to observe with certainty a counterpart of the 1604-cm^{-1} band in the deuterated spectra may reflect the extreme sensitivity of these studies to changes in experimental conditions. Mass spectrometric data for the pyrolysis of BD_3CO have not been reported. It is possible that the pyrolysis conditions for the isolation of BD_3 are even more restrictive than for BH_3.

The in-plane-bending force constant of borane was found to be 0.46 mdyn/Å, the stretching force constant 4.08 mdyn/Å. Other molecules where three coordinated boron atoms are bound to terminal hydrogen are borazine and boroxine. The B–H stretching force constants in these molecules are 3.35 and 3.68 mdyn/Å, and the in-plane-bending force constants are 0.55 and 0.65 mdyn/Å, respectively.[29,30]

Borane is most analogous to the CH_3 radical. In CH_3 the in-plane bend was observed at 1396 cm^{-1} and the force constant was found to be 0.32 mdyn/Å.[26] From the above it appears that the E′ assignments for BH_3 are reasonable. The out-of-plane-bending force constant for borane was found to be 0.59 mdyn/Å compared with 0.52 mdyn/Å for borazine,[29] but for the methyl radical a much lower value of 0.18 mdyn/Å was found.[26]

Conclusion

In these experiments weak spectra attributed to BH_3 were obtained from the pyrolysis of borane carbonyl. In order to maximize the BH_3 yield the matrix gas was used as the diluent in the pyrolysis zone. This resulted in a severe thermal load on the window, and particularly on the growing film (5 mW). A great deal of association of borane was expected and observed. As the argon film grew, its thermal conductivity dropped to such a point that association at the surface became complete. Hence there was a maximum tolerable film thickness and also a maximum amount of borane that could be isolated. In order to observe BH_3 the following conditions appear to be necessary. (a) The argon film has to be maintained below 35°K. (b) The matrix gas to borane ratio has to be greater than 1000. (c) Traces of O_2 and H_2O cannot be present. (d) The quartz surface has to be conditioned until an elemental boron surface is formed. (e) The temperature in the pyrolysis zone cannot exceed 850°K or be lower than 700°K. (f) Residence time in the pyrolysis zone has to be less than, or equal to 10^{-3} sec.

If the source and the capacity of the target to bear a larger thermal load can be improved, the amount of borane isolated might be substantially increased. Once this is accomplished, the many short-lived intermediates that make borane's chemistry exciting can be studied by producing them either (a) in the pyrolysis zone and trapping them on the target window, or (b) by codepositing borane and the second reactant in the matrix and allowing diffusion to lead to subsequent reaction.

Acknowledgments. The authors wish to thank M. Neiss and Dr. E. Lory for many helpful discussions. This work has been supported by the Army Research Office, Durham, N. C., and the Advanced Research Projects Agency through the use of the Materials Science Center at Cornell University, Ithaca, N. Y.

(29) K. E. Blick, J. W. Dawson, and K. Niedenzu, *Inorg. Chem.*, **9**, 1416 (1970).

(30) F. A. Grimm, L. Barton, and R. F. Porter, *ibid.*, **7**, 1309 (1968).

Temperature Dependence of the Proton Nuclear Magnetic Resonance Spectra of Copper(I) Borane Complexes, $B_3H_8^-$ Salts, and Icosahedral Carboranes. Quadrupole-Induced Spin Decoupling. Fluxional Behavior

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Abstract: Variable-temperature proton magnetic resonance spectroscopy has revealed efficient boron–hydrogen spin decoupling due to quadrupole-induced ^{10}B and ^{11}B spin relaxation in TlB_3H_8, $(CH_3)_4NB_3H_8$, $[(C_6H_5)_3P]_2CuBH_4$, $[(C_6H_5)_3P]_2CuB_3H_8$, *o*-carborane, and *m*-carborane. An additional temperature dependence of the proton nmr spectrum of $[(C_6H_5)_3P]_2CuB_3H_8$ provides unequivocal evidence for slowed intramolecular exchange in a $B_3H_8^-$ adduct. A total nmr line-shape analysis of the spectral behavior for $[(C_6H_5)_3P]_2CuB_3H_8$ allows calculation of the rate of pseudorotation as a function of temperature.

In a host of boron hydrides and related compounds, particularly metal derivatives of borane anions, there exists an apparent discrepancy between the crystal structure and the solution structure as studied by nuclear magnetic resonance (nmr) spectroscopy.[1] For ex-

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† Alfred P. Sloan Research Fellow, 1971–1973.

(1) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

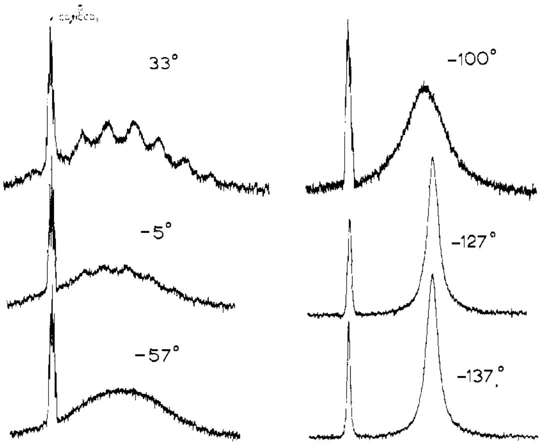


Figure 1. The pmr spectrum (60 MHz) of TlB_3H_8 in 50% CD_3OD-50% CD_3COCD_3 (v/v) as a function of temperature. The width at half height ($W_{1/2}$) of the B_3H_8 resonance is 10 Hz at −127°.

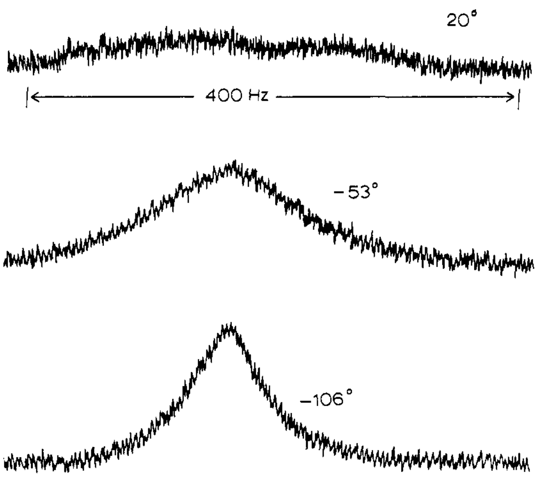
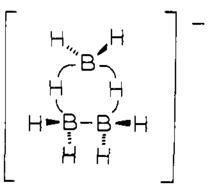


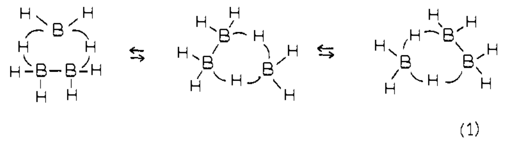
Figure 2. The temperature dependence of the pmr spectrum (60 MHz) due to the BH_4 hydrogens in $[(C_6H_5)_3P]_2CuBH_4$.

ample, the crystal structure for the $B_3H_8^-$ anion (I)



I

reveals clearly three different types of hydrogen atoms and two different kinds of boron atoms.[2] However, the ^{11}B and ^1H nmr spectra of I[3] in solution, *e.g.*, in TlB_3H_8, indicate equivalent borons and equivalent hydrogens with the respective spin–spin splitting patterns reflecting coupling of three equivalent borons to eight equivalent hydrogens. This behavior could be rationalized by rapid fluxional behavior (pseudorotation) on the nmr time scale *via* a mechanism that does not involve complete boron–hydrogen bond scission (eq 1)[4] or by a fortuitous coincidence of the respective ^{11}B and ^1H chemical shifts. Quantum mechanical "tunneling" has also been suggested to rationalize the equivalence of hydrogens in BH_4^- derivatives.[5]



(1)

In an attempt to determine the cause of the equivalence of borons or hydrogens in certain boron compounds, we have investigated the temperature dependence of the ^1H nmr spectra (60 MHz) of $[(C_6H_5)_3P]_2CuBH_4$,[6] TlB_3H_8,[3a] $(CH_3)_4NB_3H_8$,[3a] and $[(C_6H_5)_3P]_2CuB_3H_8$ (II).[3a] Two phenomena are observed. In all of the above cases, nmr spectral simplification was effected at lower temperatures (different for each compound) due to quadrupole-induced ^{10}B and ^{11}B spin relaxation ("thermal" decoupling).[3a,6,7] Indeed, thermal decoupling appears to be a general phenomenon among boranes. Evidence is also presented below for the effect in *o*- and *m*-carborane [1,2- and 1,7-dicarba-*closo*-dodecaborane(12)]. In II, additional asymmetric broadening and separation of the B_3H_8 proton resonance into several peaks at about −97° provides unequivocal evidence for the slowing of the pseudorotational rate process (eq 1) on the nmr time scale.

Results and Discussion

Examination of the pmr spectrum (60 MHz) of TlB_3H_8 (Figure 1) in 50% CD_3OD-50% CD_3COCD_3 (v/v) at room temperature revealed a typical ten-line multiplet (two outer peaks lost in the noise) reflecting eight *equivalent* hydrogens coupled to three *equivalent* ^{11}B nuclei ($I = {}^3/_2$; $J_{B-H} = 33$ Hz). Upon lowering the temperature, the spin–spin splitting pattern first coalesced and then sharpened into a constant-shape one-line spectrum at −127° (Figure 1). No evidence for any other B_3H_8 resonances was obtained at high signal amplification by sweeping 20 ppm to low and high field of the singlet observed at −127°. Below −137° (Figure 1), crystallization occurred.

$(CH_3)_4NB_3H_8$ in 50% CD_3OD-50% CD_3COCD_3 (v/v) and in 50% $(CD_3)_2NCDO$-50% CD_3COCD_3 (v/v) exhibited exactly analogous spectral transitions as TlB_3H_8, indicating at least in these two cases no significant effect of solvent or cation on the observed phenomenon.

Observation of the pmr spectrum (60 MHz) of $[(C_6H_5)_3P]_2CuBH_4$ in 50% $CDCl_3$-50% CD_2Cl_2 (v/v) at 20° revealed an extremely broad, almost indetectable resonance due to BH_4, indicating extensive ^{10}B–^1H and ^{11}B–^1H spin–spin coupling (Figure 2).[6] Upon lowering the temperature, the spectrum sharpens significantly (Figure 2) giving at −106° a broad singlet resonance of Lorentzian line shape. Crystallization occurred at −115°. This sharpening is again analogous to the behavior observed for TlB_3H_8 and $(CH_3)_4NB_3H_8$ discussed above.

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(2) C. R. Peters and C. E. Nordman, *J. Amer. Chem. Soc.*, **82**, 5758 (1960).

(3) (a) H. Beall, C. H. Bushweller, W. J. Dewkett, and M. Grace, *ibid.*, **92**, 3484 (1970); (b) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *ibid.*, **81**, 4496 (1959).

(4) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 117 (1959).

(5) R. A. Ogg, Jr., and J. D. Ray, *Discuss. Faraday Soc.*, **19**, 239 (1955).

(6) M. Grace, H. Beall, and C. H. Bushweller, *Chem. Commun.*, 701 (1970).

(7) D. Marynick and T. Onak, *J. Chem. Soc. A*, 1160 (1970).

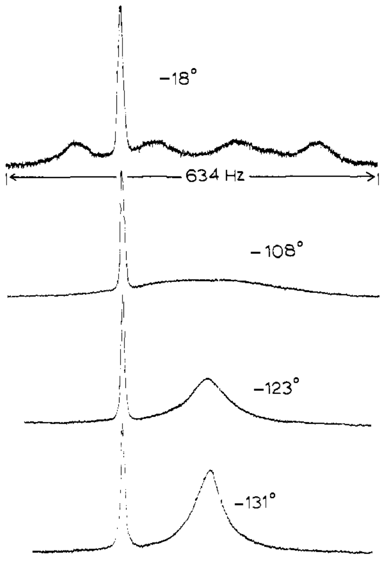
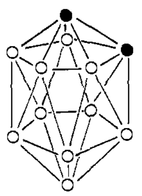
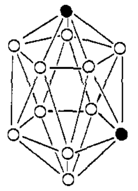


Figure 3. The temperature dependence of the pmr spectrum of *o*-carborane (III). Solvent impurity peaks due to CHD_2COCD_3, CHD_2OD, and CD_3OH have been subtracted from the spectra.

Examination of the pmr spectrum of *o*-carborane [III; 1,2-dicarba-*closo*-dodecaborane(12)] at 25° in 50% CD_3OD–50% CD_3COCD_3 (v/v) (Figure 3) shows a relatively sharp singlet due to the two C–H groups and four broad resonances due to the ten B–H groups. Since the various ^{11}B–^{1}H coupling constants (as determined from the ^{11}B nmr spectrum) are known to vary significantly (*i.e.*, 148–177 Hz)[1] depending on the type of boron, the pmr spectrum is deceptively simple (Figure 3) owing to small chemical shifts between the different kinds of hydrogens. However, upon lowering the temperature, the observed spin–spin splitting pattern coalesced and the B–H resonance sharpened into a broad singlet of Lorentzian line shape. Separated B–H pmr resonances could not be discerned at the lowest temperature at which good spectra were obtained. The C–H resonance did not undergo any dramatic changes except to sharpen somewhat at low temperatures (Figure 3), indicating the elimination of weak boron to C–H proton coupling. The pmr spectrum of *m*-carborane [IV, 1,7-dicarba-*closo*-dodecaborane(12)] in 50% CD_3OD–50% CD_3COCD_3 (v/v) was observed to be more complicated than *o*-carborane at high temperatures, indicating greater proton chemical shifts than in *o*-carborane. However, upon lowering the temperature, the spectrum collapsed in essentially the same fashion as in *o*-carborane, giving a broad asymmetric singlet resonance at very low temperatures.



III



IV

● ≡ C-H
○ ≡ B-H

The above-described phenomenon, *i.e.*, a sharpening of the pmr spectrum of boron–hydrogen compounds at *lower temperatures*, appears to be general. This behavior is inconsistent with intramolecular exchange processes which would be expected to be slower at lower temperatures resulting in a *more complicated* spectrum. These spectral transitions would seem to be best rationalized by more rapid quadrupole-induced ^{11}B and ^{10}B spin relaxation at lower temperatures effectively decoupling boron from hydrogen.[8] Although unequivocal examples of quadrupole-induced ^{11}B spin relaxation have only recently been reported,[3a,6,7] the effect of the ^{14}N quadrupole is known, *e.g.*, in nitrogen trifluoride,[9] pyrrolidine hydrochloride,[10] and the methylammonium ion.[11] The implication of the results reported here is clear. Boron quadrupolar relaxation at an appropriate temperature provides effectively an *in situ* heteronuclear spin decoupler giving more simplified nmr spectra. Such behavior should be useful in structural and mechanistic studies.

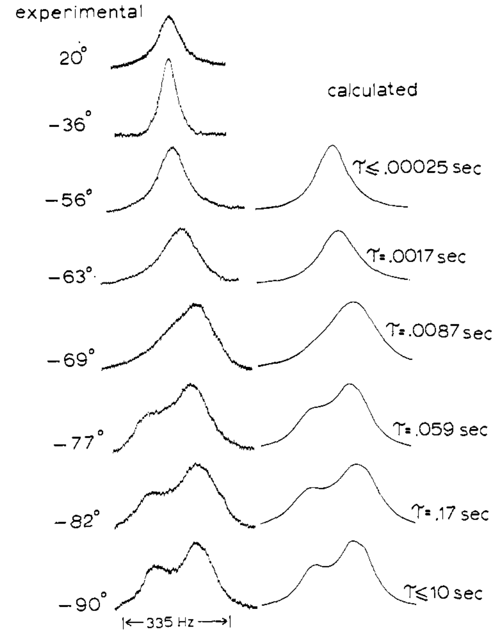


Figure 4. The experimental and theoretical pmr spectra (60 MHz) of the B_3H_8 protons in II as a function of temperature in 50% $CDCl_3$–50% CD_2Cl_2 (v/v). τ = lifetime of a proton at any site in the B_3H_8 moiety.

$[(C_6H_5)_3P]_2CuB_3H_8$(II) exhibited behavior analogous to the above results, but additional nmr spectral changes provide unequivocal evidence for slowed intramolecular exchange at low temperatures. Examination of the pmr spectrum (60 MHz) of II in 50% $CDCl_3$–50% CD_2Cl_2 (v/v) revealed a broad resonance due to the B_3H_8 hydrogens (Figure 4). The boron–hydrogen coupling is not resolved in II at 20° in contrast to TlB_3H_8 (Figure 1). Upon lowering the temperature to *ca.* −14°, the B_3H_8 proton resonance sharpened significantly (Figure 4) but at substantially higher temperatures than for TlB_3H_8 or $(CH_3)_4NB_3H_8$. It is clear that quadrupole-induced ^{11}B and ^{10}B spin relaxation is more effective at higher temperatures in II than in TlB_3H_8 and $(CH_3)_4NB_3H_8$. However, at temperatures below

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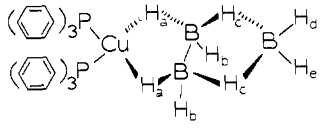
[8] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I and II, Pergamon Press, Elmsford, N. Y., 1965.

[9] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **81**, 1084 (1959); see also J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

[10] J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 4495 (1956).

[11] R. A. Ogg and J. D. Ray, *J. Chem. Phys.*, **26**, 1340 (1957).

−60°, the B_3H_8 resonance broadened in an asymmetric fashion giving a series of separate proton resonances at −97° (Figure 4) and indicating clearly hydrogens in different chemical environments. These spectral changes are consistent with the slowing of a rate process, *i.e.*, pseudorotation of the B_3H_8 moiety, on the pmr time scale and the spectrum at −97° is consistent with the static crystal structure[12] of II shown below. Although each individual resonance is not resolved, the spectrum of II at −97° (Figure 4) is consistent with three different types of terminal hydrogens (*e.g.*, H_b, H_d, and H_e in II) giving the relatively more broad downfield portion of the spectrum and only two different kinds of bridging hydrogens (H_a, H_c in II) giving the more intense upfield peak. Examination of the 100-MHz spectrum of the B_3H_8 resonances at −90° revealed clearly a series of five broad resonances, again consistent with a static form for II. Chemical shifts and widths at half height ($W_{1/2}$) obtained from the 100-MHz B_3H_8 spectrum were used to calculate a theoretical spectrum for static II. The best "fit" at −90° was obtained using the data compiled in Table I. In this analysis (Table I), it was assumed that "thermal decoupling" is effective, *i.e.*, that boron–hydrogen coupling is not present. The substantial widths at half height (Table I) observed for the various B_3H_8 proton resonances suggest that ^{10}B and ^{11}B quadrupole relaxation may shorten the proton spin–spin relaxation time (T_2), broadening the peaks. Proton–proton coupling and incomplete ^{11}B and ^{10}B or ^{63}Cu and ^{65}Cu quadrupole-induced spin decoupling may also contribute to the broadening. Examination of the temperature dependence of the pmr spectrum of II at significantly different concentrations, *e.g.*, 0.1 and 0.3 *M*, produced no apparent changes, which speaks against an intermolecular mechanism for the exchange process.



II

Table I. Nmr Spectral Parameters (^1H; 100 MHz) for the B_3H_8 Hydrogens of $[(C_6H_5)_3P]_2CuB_3H_8$

Rel chemical shift, Hz	$W_{1/2}$, Hz	Rel population
0[a]	80	2
70	80	2
150	160	2
250	94	1
280	94	1

[a] Relative chemical shift of highest field peak in the spectrum (100 MHz); all other chemical shifts are downfield from 0 Hz. The considerable width at half height of the resonance at 150 Hz might allow assignment to H_a (II) and results from the effect of quadrupole-induced spin relaxation in ^{62}Cu ($I = {}^3/_2$) and ^{65}Cu ($I = {}^3/_2$) on the H_a resonance.

The behavior of II is in contrast to TlB_3H_8 and $(CH_3)_4NB_3H_8$ in two important ways. In II, sharpening of the B_3H_8 proton resonance occurs at substantially higher temperatures than in TlB_3H_8 and $(CH_3)_4NB_3H_8$, indicating more effective quadrupole-induced ^{10}B and ^{11}B spin relaxation for II. In a qualitative sense, such behavior is not unexpected. Both intermolecular and intramolecular (*e.g.*, along a covalent bond) electric field gradients provide a mechanism for quadrupole relaxation.[8] In the samples used above, intermolecular electric field gradients are most likely averaged to zero *via* rapid molecular tumbling. However, intramolecular electric field gradients are not averaged to zero. It is clear that the effective size of II is greater than TlB_3H_8 or $(CH_3)_4NB_3H_8$, which would lead to a greater molecular correlation (reorientation) time[8] for II and more rapid ^{11}B and ^{10}B quadrupole relaxation in II. Since covalent bonding of copper to B_3H_8 in II is stronger than the corresponding bonding in TlB_3H_8 and $(CH_3)_4NB_3H_8$, it would be expected that electric field gradients along covalent bonds in II would be greater than in TlB_3H_8 or $(CH_3)_4NB_3H_8$. Therefore, quadrupole relaxation should be more rapid in II and the effect on the dynamic nmr spectrum should be observed at a higher temperature as observed (Figures 1 and 4).

The second important behavioral deviation for II as compared to TlB_3H_8 and $(CH_3)_4NB_3H_8$ involves the separation of the B_3H_8 resonance into several peaks at low temperature (Figure 4) providing unequivocal evidence for the slowing of the B_3H_8 pseudorotation on the nmr time scale. The relatively sharp singlets observed for the B_3H_8 proton resonance in the TlB_3H_8 and $(CH_3)_4NB_3H_8$ at −137° (Figure 1) are inconsistent with a static form for I and suggest strongly that the rate of B_3H_8 pseudorotation is still rapid on the nmr time scale even at these low temperatures. An upper limit to the potential barrier to pseudorotation in TlB_3H_8 and $(CH_3)_4NB_3H_8$ can be calculated to be approximately 6 kcal/mol.

In contrast to TlB_3H_8 and $(CH_3)_4NB_3H_8$, a total nmr line-shape analysis for the spectral changes observed for II from −97 to −40° (Figure 4) gave the rate of B_3H_8 pseudorotation as a function of temperature. In the computation of the theoretical dynamic nmr spectra,[13] probabilities of transitions from one nmr line to another must be introduced. These probabilities will depend on the mechanism of pseudorotation and the resultant calculated nmr line shapes will be a function of the mechanism of pseudorotation. The kinetic model used for generation of the theoretical spectra is cleavage of the Cu–H bonds followed by *total scrambling* of the B_3H_8 moeity (eq 1) and subsequent re-forming of the Cu–H bonds. In this model, the transition probability from one site to a final site will be proportional to the relative population of protons at the terminal site. One important consequence of this kinetic model is that one need not assign specific protons in II to each peak in the spectrum (Table I). Theoretical nmr spectra[13] generated using this model were matched by superposition to the experimental spectra of II obtained at various temperatures (Figure 4) at 60-MHz operating frequency.[14] The chemical

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(12) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969).

(13) C. H. Bushweller, J. Golini, G. U. Rao, and J. W. O'Neil, *J. Amer. Chem. Soc.*, **92**, 3055 (1970); see ref 5 in the above paper.

(14) The calculated nmr spectra were matched to the experimental spectra at 60-MHz operating frequency because of superior temperature control in a custom-built variable-temperature 60-MHz probe in use in this laboratory.

shift differences between the various peaks observed at 100 MHz (Table I) were reduced by the factor 60/100 in order to calculate the theoretical spectra at 60 MHz. Experimental and calculated nmr spectra are illustrated in Figure 4. In Figure 4, τ is the lifetime of a proton at any site in the B_3H_8 moeity. From the data at $-77°$, the free energy of activation ($\Delta G^{\ddagger}$) for disappearance of a proton from any B_3H_8 site (II) is calculated to be 10.0 ± 0.5 kcal/mol. For two reasons, we are hesitant to report an Arrhenius energy of activation (E_a) for the process in question. First, the temperature dependence of the various chemical shifts (Table I) for the B_3H_8 moeity is not known. Second, the temperature dependence of the various widths at half height (Table I) is not known and may be significant in light of the ^{10}B and ^{11}B quadrupole relaxation. The unknown magnitudes of these sources of error must be taken into account when perusing the τ values in Figure 4.

Another kinetic model based on Cu–H bond scission and only *one step* of pseudorotation was used to generate theoretical spectra. Peak assignments were necessary for this model and were made by analogy[1] but still somewhat arbitrarily for II (*e.g.*, H_a, 150; H_b, 70; H_c, 0; H_d or H_e, 250; and H_d or H_e, 280 Hz in Table I). The resultant calculated spectra in regions of partial peak collapse were essentially superimposable on those calculated using the total-scrambling model. Thus, a choice of mechanism is apparently impossible at least at 60 MHz. Variable-temperature nmr spectra taken at substantially higher operating frequency, *e.g.*, 220 or 300 MHz, may allow a mechanism selection.

The apparently much slower rate of B_3H_8 pseudorotation in II as compared to TlB_3H_8 and $(CH_3)_4NB_3H_8$ can be attributed to the covalently bonded Cu in II. The stronger Cu–H covalent bonds in II can be pictured as a "lock" on the pseudorotation rate process. In $B_3H_8^-$ adducts in which the pseudorotatory rate is slow at room temperature,[15] the metal–hydrogen covalent bonding is probably even stronger.

Experimental Section

Variable-temperature nmr spectra were obtained using a Varian HR-60A spectrometer equipped with a special custom-built variable-temperature probe. Temperature measurements were made simultaneously with the recording of an nmr spectrum using a calibrated copper–constantan thermocouple installed permanently in the probe. Temperature measurements are accurate to ±0.1° at the sample and the temperature gradient in the sample region is ±0.1°/3 in. at $-120°$. Spectral calibrations were performed using the audiomodulation technique.

$[(C_6H_5)_3P]_2CuBH_4$ was prepared by the method of Cariati and Naldini.[16]

$[(C_6H_5)_3P]_2CuB_3H_8$ (II) was prepared according to the procedure of Lippard and Ucko.[17]

TlB_3H_8 was prepared by the method of Amberger and Gut.[18] $(CH_3)_4NB_3H_8$ was used as received from Strem Chemicals, Danvers, Mass. *o*- and *m*-carboranes were donated by Olin Mathieson Chemical Corp. Theoretical nmr spectra were calculated using an RCA Spectra 70/46 computer.

Acknowledgment. For support of this research, H. B. is grateful to the Petroleum Research Fund, administered by the American Chemical Society, and C. H. B. to the Research Corporation and the National Science Foundation. We thank Dr. H. Schroeder of the Olin Research Center for carborane samples, the Worcester Area College Computation Center for donated computer time, and F. H. Bissett at the U. S. Army Natick Laboratories for the 100-MHz spectra.

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