CdCl_2 \cdot 2.5H_2O$ (Fisher Scientific) in a vacuum oven at 120°C for 48 h. $HgCl_2$ (Fisher Scientific) was purified by sublimation above 100°C under vacuum. KH (Alfa) obtained as a 20–25% mineral oil suspension, was washed repeatedly with pentane to remove the oil until it was a free-flowing white powder. The activity of the powder, in reactions with methanol, was 85–95%. μ,μ′-$Hg(B_5H_8)_2$ [21], 2,3-μ-$SnPh_3(B_5H_8)$ [20], μ,μ′-$Sn(B_5H_8)_2Ph_2$, μ,μ′-$Sn(B_5H_8)_2Ph_2$, μ1′-$Sn(B_5H_8)_2Ph_2$ [22], and 2,3-μ-Cu(dppe)(B_5H_8) [16] were prepared as described in the literature. NMR spectra were obtained on a 500 MHz Bruker ARX-500 NMR spectrometer operating at 500 and 160.4 MHz to observe ^1H and ^{11}B resonances, respectively. Assignments were confirmed by selective decoupling experiments and heteronuclear 2D ^{11}B–^1H correlation spectra. ^{11}B chemical shifts are reported in ppm, positive signs denoting a shift at a lower field with respect to $Et_2O \cdot BF_3$ reference (0.0 ppm). ^1H-NMR shifts was measured relative to $SiMe_4$. Mass spectra were run as solids at 70 eV on a Varian/Mat 311A spectrometer equipped with a Technivent data system. IR spectra were run as KBr pellets on a Perkin–Elmer 1604 FTIR spectrometer. Elemental analysis for Cd were obtained on a GBC Model 904BT double-beam AAS instrument in the flame atomization mode by comparison with standard Cd^{2+} solutions.

2.2. Preparation of $Cd(B_5H_8)_2$

Potassium hydride (250 mg, 5.3 mmol calc. from 85% activity) was weighed in a glove box into a 50 ml two neck reaction flask, equipped with a extractor on one neck and a glass stopper on the other. After evacuation on the vacuum line, an excess of 0.8 ml of B_5H_9 (7.7 mmol) and 15 ml of THF were condensed in the vessel at −198°C. Deprotonation of the B_5H_9 was carried out by stirring at −78°C for about 2 h until H_2 evolution ceased. The mixture was cooled again to −198°C, and evacuated, flushed with N_2 and a tipper tube containing 550 mg anhydrous $CdCl_2$ (3.0 mmol) was attached to the vessel under positive pressure of N_2. After evacuation, the $CdCl_2$ was tipped in the flask and the reaction mixture was stirred at −78°C overnight and at −35°C for 3 h. The reaction mixture was then warmed to 0°C over a period of 2 h and stirred at that temperature for an additional 1.5 h. Traces of a greenish metallic-like deposit, assumed to be Cd, were observed. THF was removed under vacuum at room temperature (r.t.) to give a viscous residue, which was extracted with 10 ml of CH_2Cl_2. The contents of the flask were filtered at −78°C by suction through a frit on the vacuum line to remove KCl. The product crystallized from CH_2Cl_2 during filtration. Element analysis for Cd before the crystals were dried gave 28.56% and 29.45% obs. (calc. for $Cd(B_5H_8)_2 \cdot 2THF$: 29.53%). ^1H-, ^{11}B-NMR and IR spectra confirmed the composition to be $Cd(B_5H_8)_2 \cdot (THF)_x$ after evacuation at ambient temperature for 15 min on the vacuum line. This species is soluble in THF, Et_2O, CH_2Cl_2 and $CHCl_3$ and sparingly soluble in pentane, hexane. The product was dried further at r.t. affording 410 mg of white solid $Cd(B_5H_8)_2$ (65% yield) which melts at 95°C with decomposition. Analysis for Cd gave 49.06% and 48.28% (calc. for $Cd(B_5H_8)_2$: 47.55%). Commercial elemental analyses on $Cd(B_5H_8)_2$ were unsuccessful due to its high sensitivity to air and moisture, and also to incomplete combustion since the compound does not contain carbon. Schwarzkopf Microanalytical Laboratory reported that the species exploded when treated with nitric acid. $Cd(B_5H_8)_2$ is slightly soluble in CH_2Cl_2 and $CHCl_3$. If dry isolated $Cd(B_5H_8)_2$ is dissolved THF at ambient temperature, it completely decomposes to $[B_9H_{14}]^-$. Attempts to grow crystals resulted in the formation of good crystals of $K[B_9H_{14}]$ if traces of KCl were present [25]. The IR spectrum of $Cd(B_5H_8)_2 \cdot (THF)_x$ run as a KBr pellet, showed weak absorbencies of the coordinated THF at 2965(w), 2878(w), 1024(w), 884(w). Absorbencies were observed for the B_5H_8 cage at 2522(s), 1797(w). Unassigned bands are 1376(m, br), 1263(m), 1089(w), 959(s), 806(m), 708(w), 605.8(w), 565(w). NMR data are given in Table 1. The mass spectrum exhibited the expected $Cd(B_5H_8)_2$ envelope with a cutoff at m/q 242 attributed to $[B_{10}H_{16}Cd]^+$. The observed m/q values (relative intensity) for the $Cd(B_5H_8)_2$ molecular ion cluster were 231(0), 232(6.17), 233(27.66), 234(48.83), 235(60.04), 236(85.90), 237(100), 238(87.12), 239(73.24), 240(50.45), 241(17.70), 242(7.00). The calculated m/e data were 231(5.25), 232(11.25), 233(26.15),

Table 1
^{1}H-NMR data for Group 12 metal-bis[pentaboranyl(9)] complexes [a]

Compound	^{1}H	^{1}H{^{11}B)
μ,μ'-$Zn(B_5H_8)_2\cdot 2THF$	−3.61[s, br, 4H, Hμ(3,4), Hμ(2,5), Hμ(3′,4′), Hμ(2′,5′)]	
	−2.19 [s, br, 2H, Hμ(4,5), Hμ(4′,5′)]	
	0.44 [q, 2H, H(1), H(1′), $J(^{11}B–^1H) = 170$ Hz]	0.44 [s, 2H, H(1), H(1′)]
	1.3–3.0 [m, br, 8H, Ht(2–5), Ht(2′-5′), *J*unres]	1.82 [s, 4H, Ht(2,3), Ht(2′,3′)]
	1.96 [s, 6H, H_β THF], 3.89 [s, 6H, H_α THF]	2.39 [s, 4H, Ht(4,5), Ht(4′,5′)]
μ,μ'-$Cd(B_5H_8)_2$-$(THF)_x$	−3.61 [s, br, 4H, Hμ(3,4), Hμ(2,5) Hμ(3′,4′), Hμ(2′,5′)]	
	−2.03 [s, br, 2H, Hμ(4,5), Hμ(4′,5′)]	
	0.68 [q, 2H, H(l), H(1′), J ($^{11}B–^1H) = 172$ Hz]	0.68 [s, 2H, H(1), H(1′)]
	1.3–3.1 [m, br, 8H, Ht(2–5), Ht(2′–5′), *J*unres]	1.88 [s, 4H, Ht(2,3), Ht(2′,3)]
	1.93 [s, 2H, Hp THF], 3.81 [s, 2H, Ha THF]	2.49 [s, 4H, Ht(4,5), Ht(4′,5′)]
μ,μ'-$Cd(B_5H_8)_2\cdot PPh_3$ [b,c]	−3.41 [s, br, 4H, Hμ(3,4), Hμ(2,5), Hμ(3′,4′), Hμ(2,5′)]	
	−2.38 [s, br, 2H, Hμ(4,5), Hμ(4′,5′)]	−2.51 [s, 4, Ht(4,5), Ht(4′,5′)]
	0.49 [q, 2H, H(l), H(1′), $J(^{11}B–^1H) = 165$ Hz]	0.49 [s, 2H, H(1), H(1′)]
	1.3–3.1 [m, br, 8H, Ht(2–5), Ht(2′–5′), *J*unres]	1.84 [s, 4H, Ht(2,3), Ht(2′,3′)]
	2.26 [s, 4H, Ht(4,5), Ht(4′,5′)]	
μ,μ'-$Hg(B_5H_8)_2$	−2.48 [s, br, 4H, Hμ(3,4), Hμ(2,5) Hμ(3′,4′), Hμ (2′,5′)]	−2.48 [s, sh, 4H, Hμ(3,4), Hμ(2,5), Hμ (3′,4′), Hμ (2′,5′), $J(^{199}Hg–^1H\mu = 100$ Hz]
	−1.44 [s, br, 2H, Hμ(4,5), Hμ(4′,5′)]	−1.44 [s-sh, 2H, Hμ(4,5), Hμ(4′,5′), J ($^{199}Hg–^1H\mu\mu = 152$ Hz]
	−1.58 [q, 2H, H(1), H(1′), J ($^{11}B–^1H) = 176$ Hz]	−1.58 [s, 2H, H(1), H(1′)]
	2.47 [q, 4H, Ht(2,3), Ht(2′,3′), *J*unres]	2.47 [s, 4H, Ht(2,3), Ht(2′,3′), $J(^{199}Hg–^1Ht) = 160$ Hz]
	2.51 [q, 4H, Ht(4,5), Ht(4′,5′), *J*unres]	2.51 [s, 4, Ht(4,5), Ht(4′,5′)]

[a] All spectra were recorded at 500 MHz at room temperature in $CDCl_3$ and assigned by ^1H-{$^{11}B_{selective}$} and 2D-HETCOR experiments. Abbreviations: s, singlet; d, doublet; q, quartet; m, multiplet; br, broad; sh, sharp; unres, unresolved coupling.

[b] Resonances for the phenyl groups on PPh_3 and omitted.

[c] ^{31}P data: $\delta(^{31}P)$ ($CDCl_3$, 223 K) +20.83, singlet {^{1}H}.

234(51.38), 235(79.09), 236(97.34), 237(100), 238(87.00), 239(60.43), 240(30.81), 241(11.68), 242(4.67). The fit is not perfect, and this may be ascribed to the low intensity of the molecular ion cluster, which is affected by baseline noise. The $[M-B_5H_8]^+$ cluster, has a base peak at *m*/*e* 175, and cut off at *m*/*e* 179 corresponding to $[B_5H_8Cd]^+$. The observed *m*/*e* data were 170(12.83), 171(27.58), 172(57.86), 173(76.26), 174(98.93), 175(100), 176(98.36), 177(59.28), 178(8.44), 179(19.92), and the calculated *m*/*e* data were 170(5.80), 171(19.33), 172(47.81), 173(79.73), 174(95.59), 175(100), 176(86.05), 177(58.36), 178(16.566), 179(13.22). This fit is very good. A qualitative test 0.2 M $AgNO_3$ confirmed the absence of Cl^-.

2.3. Preparation of $Zn(B_5H_8)_2$

KH 260 mg (5.52 mmol, calc. as 85% activity) was placed in a 50 ml two-necked flask with one neck fitted with an extractor and the other neck stoppered. B_5H_9 (0.8 ml, 0.77 mmol) was condensed at −198°C. The mixture was warmed to −78°C and stirred for 3 h after which time deprotonation was complete. The H_2 was pumped away at 198°C and under positive N_2 flow, a side arm tip tube containing $ZnCl_2$ (410 mg, 3 mmol) was attached to the second neck of the reaction flask. The reaction mixture was stirred at −78°C overnight. The $ZnCl_2$ appeared to dissolve in the THF. The mixture was warmed to −35°C and stirred for 3 h and then at 0°C for an additional 0.5 h. The solvent was removed in vacuum to give a viscous compound, which was evacuated for 15 min at ambient temperature. The residue was extracted with 15 ml of CH_2Cl_2 and the resulting solid KCl was filtered. Some crystals formed under the filter frit. The resultant clear filtrate was reduced to 2 ml under vacuum and 10 ml pentane resulted in a trace of precipitate so the solvent was removed and the resulting compound was dried under vacuum for 1 h at r.t. to afford a white solid 390 mg, 42% yield of $Zn(B_5H_8)_2\cdot 2THF$. The compound melts with decomposition above 98°C and is soluble in $CHCl_3$, CH_2Cl_2, THF, Et_2O and C_6H_6. Some decomposition to $[B_9H_{14}]^-$ can be observed from solutions in THF, Et_2O and C_6H_6. Mass spectra data were supportive of the formulation. The observed *m*/*e* values for the molecular ion $[\mathrm{Zn(B_5H_8)_2}]^+$ were: (relative intensity) 183(0), 184(0.73), 185(5.65), 186(22.68), 187(56.29), 188(93.01), 189(100), 190(84.92), 191(67.48), 192(50.30), 193(25.95), 194(8.56) and the calculated data are 183(0.20), 184(1.38), 185(6.68), 186(22.71), 187(54.03), 188(88.80), 189(100), 190(82.68), 191(64.24), 192(50.38), 193(28.78), 194(11.31). The fit is excellent; details of the molecular ion envelopes, along with the calculated ones are available as supplemental information. The IR spectrum clearly indicated THF coordination with absorbencies ($\mathrm{cm^{-1}}$) at 2982(m), 2889(m), 1458(w) 1346(m), 1177(w), 1022(s), 883(s). Two bands for $\nu_{\mathrm{B-H_t}}$ at 2579(s), and 2517(s) and one bond for $\nu_{\mathrm{B-H\mu}}$ at 1803(w, br) and unassigned bonds at 1376(m), 1296(w), 1262(w), 1095(w), 1049(m), 960(m), 943(m), 922(m), 859(m), 808(w), 749(w), 713(w), 651(w), 605(s) and 578(m) were observed. $\mathrm{Cl^-}$ was shown to be absent using the $\mathrm{AgNO_3}$ test.

2.4. Tests for possible rearrangement

Samples of about 20 mg [μ,μ′-$\mathrm{Cd(B_5H_8)_2{\cdot}2THF}$] was dissolved in THF, $\mathrm{Et_2O}$ and $\mathrm{CDCl_3}$ separately in NMR tube at r.t., and NMR sample was sealed under vacuum. The ^{11}B spectra were monitored periodically over several months. The only change detected was the appearance of a small amount of $[\mathrm{B_9H_{14}}]^-$.

2.5. Reaction of μ,μ′-$\mathrm{Cd(B_5H_8)_2{\cdot}2THF}$ with $\mathrm{PPh_3}$

[μ,μ′-$\mathrm{Cd(B_5H_8)_2{\cdot}2THF}$], 30 mg (0.08 mmol), was stirred with 30 mg (0.12 mmol) $\mathrm{PPh_3}$ at −78°C in $\mathrm{CH_2Cl_2}$ for 8 h, solvent was evaporated at −35°C until the solid was dry. An NMR sample was prepared in $\mathrm{CDCl_3}$ and ^{11}B and ^{1}H are given in Table 1, implying the existence of μ,μ′-$\mathrm{Cd(B_5H_8)_2PPh_3}$.

3. Results and discussion

The reaction between $\mathrm{K(B_5H_8)}$ and anhydrous $\mathrm{CdCl_2}$ in 2:1 ratio in THF affords [μ,μ′-$\mathrm{Cd(B_5H_8)_2}$] (**I**) in 65% yield. The product is slightly soluble in $\mathrm{CH_2Cl_2}$ and $\mathrm{CHCl_3}$. Elemental analysis and mass spectral data support the proposed formulation. **I** is quite different from [μ,μ′-$\mathrm{Cd(B_5H_8)_2{\cdot}2THF}$], which is very soluble in $\mathrm{CHCl_3}$, $\mathrm{CH_2Cl_2}$, THF, $\mathrm{Et_2O}$ and pentane. Elemental analysis for Cd were obtained for both μ,μ′-$\mathrm{Cd(B_5H_8)_2{\cdot}2THF}$, before removal of solvent, and μ,μ′-$\mathrm{Cd(B_5H_8)_2}$ after drying. Invariably THF solvates the complex in amounts ranging from 0 to 2 mol. The ^{1}H-NMR spectrum in $\mathrm{CDCl_3}$ gives broad resonances at −3.46 ppm and −2.03 ppm in 1:2 area ratio, respectively, in the upfield region assigned to bridging H atoms, together with a quartet at 0.68 ($J = 172$ Hz) ppm assigned to the apical H atom and overlapped broad quartets between 1 and 3 ppm. On ^{11}B-decoupling, the two upfield resonances become sharper, the apical H resonance becomes a singlet and the low field overlapped resonances are seen as two singlets at 1.88 and 2.49 ppm, in area ratio 2:2. These latter are assigned to the basal boron atoms suggesting that the two $\mathrm{B_5H_8}$ cages are each bonded to Cd at positions bridging basal H atoms. The 160.4 MHz ^{11}B-NMR spectrum of **I** in $\mathrm{CDCl_3}$ affords a high-field doublet, of relative area 1, at −49.0 ppm, assigned to the apical boron atoms, and two well-separated, equally intense doublets at −18.3 ppm, ($J = 130$ Hz) and −8.5 ppm ($J = 152$ Hz) assigned to the basal boron atoms. These observations are in contrast to the spectra of the only known cadmium complexes, Cd(μ-$\mathrm{B_5H_8}$)Cl($\mathrm{PPh_3}$) and Cd(μ-1-Br–$\mathrm{B_5H_7}$)Cl($\mathrm{PPh_3}$), for which ^{11}B-NMR spectra were run at 28.87 MHz affording broad overlapped basal boron resonances with ca. 4 and 5 ppm separation, respectively [18]. The ^{11}B resonances for **I** and μ,μ′-$\mathrm{Cd(B_5H_8)_2{\cdot}2THF}$ collapse to singlets on proton-decoupling. Unfortunately we were unable to grow crystals suitable for X-ray diffraction analysis; however, elemental analysis and mass spectral data support the formulation derived from the NMR data. Similar data were obtained for [μ,μ′-$\mathrm{Zn(B_5H_8)_2}$] (**II**), also a new compound, and for [μ,μ′-$\mathrm{Hg(B_5H_8)_2}$] (**III**), which was prepared for comparisons purposes. NMR data for **I**–**III** are given in Table 1 and a proposed structure for **I**, typical of the class of compounds, is given in Fig. 2.

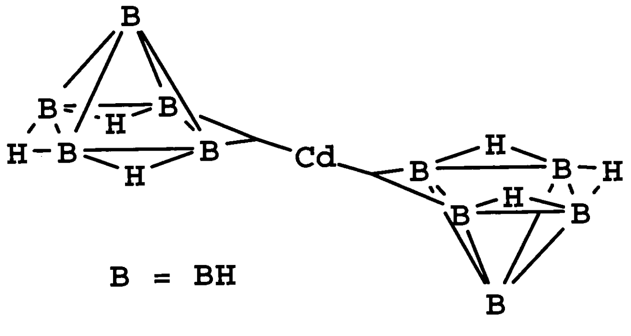

Fig. 2. Proposed structure for species **I**.

The assignments of the ^{11}B-NMR spectra for **I**–**III** differ from those previously published for pentaborane(9) derivatives with a substituent in a bridging position replacing a bridging hydrogen atom. The original assignments of the ^{11}B-NMR spectra were based on the assumption that the basal boron resonances which were shifted the least from those in pentaborane(9) would be the B(4,5) atoms [8a–c,8f,18] (see Fig. 1). Thus the lowest field resonances in the ^{11}B-NMR spectra of 2,3-μ-bridge-substituted *nido*-pentaboranes were assigned to the boron atoms bonded to the metal substituent. This was based on the observation that these resonances were shifted from those in $\mathrm{B_5H_9}$ itself whereas the upfield resonance was not and on the assumption that the boron atoms B(2,3), to which the metal substituent is bonded, are most likely to be shifted and broadened.

Thus in the original series of Group 14 derivatives discovered and several others since then, assignments were based on this premise. For example, in 2,3-μ-$(Me_3Si)B_5H_8$, the lower field basal boron resonance which is seen at $\delta = 8.7$ ppm was assigned to B(2,3) and the higher field resonance, observed at 13.2 ppm (versus 12.5 ppm for B_5H_9 [26]), was assigned to B(4,5) [8b]. Analogous assignments persisted in more recent work [8c,18,13,20,27] but we noticed some anomalies with these assignments, first when examining the spectra of [μ,2-$SnPh_2(B_5H_8)_2$] [22,28]. We found for this system that B(4), which is the boron atom furthest from the basal boron atom to which a tin atom is sigma-bonded, falls at the lowest field strength. This conflicts with previous assignments for pentaboranes(9) substituted at the 2-position [8c,20]. Thus, we reexamined the spectra of some related bridged-substituted pentaborane(9) species we had prepared previously by conducting 500 MHz $^1H\{^{11}B\}$-NMR selective decoupling experiments. The bridging H atoms in 2,3-μ-substituted pentaboranes(9) exhibit two broad resonances in area ratio 1:2, corresponding to Hμ(4,5) and Hμ(3,4)/Hμ(2,5), respectively (see Fig. 1). We observed that when the frequency corresponding to the higher field basal boron resonance in [2,3-μ-$(SnPh_3)B_5H_8$] was irradiated, the bridging H atom resonance of relative area 2 sharpened. Also, irradiation at the other (lower field) basal boron atom field position resulted in the sharpening of both bridging H atom resonances, the one of area 1 being the most affected. This implies that the lower field resonance, which couples to all the Hμ resonances, is B(4,5) and the higher field resonance which only couples to the Hμ resonance of area 2, is B(2,3), the B atoms adjacent to the metal. Analogous experiments for the species μ,μ′-$SnPh_2(B_5H_8)_2$, μ,1′-$SnPh_2(B_5H_8)_2$, 2,3-μ-Cu-(dppe)B_5H_8 afforded similar results. In each case the low field resonance in the ^{11}B-NMR spectrum was assigned to B(4,5).

Our ^{11}B-NMR assignments for **I–III** were also made on the basis of selective ^{11}B decoupling of the proton spectra and the data we obtained were in accord with our new results for [2,3-μ-$(SnPh_3)B_5H_8$], which had been obtained simultaneously, and the other species listed above. That is the low field resonance in the ^{11}B spectra of all these species corresponds to the atoms B(4,5). In order to confirm these results, we conducted heteronuclear $^{11}B-^1H$ chemical shift correlation spectroscopy experiments. Fig. 3 shows the $^{11}B-^1H$ correlated 2D-NMR spectra for 2,3-μ-$(SnPh_3)B_5H_8$, μ,μ′-$Zn(B_5H_8)_2$, μ,μ′-$Cd(B_5H_8)_2$, μ,μ′-$Hg(B_5H_8)_2$. All give similar results. The low field basal ^{11}B resonance correlates with all three bridging H atoms and thus is assigned to B(4,5) and the upfield basal boron resonance correlates only with the bridging H resonance of area 2, and is assigned to B(2,3). We conducted the same experiments for μ,μ′-$SnPh_2(B_5H_8)_2$, μ,1′-$SnPh_2(B_5H_8)_2$, and 2,3-μ-Cu(dppe)B_5H_8, obtaining similar results in each case thus confirming our reassignments. Since we ran spectra on a 500 MHz spectrometer which had been previously obtained at lower field strength, we report herein the newly recorded spectra for 2,3-μ-$(SnPh_3)B_5H_8$, and 2,3-μ-Cu(dppe)B_5H_8. The data are tabulated in Table 2 and they provide much more details than was available from spectra run at lower field strength. Of note is our observation of the $^{119}Sn-^1H$ coupling constant of 67 Hz for the terminal H atoms on the B atoms which are bridged by the Sn

Table 2

^1H- and ^{11}B-NMR data for 2,3-μ-$(SnPh_3)(B_5H_8)$ and 2,3-μ-Cu(dppe)B_5H_8 [a]

Compound	^{11}B	H	$^1H\{^{11}B\}$
2,3-μ-$(SnPh_3)(B_5H_8)$	−9.7 [d, 2B, B(4,5), $J(^{11}B–^1H) = 151$ Hz]	−2.58 [s, br, 2H, Hμ(3,4), Hμ(2,5)	
	−13.6 [d, 2B, B(2,3), $J(^{11}B–^1H) = 148$ Hz]	−1.97 [s, br, 1H, Hμ(4,5)]	
	−49.4 [d, 1B, B(1), $J(^{11}B–^1H) = 176$ Hz]	0.91 [q, 1H, H(1), $J(^{11}B–^1H) = 175$ Hz]	0.91 [s, 1H, H(1)] 2.58 [s, 2H, Ht(4,5)]
		2.0–3.5 [m, br, 4H, Ht(2–5), $J_{unres.}$]	2.39 [s, 2H, Ht(2,3) $J(^{119}Sn–^1H) = 67$ Hz]
2,3-μ-Cu(dppe)B_5H_8	−13.1 [d, 2B, B(4,5), $J(^{11}B–^1H) = 149$ Hz]	−3.00 [s, br, 2H, Hμ(3,4), Hμ(2,5)]	
	−16.37 [d, 2B, B(2,3), $J(^{11}B–^1H) = 124$ Hz]	−2.67 [s, br, 1H, Hμ(4,5)]	
	−49.1 [d, 1B, B(1), $J(^{11}B–^1H) = 161$ Hz]	0.12 [q, 1H, H(1), $J(^{11}B–^1H) = 161$ Hz]	0.12 [s, 1H, H(1)] 1.96 [s, 2H, Ht(2,3)]
		1.3–3.1 [q, br, 4H, Ht(2–5), $J_{unres.}$]	2.09 [s, 2H, Ht(4,5)]
		2.47 [s, 4H, from $CH_2–CH_2$]	

[a] All spectra are recorded at 500 MHz at room temperature in $CDCl_3$ and assigned by ^1H-$\{^{11}B_{selective}\}$ and 2D HETCOR experiments. Abbreviations: s = singlet, d = doublet, q = quartet, m = multiplet, br = broad, sh = sharp, unres = unresolved coupling.

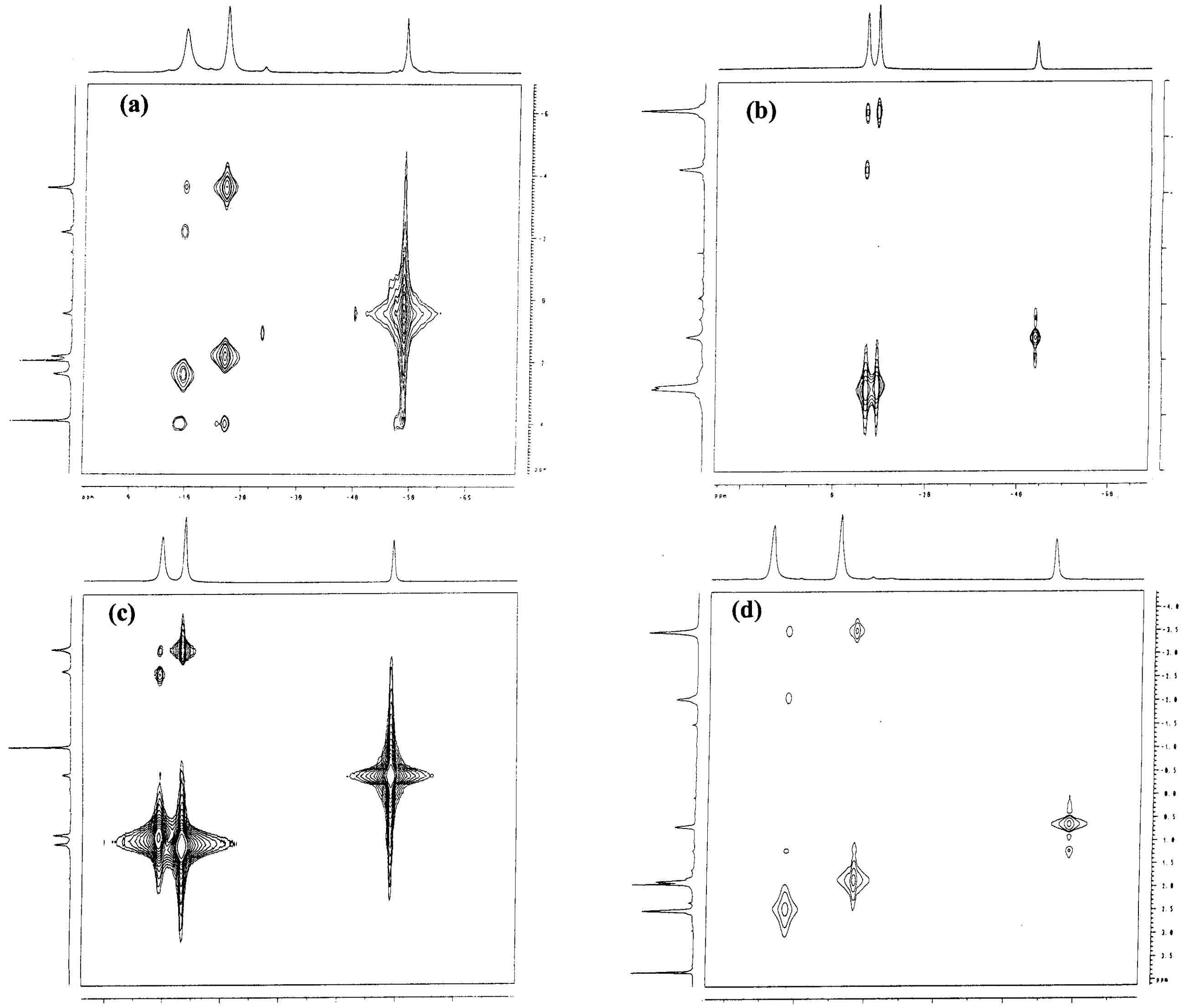

Fig. 3. ^{11}B–^{1}H correlated 2D-NMR spectra for (a) μ,μ′-$Zn(B_5H_8)_2$, (b) μ,μ′-$Hg(B_5H_8)_2$, (c) 2,3-μ-$(SnPh_3)B_5H_8$, and (d) μ,μ′-$Cd(B_5H_8)_2$.

moiety. Such values have not been reported previously. For μ,μ′-$Hg(B_5H_8)_2$, which has been previously described [18], we note from our results a large $^{4}J(^{199}Hg$–$^{1}H)$ coupling of 152 Hz to the bridging proton H(4,5) comparable in magnitude to the two-bond coupling to the terminal protons H(2) and H(3) [$^{2}J(^{199}Hg$–$^{1}H)$] 160 Hz and previously unseen in the lower dispersion 32 MHz spectrum. The coupling is large although ^{4}J and $^{5}J(^{199}Hg$–$^{1}H)$ couplings of 39 Hz have been observed to the pendant methyl groups in μ,μ′-$[(CH_3)_2C_2B_4H_5H_8]_2$-Hg [18]. Also of note is our observation that ^{199}Hg coupling to the distal Hμ atoms in μ,μ′-$Hg(B_5H_8)_2$ is larger than that to the proximal Hμ atoms {$J(^{199}Hg$–$^{1}H\mu_{45}) = 152$ Hz versus $J(^{199}Hg$–$^{1}H\mu_{34,25}) = 100$ Hz}. This is presumably due to enhanced long-range coupling due to the W effect [29]. Direct coupling between adjacent ^{11}B nuclei is known to be quite small when they are H-bridged [30], but coupling through the bridging H atoms is not [31]. Although we were able to discern the presence of ^{113}Cd satellites in the proton spectra of **I**, they were too much overlapped to allow the reporting of $J(^{113}Cd$–$^{1}H)$ values.

Thus, we conclude that for all 2,3-μ derivatives of B_5H_9, the basal boron resonance at low-field arises from B(4,5) and the upfield one from B(2,3). The only other system for which the assignment of the basal boron resonances is the same as ours was for 2,3-μ-$(C_6H_5)_2P$-B_5H_8, although this system is not quite the same in that the bridging moiety, $(C_6H_5)_2P$ is bonded to the boron atoms through two normal two-center, two electron bonds, rather than by a three-center two-electron bond [32]. Using hindsight, the assignments we describe herein are obvious. The downfield resonance is usually broader and this broadening was ascribed to the influence of the metal atom. Now we can see that it really is due to coupling to the bridging hydrogen atoms rather than to the substituent. The assignment of the ^{11}B spectra from comparisons with that of the parent B_5H_9 is not reasonable, because these 2,3-μ-M(B_5H_8) species are formed from the reaction of $[B_5H_8]^-$ salts with complex metal halides. The chemical shifts of the 2,3-μ-M(B_5H_8) systems are more appropriately compared to those of the anion $[B_5H_8]^-$, for which the basal boron resonance is observed at 17 ppm [33]. Actually, when the anion $[B_5H_8]^-$ bonds to bridging metal or metalloid substituents, the electron distribution is changed. One may expect that the boron atom bonded to the metal have higher charge density than the basal boron atoms further away from metal. Thus one would expect the B atoms closest to the metal to be more shielded. This pertains in organolithium compounds when for example in *n*-butyllithium [34] and *n*-propyllithium [35], the resonance for the carbon atom is which closest to the metal is at the highest field, because it is strongly shielded.

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References

[1] (a) T.P. Onak, G.B. Dunks, I.W. Searcy, J. Spielman, Inorg. Chem. 6 (1967) 1465. (b) D.F. Gaines T.V. Iorns, J. Am. Chem. Soc. 89 (1967) 3375. (c) R.A. Geanangel, S.G. Shore, J. Am. Chem. Soc.89 (1967) 6771.

[2] (a) D.F. Gaines, Acc. Chem. Res. 6 (1973) 416. (b) S.G. Shore, Pure Appl. Chem. 69 (1977) 717. (c) N.N. Greenwood, Pure Appl. Chem. 69 (1977) 791.

[3] H.D. Johnson, S.G. Shore, J. Am. Chem. Soc. 93 (1971) 3798.

[4] (a) D.F. Gaines, in: R.W. Parry, G.J. Kodama (Eds.) Boron Chemistry 4, Plenary Lectures at the 4th International Meeting on Boron Chemistry, Salt Lake City, Pergamon Press, Oxford, 1979, pp. 73–82. (b) L.J. Todd, Chapter 4, in: R.N. Grimes (Ed.), Metal Interactions with Boron Clusters, Plenum Press, New York, 1982.

[5] (a) K.B. Gilbert, S.K. Boocock, S.G. Shore, Part 6, Chapter 41, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Oxford, Pergamon Press, 1982, pp. 879–945. (b) J.D. Kennedy, Prog. Inorg. Chem. 32 (1984) 651. (c) L. Barton, D.K. Srivastava, Chapter 8, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.) Comprehensive Organometallic Chemistry II, Pergamon Press, Oxford, 1995, Vol. 1, pp. 275–373.

[6] (a) D.F. Gaines, K.M. Coleson, J.C. Calabrese, J. Am. Chem. Soc. 101 (1979) 3979. (b) D.F. Gaines, K.M. Coleson, J.C. Calabrese, Inorg. Chem. 20 (1981) 2185.

[7] (a) D.F. Gaines, T.V. Iorns, J. Am. Chem. Soc. 92 (1970) 4571. (b) M.A. Nelson, M. Kameda, S.A. Snow, G. Kodama, Inorg. Chem. 21 (1982) 2898.

[8] (a) D.F. Gaines, T.V. Iorns, J. Am. Chem. Soc. 89 (1967) 4249. (b) D.F. Gaines, T.V. Iorns, J. Am. Chem. Soc. 90 (1968) 6617. (c) D.F. Gaines, J. Ulman, Inorg. Chem. 13 (1974) 2792. (d) T.C.Geisler, A.D. Norman, Inorg. Chem. 9 (1970) 2167. (e) A.B. Burg, Inorg. Chem. 13 (1974) 1010. (f) J.B. Leach, G. Oates, S. Tang, T. Onak, J. Chem. Soc. Dalton Trans (1975) 1018. (g) L. Barton, H. Fang, D.K. Srivastava, T.A. Schweitzer, N.P. Rath, Appl. Organomet. Chem. 10 (1996) 183.

[9] (a) A.B. Burg, H. Heinen, Inorg. Chem. 7 (1968) 1021. (b) D.F. Gaines, D.E. Coons, Inorg. Chem. 25 (1986) 364. (c) D.E. Coons, D.F. Gaines, Inorg. Chem. 27 (1987) 1985. (d) R.W. Miller, K.J. Donaghy, J.T. Spencer, Organometallics 10 (1991) 1161. (e) B.H. Goodreau, R.L. Ostrander, J.T. Spencer, Inorg. Chem. 30 (1991) 2066. (f) R.W. Miller, K.T. Donaghy, J.T. Spencer, Phosphorus Sulfur Silicon 57 (1991) 287.

[10] (a) V.T. Brice, S.G. Shore, J. Chem. Soc. Chem. Commun. (1970) 1312, (b) V.T. Brice, S.G. Shore, J. Chem. Soc. Dalton Trans. (1975) 334.

[11] N.N. Greenwood, J.A. Howard, W.S. McDonald, J. Chem. Soc. Dalton Trans. (1975) 334.

[12] N.N. Greenwood, J. Staves, J. Chem. Soc. Dalton Trans. (1977) 1788.

[13] J.D. Kennedy, J. Staves, Z. Naturforsch. Teil B 34B (1979) 808.

[14] N.N. Greenwood, J. Staves, J. Chem. Soc. Dalton Trans. (1978) 1146.

[15] N.N. Greenwood, J. Staves, J. Chem. Soc. Dalton Trans. (1978) 1144.

[16] P.K. Rush, L. Barton, Polyhedron 4 (1985) 1741.

[17] N.W. Alcock, L. Parkhill, M.G.H. Wallbridge, Acta Crystallogr. Sect. C 41 (1985) 716.

[18] N.N. Greenwood, J. Staves, J. Chem. Soc. Dalton Trans. (1977) 1786.

[19] J.C. Calabrese, L.F. Dahl, J. Am. Chem. Soc. 93 (1971) 6042.

[20] D.K. Srivastava, N.P. Rath, L. Barton, Organometallics. 11 (1992) 2263.

[21] N.S. Hosmane, R.N. Grimes, Inorg. Chem. 18 (1979) 2886.

[22] H. Fang, D. Zhao, N.P. Rath, L. Brammer, L. Barton, Organometallics. 14 (1995) 1700.

[23] Presented at BUSA-V-MEX, Guanajuato, Mexico (1996) Paper No. 1, 1996.

[24] D.F. Shriver, M.A. Drezdon, The Manipulation of Air-Sensitive Compounds, John Wiley, New York, 1986.

[25] J. Bould, J.D. Kennedy, M.Thornton-Pett, H. Fang, N.P. Rath and L. Barton (in preparation).

[26] (a) T. Onak, H. Landesman, R.E. Williams, I. Shapiro, J. Phys. Chem. 63 (1959) 1533. (b) J.D. Odom, P.D. Ellis, H.C. Walsh, J. Am. Chem. Soc. 93 (1971) 3529. (c) H.D. Johnson II, S.G. Shore, in: E.L. Muetterties (Ed.), Boron Hydrides, Academic Press, New York, 1975, p. 101.

[27] H. Fang, D. Zhao, L. Brammer and L. Barton, J. Chem. Soc. Chem. Commun. (1994) 1531.

[28] H. Fang, PhD Dissertation, University of Missouri-St. Louis, 1985.

[29] P. Hore, Nuclear Magnetic Resonance, Oxford Science Publications, Oxford University Press, Oxford, 1995.

[30] D.F. Gaines, G.M. Edvenson, B.R. Adams, Inorg. Chem. 26 (1987) 1813.

[31] H. Nöth, B. Wrackmeyer, Chapter 8, in: Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, Springer, Heidelberg, 1978.

[32] B.H. Goodreau, R.L. Ostrander, J.T. Spencer, Inorg. Chem. 30 (1991) 2066.

[33] H.D. Johnson, II, R.A. Geanangel, S.G. Shore, Inorg. Chem. 9 (1970) 908.

[34] G. Fraenkel, A.M. Fraenkel, M.J. Geckle, F. Schloss, J. Am. Chem. Soc. 101 (1979) 4745.

[35] S. Bywater, P. Lachance, D.J. Worsfold, J. Phys. Chem. 79 (1975) 2148.