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Stereodynamics of $L_2CuB_3H_8$. Rate of $B_3H_8^-$ Rearrangement as a Function of L

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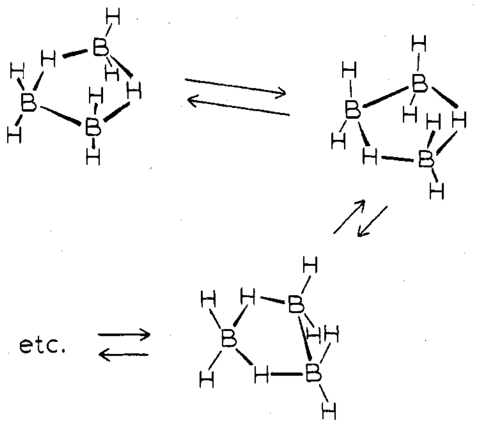
In previous papers, we reported changes in the ^1H DNMR spectra of various triborohydride ion ($B_3H_8^-$) derivatives which may be attributed to two fundamentally different rate processes.[2,3] One phenomenon involves quadrupole-induced ^{10}B and ^{11}B spin relaxation which becomes more efficient with increasing solution viscosity and/or decreasing temperature and leads to eventual decoupling of ^{10}B and ^{11}B from ^1H and a *simplification* of the ^1H DNMR spectra.[2,3] The other phenomenon involves a slowing of $B_3H_8^-$ "pseudorotation" or rearrangement on the DNMR time scale and a separation of the ^1H DNMR spectrum into several signals corresponding to protons in different environments in an essentially static $B_3H_8^-$ system.[2,3] For example, the ^1H DNMR spectra of TlB_3H_8 and $(CH_3)_4NB_3H_8$ show a typical ten-line multiplet for the $B_3H_8^-$ protons at 33 °C which collapses to a relatively sharp *singlet* at −137 °C consistent with efficient quadrupole-induced boron spin relaxation. The observation of a singlet resonance at −137 °C reveals all $B_3H_8^-$ protons to be equivalent due most likely to *rapid* $B_3H_8^-$ rearrangement on the DNMR time scale (eq 1). In contrast, the $B_3H_8^-$ proton resonance of $[(C_6H_5)_3P]_2CuB_3H_8$ shows spectral sharpening from room temperature to about −40 °C (i.e., quadrupole-induced boron spin relaxation) but at lower temperatures (−40 to −90 °C) broadens and separates into several ^1H resonances consistent with slowing $B_3H_8^-$ rearrangement on the DNMR time scale [eq 2; L = $(C_6H_5)_3P$].



(1)

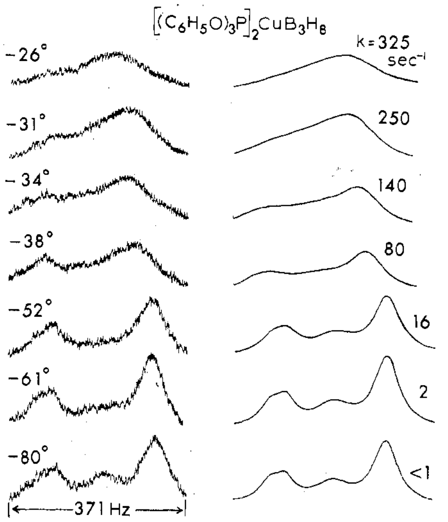
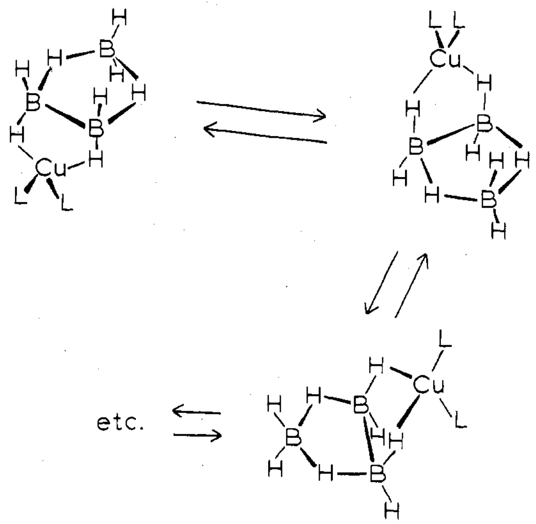


Figure 1. The ^1H DNMR spectra (60 MHz) of $[(C_6H_5O)_3P]_2CuB_3H_8$ in 50% $CDCl_3$/50% CD_2Cl_2 (v/v) and theoretical spectra calculated as a function of the rate of $B_3H_8^-$ scrambling (*k* is the first-order rate constant for disappearance of a proton from any site on the $B_3H_8^-$ moiety).



(2)

Thus, it appears that the upper limit to the barrier to $B_3H_8^-$ scrambling in the "free" $B_3H_8^-$ anion [i.e., TlB_3H_8 and $(CH_3)_4NB_3H_8$] is below 6.5 kcal/mol consistent with recent theoretical calculations.[4] It is also apparent that complexation of $B_3H_8^-$ in $[(C_6H_5)_3P]_2CuB_3H_8$ provides an effective "brake" on $B_3H_8^-$ scrambling and this rate process slows significantly relative to TlB_3H_8 and $(CH_3)_4NB_3H_8$.[2] In contrast to these systems, the ^{11}B NMR spectrum of the $(OC)_4MB_3H_8^-$ ion (M = Cr, Mo, W) reveals a *static* B_3H_8 moiety at room temperature.[5]

In light of these observations, it was intriguing to consider what effect variation of the electron-donating properties of L (eq 2) would have on the rate of $B_3H_8^-$ rearrangement in $L_2CuB_3H_8$.

Examination of the ^1H DNMR spectrum (60 MHz) of the $B_3H_8^-$ protons of $[(C_6H_5O)_3P]_2CuB_3H_8$ in 50% $CDCl_3$/50% CD_2Cl_2 (v/v) at room temperature showed a broad resonance which first sharpened at lower temperatures followed by asymmetric broadening and separation into several resonances by −80 °C (Figure 1). The spectrum of $[(C_6H_5O)_3P]_2CuB_3H_8$ at −80 °C (Figure 1) is consistent with slow $B_3H_8^-$ rearrangement [eq 2; L = $(C_6H_5O)_3P$] on the DNMR time scale. A complete ^1H DNMR line shape analysis for the $B_3H_8^-$ group of $[(C_6H_5O)_3P]_2CuB_3H_8$ was performed in exactly the same manner as reported previously for $[(C_6H_5)_3P]_2CuB_3H_8$.[2] Chemical shift values, widths at half-height, and relative peak areas are compiled in Table I. The kinetic model used to simulate the exchange-broadened spectra, e.g., −26 to −61 °C, is the random exchange system employed previously for

Table I. ^{1}H DNMR Parameters (60 MHz) for the Static $B_3H_8^-$ Group in $L_2CuB_3H_8$

L	Rel chem shift,^{a} ppm	$W_{1/2}$, Hz	Rel area under peak
$(C_6H_5O)_3P$	0.00	92	4
	1.52	143	2
	3.02	50	1
	3.44	50	1
$(C_6H_5)_3As$	0.00	96	2
	0.57	108	2
	1.02	64	2
	2.70	60	2

^{a} The resonance at 0.00 ppm is the highest field peak in the $B_3H_8^-$ spectrum.

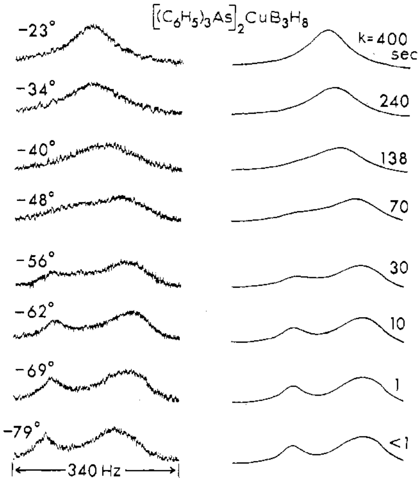


Figure 2. The ^{1}H DNMR spectra (60 MHz) of $[(C_6H_5)_3As]_2CuB_3H_8$ in 50% $CDCl_3$/50% CD_2Cl_2 (v/v) and theoretical spectra calculated as a function of the rate of $B_3H_8^-$ scrambling (see caption to Figure 1).

$[(C_6H_5)_3P]_2CuB_3H_8$[2]. Similar behavior was observed for $[(C_6H_5)_3As]_2CuB_3H_8$ (Figure 2) in the same solvent system although the relative chemical shift values differ (Table I). Dissolution of $[(C_6H_5)_3Sb]_3CuB_3H_8$ and $[(C_6H_5)_3P]_2AgB_3H_8$ in a variety of solvents resulted in decomposition (gas evolution) and it was not possible to obtain reliable DNMR spectra of these complexes.

Although the complete DNMR line shape analyses illustrated in Figures 1 and 2 are subject to errors discussed previously for $[(C_6H_5)_3P]_2CuB_3H_8$,[2] it is possible to use the derived rates of $B_3H_8^-$ exchange to obtain activation parameters for this rate process. Those activation parameters for $L_2CuB_3H_8$ [L = $(C_6H_5)_3P$, $(C_6H_5O)_3P$, $(C_6H_5)_3As$] and related compounds are compiled in Table II.

Table II. Activation Parameters for $B_3H_8^-$ Rearrangement

Compd or ion	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, gibbs	$\Delta G^{\ddagger}$, kcal/mol (T, °C)	Ref
$(CO)_4MB_3H_8^-$ (M = Cr, Mo, W)			>16^a	5
$[(C_6H_5O)_3P]_2CuB_3H_8$	14 ± 3	10 ± 8	11.8 ± 0.5 (−51)	This work
$[(C_6H_5)_3As]_2CuB_3H_8$	13 ± 3	4 ± 8	11.8 ± 0.5 (−48)	This work
$[(C_6H_5)_3P]_2CuB_3H_8$	12 ± 3	11 ± 8	10.2 ± 0.5 (−69)	2
TlB_3H_8			<6.5^b	2
$(CH_3)_4NB_3H_8$			<6.5^b	2

^{a} Rearrangement is slow at room temperature. ^{b} Rearrangement is fast at −137 °C.

Although the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in Table II must be viewed with discretion due to the possibility of systematic errors in the DNMR line shape analyses,[2] the generally positive values of $\Delta S^{\ddagger}$ are consistent with at least a partial dissociation (e.g., Cu–H bond scission) in the rate-determining step for $B_3H_8^-$ rearrangement. Since the values of $\Delta G^{\ddagger}$ (Table II) are usually less subject to systematic errors, it is instructive to consider these. The first observation that one makes after a perusal of Table II is that the three different ligands of the $L_2CuB_3H_8$ complexes are not dramatically different in their effect on the rate of $B_3H_8^-$ scrambling. $(C_6H_5O)_3P$ and $(C_6H_5)_3As$ are very comparable while $(C_6H_5)_3P$ induces a somewhat faster rate of rearrangement than the other two. A simple model for the effectiveness of L_2Cu to "lock" the $B_3H_8^-$ pseudorotatory rate process (eq 2) could be based on the effective positive charge on copper. As the positive charge on copper increases, binding to $B_3H_8^-$ would become stronger and the rate of scrambling will slow down. The effective positive charge on copper will in turn depend on the electron-donating ability of L. The greater the propensity of L to donate electron density to copper, the lower the positive charge is on copper and the less efficient L_2Cu is as a "brake" to $B_3H_8^-$ rearrangement. Based on a π-acceptor theory[6] of electronic effects, the order of ability to accept electron density for the ligands of interest is $(C_6H_5O)_3P > (C_6H_5)_3As > (C_6H_5)_3P$. Using a σ-donor model for electron donation,[7] the order of effective basicity is $(C_6H_5)_3P > (C_6H_5)_3As > (C_6H_5O)_3P$. Using either model, $(C_6H_5)_3P$ is less effective than $(C_6H_5)_3As$ and $(C_6H_5O)_3P$ in net electron withdrawal from copper leading to a decreased positive charge on copper in $[(C_6H_5)_3P]_2CuB_3H_8$ and a faster rate of rearrangement as compared to the $(C_6H_5O)_3P$ and $(C_6H_5)_3As$ analogues (Table II). The very similar rates of rearrangement in the $(C_6H_5O)_3P$ and $(C_6H_5)_3As$ derivatives (Table II) point up the possible inadequacy of the above model. However, the barrier differences (Table II) are so small as to obscure subtle differences in the effect of the various ligands.

Experimental Section

$L_2CuB_3H_8$ complexes were prepared by the general method of Lippard and Ucko[8] which is itself a modification of the method of Cariati and Naldini.[9] Elemental analyses and spectroscopic data are consistent with the structures of the individual complexes.

The 60-MHz ^{1}H DNMR spectra were obtained using a Varian HR-60A NMR spectrometer equipped with a custom-built variable-temperature probe.[10] Theoretical DNMR spectra were calculated using DEC PDP-10 and RCA Spectra 70/46 computers and plotted using a Calcomp plotter as described previously.[2]

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Registry No. $((C_6H_5O)_3P)_2CuB_3H_8$, 34652-39-6; $((C_6H_5)_3As)_2CuB_3H_8$, 12376-41-9; $B_3H_8^-$, 33055-82-2.

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