

The $\text{HMn}_2(\text{CO})_6\text{B}_2$ group in $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$ possesses a configuration similar to that found in $\text{S}_2\text{Fe}_2(\text{CO})_6$ ¹⁶ for which a bent metal-metal bond arising from the overlap of octahedral-type iron orbitals is presumed to be mainly responsible for the molecular geometry with a resulting nonplanar S_2Fe_2 system. Furthermore, the coordination site of the binuclear hydride atom in $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$ corresponds within experimental error to the intersection of the octahedral-type manganese orbitals as determined by the apical carbonyl groups of the $\text{HMn}_2(\text{CO})_6\text{B}_2$ fragment. The similar localized environments of the metal atoms in the $\text{HMn}_2(\text{CO})_6\text{B}_2$ group and the $\text{S}_2\text{Fe}_2(\text{CO})_6$ molecule with the hydrogen in the former compound substituted in place of the bent metal-metal bond in the thio-iron carbonyl complex may be considered as support for the existence of a bent metal-metal bond occupying a regular coordination site in $\text{S}_2\text{Fe}_2(\text{CO})_6$ (and in the structurally related complexes $[\text{C}_2\text{H}_5\text{SFe}(\text{CO})_3]_2$ ¹⁷ and $[(\text{C}_6\text{H}_5)_2\text{PCoC}_5\text{H}_5]_2$ ¹⁸). Other borane metal carbonyl complexes of the type described above are being sought.

needs only $1/2$ electron from each boron to fill the two three-center bonding Mn-H-B orbitals and thereby to obtain the closed-shell configuration. Consequently, each of the two boron atoms has $1\frac{1}{2}$ electrons remaining, of which $3/4$ electron is contributed via three-center Mn-H-B bonds to each of the symmetry-related manganese atoms. Since the three carbonyl groups together with the two hydrogen and two boron atoms can be considered as "effectively" donating $9\frac{1}{2}$ electrons to each of these zerovalent manganese atoms, the binuclear hydrido Mn-H-Mn interaction also may be described in terms of bent three-center MO's (with each of the three MO's constructed from a σ -type metal orbital and the bridging 1s hydrogen orbital), of which again only the bonding one is occupied with $1/2$ electron from each of the two manganese atoms and one from the hydrogen atom. By this electron-counting scheme, in which the electrons in the three-center bonds are delocalized, the symmetry-related manganese atoms also conform to the closed-shell configuration.

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Unsymmetrical Cleavage of Diborane by Methylamine and Dimethylamine

Sir:

Most of the known reactions of diborane with Lewis bases appear, or are believed, to result in symmetrical cleavage of the boron-hydrogen bridge system.¹ Relatively few examples of unsymmetrical cleavage have been reported. Direct reaction of ammonia with diborane produces $\text{H}_2\text{B}(\text{NH}_3)_2^+\text{BH}_4^-$, the best documented example of unsymmetrical cleavage by a nitrogen base.² Conversely, reactions of diborane with methylamines have been reported to produce symmetrical cleavage products, amine boranes.^{3,4}

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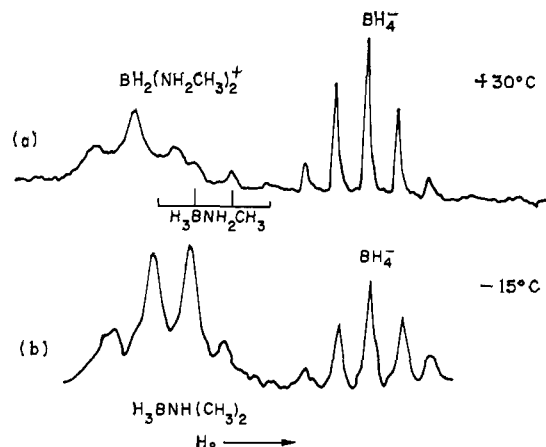


Figure 1. B^{11} n.m.r. spectra of cleavage products: (a) reaction of B_2H_6 with CH_3NH_2 in liquid CH_2NH_2 ; (b) reaction of B_2H_6 with $(\text{CH}_3)_2\text{NH}$ in liquid $(\text{CH}_3)_2\text{NH}$.

We have found that procedures equivalent to those used to prepare $\text{H}_2\text{B}(\text{NH}_3)_2^+\text{BH}_4^-$ ^{2,5} can produce unsymmetrical as well as symmetrical cleavage when B_2H_6 reacts directly with excess CH_3NH_2 or $(\text{CH}_3)_2\text{NH}$ at low temperature (-80 to -90°). Relative yields of cleavage products (estimated from B^{11} n.m.r. spectra) from individual reactions of diborane with CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, and $(\text{CH}_3)_3\text{N}$ were found to be: $\text{H}_2\text{B}(\text{NH}_2\text{CH}_3)_2^+\text{BH}_4^- \gg \text{H}_3\text{BNH}_2\text{CH}_3$; $\text{H}_3\text{BNH}(\text{CH}_3)_2 > \text{H}_2\text{B}(\text{NH}(\text{CH}_3)_2)_2^+\text{BH}_4^-$; $\text{H}_3\text{BN}(\text{CH}_3)_3$, only detectable product.

Figure 1a shows B^{11} n.m.r. spectra of products of direct reaction of B_2H_6 with CH_3NH_2 under conditions cited in ref. 2 and 5. The predominant product, $\text{H}_2\text{B}(\text{NH}_2\text{CH}_3)_2^+\text{BH}_4^-$, is that of unsymmetrical cleavage. Only a barely detectable amount of symmetrical cleavage product, $\text{H}_3\text{BNH}_2\text{CH}_3$, is formed. The coupling constant ($J_{\text{BH}} = 82$ c.p.s.) and the chemical shift ($\delta = 40.5$ p.p.m., with respect to $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$) for the quintet are in agreement with reported values for BH_4^- .⁶ The triplet assigned to $\text{H}_2\text{B}(\text{NH}_2\text{CH}_3)_2^+$ has peak heights in the expected ratio 1:2:1, with $J_{\text{BH}} = 104$ c.p.s. and $\delta = 9.2$ p.p.m. Peaks assigned to the symmetrical cleavage product, $\text{H}_3\text{BNH}_2\text{CH}_3$, were duplicated by an authentic sample of this compound⁷; J_{BH} and δ were in agreement with reported values.⁸

Figure 1b presents B^{11} n.m.r. spectra of products of direct reaction of B_2H_6 with $(\text{CH}_3)_2\text{NH}$ under conditions cited in ref. 2 and 5; J_{BH} and δ of the quartet assigned to the symmetrical cleavage product were in agreement with reported values.⁸ Of the unsymmetrical cleavage product, only BH_4^- could be detected with certainty. In addition to the possibility that the spectrum of $\text{H}_2\text{B}(\text{NH}(\text{CH}_3)_2)_2^+$ most likely overlaps that of $\text{H}_3\text{BNH}(\text{CH}_3)_2$, results discussed below suggest that the spectrum of this ion would not be detected easily at the temperature at which the spectra were obtained.

The spectrum of $\text{H}_2\text{B}(\text{NH}_2\text{CH}_3)_2^+$ is markedly temperature dependent. Below -5° , this ion could not be detected at radiofrequency transmitter powers which produced the well-resolved quintet of BH_4^- . Only at a

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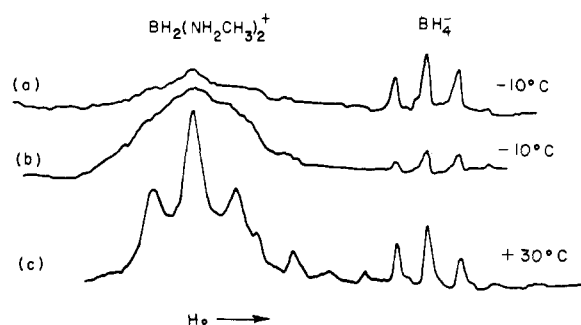


Figure 2. Effect of radiofrequency power temperature on B^{11} n.m.r. spectra of cleavage products whose normal spectra are shown in Figure 1a: (a) radiofrequency power increased to produce noticeable saturation of BH_4^- ; (b) additional increase in radiofrequency power; (c) increased temperature at the same radiofrequency power as (a).

high radiofrequency power, sufficient to produce significant attenuation (saturation) of the BH_4^- signal, was the cation signal detectable, but as a broad band rather than the expected triplet (Figure 2a,b). However, at ambient temperature, a well-defined triplet was observed. Figure 2c is the exaggerated spectrum at high radiofrequency power and Figure 1a is the normal spectrum. The temperature dependence of the $H_2B(NH_2CH_3)_2^+$ spectrum indicates that nuclear quadrupole spin-lattice relaxation⁹ is responsible for the absence of a detectable triplet at low temperature. This appears to be the first such example which has been identified for B^{11} . However, unsymmetrical cleavage of B_2H_6 by $(CH_3)_2SO$ ¹⁰ and B_4H_{10} by tetrahydrofuran¹¹ have been reported recently, and the characteristic triplets of the cations were not detected in the B^{11} n.m.r. spectra. Conceivably, quadrupole relaxation occurs in these systems also.

Discrepancies in reported^{3,4,7,12} properties of $H_3BNH_2CH_3$ and $H_3BNH(CH_3)_2$ are resolved by the present investigation. Authentic samples⁷ of these compounds are crystalline solids at room temperature which show no tendency to decompose *in vacuo*. On the other hand, the products of direct addition of diborane to amine, unsymmetrical cleavage products, which are reported as symmetrical cleavage products in investigations prior to this one,^{3,4} are liquids at room temperature which evolve hydrogen *in vacuo*. The only evidence for symmetrical cleavage in the products of direct reaction in earlier work was based upon molecular weight studies of the CH_3NH_2 and $(CH_3)_2NH$ adducts in liquid ammonia by vapor pressure depression.⁴ We have found, however, that the molecular weight of the product of direct reaction of B_2H_6 with CH_3NH_2 by cryoscopy in liquid CH_3NH_2 is consistent with the formula of the unsymmetrical cleavage product (theory for $H_2B(NH_2CH_3)_2^+BH_4^-$: 89; found: 100).

Results of this study and other recent investigations^{10,11} indicate that unsymmetrical cleavage of the bridge system of diborane by Lewis bases may be more prevalent than previously suspected. One of the factors which determines the course of cleavage is most

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likely steric, considering the change in type of cleavage observed with progressive methyl substitution on nitrogen in the methylamines.¹³ However, more subtle factors are probably involved also. Work on new examples of unsymmetrical cleavage and factors which determine the course of cleavage is continuing in this laboratory.

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged. S. G. S. thanks The Ohio State University for assigned research duty.

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On the Conformation of Horse Heart Ferri- and Ferrocyanochrome *c*

Sir:

Much indirect evidence has accumulated suggesting a difference in the conformations of ferri- and ferrocyanochrome *c*, e.g. separation on cation-exchange resins,¹ differing susceptibility to digestion by bacterial proteinase,² and differing crystal forms.³ This preliminary report on the optical rotatory dispersion (ORD) of cytochrome *c* in the range 195–600 $m\mu$ presents relatively detailed information as to the nature of these differences. Earlier work^{4,5} was neither of sufficient spectral range nor of the resolution required to make the observations reported here.

Horse heart cytochrome *c* (Sigma Chemical Co. Type III) in 0.05 *M* phosphate at pH 7 was treated with β -diphosphopyridine nucleotide and phenazine methosulfate⁶ or sodium dithionite (in the absence of oxygen) to effect reduction or with potassium ferricyanide to complete oxidation. The mixture was then passed through a Sephadex G-75 column to free the protein of reductant or oxidant and their products and to be assured of the monomeric form.⁷ The ORD curves of each sample, initially free of oxidant or reductant, were determined on a Cary Model 60 spectropolarimeter. Solid dithionite was then added to the oxidized protein or crystalline potassium ferricyanide to the reduced protein and the curves were rerun so that the same molecules were studied in both states without a significant change in concentration. This procedure also allowed comparison of the curves in the absence of oxidant or reductant. The concentration of each sample was spectrophotometrically determined in both states of oxidation on a Cary Model 14 spectrophotometer under conditions of sufficiently narrow spectral band widths. Using the extinction coefficients of Van Gelder and Slater,⁶ the calculated concentrations of the same sample in both

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