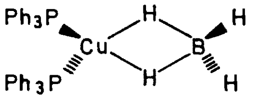
"Thermal" Decoupling and Apparent Rapid Intramolecular Exchange in $(Ph_3P)_2CuBH_4$: ^1H Nuclear Magnetic Resonance Study

By MICHAEL GRACE, HERBERT BEALL,* and C. HACKETT BUSHWELLER
(*Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts* 01609)

Summary The sharpening of the ^1H n.m.r. spectrum of the BH_4 hydrogens of $(Ph_3P)_2CuBH_4$ into a singlet resonance at low temperature indicates efficient quadrupole induced ^{10}B and ^{11}B spin relaxation ("thermal" decoupling) and apparent rapid intramolecular exchange on the ^1H n.m.r. time scale at $-110°$.

AVAILABLE n.m.r. spectra (^{11}B and ^1H) of various metal derivatives of BH_4^- in solution indicate equivalent borohydride hydrogens although these hydrogens are nonequivalent in the pertinent crystal structures. This behaviour suggests a rapid intramolecular exchange process on the n.m.r. time scale.



(I)

In order to determine the nature of this apparently rapid rate process, we investigated the temperature dependence of the ^1H n.m.r. spectrum (60MHz) of $(Ph_3P)_2CuBH_4$ (I)[1] in 50% $CDCl_3$–50% CH_2Cl_2 (v/v) as solvent. Examination of the ^1H n.m.r. spectrum of the BH_4 hydrogens of (I) at 25° reveals an extremely broad, almost indetectable resonance indicating extensive ^{10}B and ^{11}B coupling to hydrogen (Figure). Upon lowering the temperature, the spectrum sharpens significantly (Figure) giving a singlet of Lorentzian line shape at $-106°$. Crystallization occurred at $-115°$. The sharpening of the BH_4 proton resonance at low temperatures indicates effective quadrupole induced ^{10}B and ^{11}B spin relaxation ("thermal" decoupling). The singlet resonance for the BH_4 hydrogens at $-106°$ suggests a rapid intramolecular exchange process or equivalence of all hydrogens in a static form of (I). Investigations at lower temperature may shed some light on this problem.

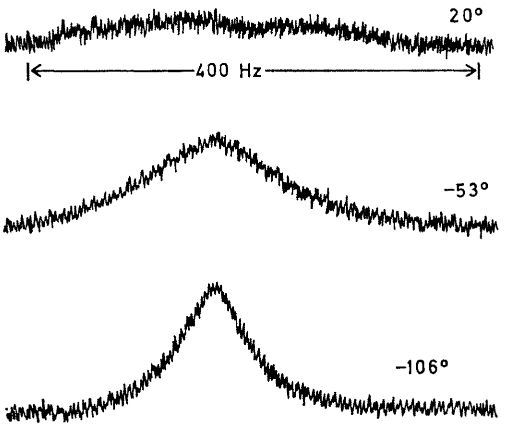


FIGURE. *The temperature dependence of the* ^1H *n.m.r.* (60*MHz*) *due to the* BH_4 *hydrogens of* (I).

Indeed, "thermal" decoupling appears to be general for many boron–hydrogen neutral compounds and anions, giving much simplified spectra at lower temperatures.[3] In the case of $(Ph_3P)_2CuB_3H_8$, both the effects of thermal decoupling (at $-20°$) and an intramolecular exchange process (at $-80°$) are evident in the ^1H n.m.r. spectrum.[2]

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[2] H. Beall, C. H. Bushweller, W. J. Dewkett, and M. Grace, *J. Amer. Chem. Soc.*, in the press.