Detection of Stereochemical Nonrigidity in a Metal Tetrahydroborate and Estimation of the Barrier: ^1H Nuclear Magnetic Resonance Study

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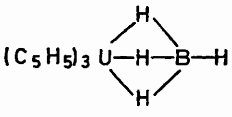
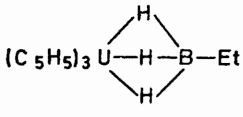
Summary Slowing of the dynamic interchange of bridge and terminal hydrogens in a metal tetrahydroborate has been observed for the first time in the low temperature ^1H n.m.r. spectra of $(C_5H_5)_3UBH_4$; at coalescence, ΔG^* is *ca.* 5·0 ± 0·6 kcal mol^{-1} (21 ± 2·5 kJ mol^{-1}).

^1H Nuclear magnetic resonance spectra of covalent metal tetrahydroborates invariably show the bridging and terminal BH_4 protons to be magnetically equivalent. It has been thought that this anomaly was due to rapid intramolecular rearrangement,[1] but attempts at elucidation (or confirmation) have been deterred by extraneous quadrupolar effects[2] and the apparent extreme rapidity of the process. We report an experiment which allows for the first time, detection of the fluxional behaviour and estimation of the free energy barrier.

The compound chosen for study was $(\eta\text{-}C_5H_5)_3UBH_4$[3] (**1**) which has been shown[4] by vibrational spectroscopy to have a triple hydrogen bridge. Amplification of the chemical shift difference between terminal and bridging hydrogens (the exchanging sites) is achieved *via* the demonstrated[5] ability of the $(C_5H_5)_3U$ (IV) moiety to function as an efficient (large shifts, short electron spin relaxation time) shift reagent. Broad-band decoupling of ^{11}B is essential for simplifying the temperature dependence[2] of the spectrum. The observed complete collapse of the BH_4 singlet resonance by −120° was shown not to arise from relaxation phenomena[6] unrelated to the slowing of a chemical exchange process since the lineshape changes are essentially independent of concentration, solvent (diethyl ether, dimethyl ether, toluene), and solvent viscosity. The C_5H_5 resonance remains sharp throughout the temperature range +25 to −121°. The temperature dependence of the chemical shifts exhibits approximate Curie–Weiss behaviour. Furthermore, we have synthesized the nonfluxional molecule (**2**) *via*



(1)



(2)

reaction[7] of (**1**) with triethylborane. The hydride resonance of this molecule broadens only slightly over the temperature range +25 to −121°. These results indicate the fluxional process in (**1**) is becoming slow at −120°. The low solubility and great reactivity of (**1**) have prevented studies at lower temperatures and in other solvent systems.

The frequency separation between bridge and terminal hydrogens in (**1**) can be estimated by combining the chemical shift data from (**1**) and (**2**). At the coalescence point which we estimate to be $-140 \pm 20°$, $\Delta\nu = 15{,}000$—$36{,}000$ Hz. Assuming that $\tau \approx 2/\pi\Delta\nu$,† where τ is the mean lifetime, we obtain $\tau \approx 22 \pm 8\,\mu$s and $\Delta G_c^* \approx 5{\cdot}0 \pm 0{\cdot}6$ kcal mol^{-1} ($21 \pm 2{\cdot}5$ kJ mol^{-1}). This result, of admittedly limited accuracy, represents the first rate data on such fluxional systems. In addition, the use of paramagnetic probes in dynamic n.m.r. may be of general utility. Further studies are in progress.

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† This equation is only strictly valid if the exchanging sites have equal populations, but is a reasonable approximation.

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