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Singly Bridged Hydroborates: Fluxional Character in $[(MeO)_3P]_2CuBH_4$ and a Calculation of $\Delta G^\ddagger$ for the Process

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A $\Delta G^\ddagger$ for the fluxional process in $[(MeO_3P]_2CuBH_4$ has been determined utilizing data on a related compound $[(MeO_3P]_2CuH_3BCO_2C_2H_5$. Results are related to a model for the permutation process and they indicate that the difference between $\Delta G^\ddagger$ values for the bidentate copper complex (4.3 kcal/mol) and the bidentate vanadium complex (7.6 kcal/mol) is dependent on the greater covalency of the B–H bond in the vanadium complex rather than a difference in geometry of the fluxional intermediate.

Introduction

Very few covalent metal tetrahydroborate complexes have been reported which exhibit a slowing of the fluxional process involving bridge and terminal hydrogens [1–4]. This phenomenon has been studied using NMR in both paramagnetic and diamagnetic tetrahydroborate complexes, but only in the bidentate series with the $(\eta^5\text{-}C_5H_5)_2VBH_4$ paramagnetic species could the free energy of activation for the exchange process be calculated directly [2, 3]. This was a direct result of the fact that not only was the coalescence temperature obtainable, but upon continued temperature lowering, the bridging hydrogen (H_b) resonance was observed and the terminal hydrogen (H_t) resonance could be observed, or estimated if obscured by solvent. The latter resonances give a measure of the site frequency separation (δw), a necessary parameter for calculating $\Delta G^\ddagger$ for the permutation process [3]. Although in the variable temperature NMR study on $[(MeO)_3P]_2CuBH_4$ [4] the H_t and H_b resonances were not obtained (only the upper exchange limit could be reached), we have been able to calculate an approximate $\Delta G^\ddagger$ for this compound using data on the related compound $[(MeO)_3P]_2CuH_3BCO_2C_2H_5$ [5]. The coalescence point for $[(MeO)_3P]_2CuBH_4$ was estimated in a manner similar to that used by Marks and Kolb for the coalescence point of $(\eta^5\text{-}C_5H_5)_3UBH_4$, *i.e.* by comparison to $(C_5H_5)_3U(\eta^1\text{-allyl})$, for which the slow exchange limit could be reached [1]. Details of our calculations are presented below. The results show $\Delta G^\ddagger$ for the bidentate vanadium and copper complexes to be dependent upon the degree of M–H–B covalent bonding rather than a difference in the nature of the fluxional intermediate.

Discussion

Similarity between $[(MeO)_3P]_2CuBH_4$ and $[(MeO)_3P]_2CuH_3BCO_2C_2H_5$ suggested that the chemical shifts of the terminal and bridging hydrogen atoms in $[(MeO)_3P]_2CuBH_4$ might be obtainable by utilizing available data on both complexes. The accuracy of the calculations to determine the chemical shifts for the terminal and bridging hydrogens hinges on the following assumptions: 1) the hydroborate ligand–metal bonding in the tetrahydroborate complex and (ethoxycarbonyl)trihydroborate complex is very similar. Specifically, upon complexation using either anion, the inductive effect on the terminal hydrogens and the absolute effect upon their chemical shifts must be comparable; 2) the electronic properties of the B–C bond in the (ethoxycarbonyl)trihydroborate are not greatly enough different from the electronic properties of the B–H bonds to significantly alter the inductive effect which occurs with the borane hydrogens of the (ethoxycarbonyl)trihydroborate upon coordination as compared to the effect experienced by the borane hydrogens of BH_4^- upon coordination. Assumptions 1) and 2) are supported by the fact that the frequency separation between the bridging and terminal B–H stretching frequencies in the infrared spectra for both complexes is very similar [4, 5]. Since this separation is accepted as a measure of the covalency of the M–H bond [6], the extent of interaction with the copper is very similar for both anionic ligands. It is therefore likely that the change in chemical shifts for the terminal and bridging hydrogens and related inductive effects are comparable for the two complexes.

The chemical shifts of the terminal and bridging hydrogens, and subsequently the site frequency separation, δw, are estimated by calculating the

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TABLE I. NMR Data on Hydroborate Complexes.

Designation	Complex	$^1H\ \delta$ (ppm) [9]	$\Delta G^\ddagger$ (kcal/mol)
X	$[(MeO)_3P)]_2Cu(H_b)_2B(H_t)_2$	+0.69 ppm [5] (vinyl chloride–vinyl fluoride)	4.3 ± 0.5
Y	$[(MeO)_3P]_2Cu(H_b)_2B(H_t)CO_2C_2H_5$	+1.02 ppm ($CDCl_3$) [5]	
	BH_4^-	+0.36 ppm ($CDCl_3$) (this work)	
	$H_3BCO_2C_2H_5^-$($ECTB^-$) [5a]	+0.60 ppm (DMSO)	
	$(C_5H_5)_2VBH_4$		7.6 ± 0.3 [2]
	$(C_5H_5)_2NbBH_4$		too rapid to observe on NMR time scale [2]

chemical shift which $[(MeO)_3P]_2CuBH_4$, designated as complex X (Table I), would exhibit if one of the terminal hydrogens were replaced by a deuterium; the latter hypothetical complex will be called X′and its chemical shift $\delta_{x'}$. On the basis of the rationale just given, the change in chemical shift of BH_3D^- upon complexation would be approximately the same as the change in chemical shift upon complexation of the (ethoxycarbonyl)trihydroborate anion (ECTB), $\delta_{BH_3D}-\!-\delta_x \approx \delta_{ECTB}-\delta_y$ where y is $[(MeO)_3P]_2CuH_3BCO_2C_2H_5$. It is self evident that the chemical shift of BH_3D^- would equal the chemical shift of BH_4^-. Using this and the values in Table I, $\delta_{X'} \approx +0.06$ ppm. Since the chemical shift of the B–H protons is a weighted average of the individual environments, the following independent equations may be written.

$$\delta_X = +0.69 = (2\delta_t + 2\delta_b)/4 \qquad (1)$$

$$\delta_{X'} \approx +0.06 \approx (\delta_t + 2\delta_b)/3 \qquad (2)$$

Simultaneous solution of these equations yields $\delta_b \approx -1.20$ ppm and $\delta_t \approx 2.58$ ppm. The difference ($\delta_t - \delta_b$) ≈ 3.8 ppm (δw), is reasonable compared to the separation for diborane (4.5 ppm) [7] and $(C_5H_5)_2VBH_4$ (2.8 ppm) [2].

The second step in the calculation of the activation energy involves consideration of line shape functions. The line shape function is:

$$g(\nu) = K\tau(\nu_a - \nu_b)^2/\{[1/2(\nu_a + \nu_b) - \nu]^2 + + 4\pi^2\tau^2(\nu_a - \nu)^2(\nu_b - \nu)^2\} \qquad (3)$$

where K is a normalizing constant, τ = half of the lifetime of either site, and ν_a and ν_b are the frequencies of the two sites [8]. The actual line shape depends only upon the product $\tau|\nu_a - \nu_b|$. The line shape function for two similar systems should be the same at the temperatures at which collapse of the signal occurs. The borane peak for the complex $(\eta^5 - C_5H_5)_2VBH_4$ [2] collapses to the baseline at a temperature of approximately −70 ± 5 ℃, and the peak for the bis(methylphosphite)–copper complex collapses at approximately −165 ± 5 ℃. Therefore:

$$[\tau_{V(-70^\circ)}]_b|\nu_a - \nu_b|V = [\tau_{Cu(-165^\circ)}]_b|\nu_a - \nu_b|_{Cu}$$

where τ_b = the mean preexchange lifetime for a bridging hydrogen and $\tau_b = 2\tau$ for both V and Cu systems. $[\tau_{V(-70^\circ)}]_b$ indicates the mean preexchange lifetime for a bridging hydrogen in the vanadium complex at −70 ℃. ν_a and ν_b are frequencies of bridging and terminal hydrogen resonances so the difference between them $\delta w = |\nu_a - \nu_b| \approx 378$ Hz for the bis-methylphosphite copper complex. Assume $\delta w = |\nu_a - \nu_b| \approx 2500$ Hz for the vanadium complex at −70 ℃ since this is the value which was used by Marks and Kennelly for the complex at −87 ℃ [2].

Use of the Boltzmann equation [9] $1/\tau_b = (kT/h)(e^{-\Delta G\ddagger/RT})$ in conjunction with equation (5) allows calculation of $\Delta G^\ddagger$ for the related copper system using data for the vanacium complex:

$$\delta w(Hz)_{Cu}/\delta w(Hz)_V = (\tau_V)_b/(\tau_{Cu})_b = (T_{Cu}/T_V)e^{(\Delta G^\ddagger/RT)V - (\Delta G^\ddagger/RT)Cu} \qquad (4)$$

$$378\ Hz/2500\ Hz = (108\ {}^\circ K/203\ {}^\circ K)\, e^{(7600\ cal/R(203\ K) - \Delta G^\ddagger{}_{Cu}/R(108\ K)} \qquad (5)$$

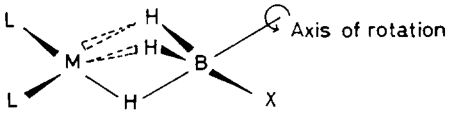
$$\Delta G^\ddagger{}_{Cu} = 4.3\ kcal/mol \qquad (6)$$

The values for calculating the upper and lower range for $\Delta G^\ddagger$ follow and are based upon the upper and lower limits of error expected for these parameters:

Upper range of $\Delta G^\ddagger$	*Lower range of $\Delta G^\ddagger$*
Peak collapse Cu:	Peak collapse Cu:
−160 ℃ (113 K)	−170 ℃ (103 K)
Peak collapse V:	Peak collapse V:
−75 ℃ (198 K)	−65 ℃ (208 K)
δw (Cu) 278 Hz	δw (Cu) 478 Hz
δw (V) 2600 Hz	δw (V) 2400 Hz
$\Delta G^\ddagger{}_V$ 7.9 kcal/mol	$\Delta G^\ddagger{}_V$ 7.3 kcal/mol
$\Delta G^\ddagger{}_{Cu}$ = 4.9 kcal/mol	$\Delta G^\ddagger{}_{Cu}$ = 3.8 kcal/mol

The above arguments only hold if the collapse of the 'thermally' decoupled resonance occurs at the same temperature as the collapse of a resonance which is white noise ^{11}B decoupled as well as 'thermally' decoupled. Our work with copper complexes did not utilize white noise decoupling while the spectra of the vanadium complex were taken using this technique. Support for the similarity of behavior for white noise decoupled and nondecoupled systems if thermal decoupling is in a fairly advanced stage comes from work by Marks and Kolb with $(\eta^5\text{-}C_5H_5)_3UBH_4$ in which both the white noise decoupled and 'thermally' decoupled (without white noise decoupling) B–H resonances collapsed at approximately –125 °C [1].

Factors affecting the dynamic hydrogen interchange process in covalent metal tetrahydroborates may now be considered. A plausible transition state intermediate for the fluxional behavior in hydroborate complexes has been suggested as one in which one metal–hydrogen bond remains substantially unchanged while the leaving bridging hydrogen and the terminal hydrogen which is replacing it occupy equivalent positions intermediate between terminal and bridging [3]. This may alternately be described as a rotation of the hydroborate around an axis described by the stationary bridging hydrogen and the boron (see *I*). The intermediate could then be described as a hybridization between unidentate and tridentate coordination with the contribution from each dependent upon the metallic radius and the degree of steric crowding. (Tridentate coordinated complexes are known [3] and recent neutron diffraction work on $Cu(PPh_2Me)_3(BH_4)$ [10] provides evidence that a contribution to the intermediate by a unidentate structure is reasonable in the BH_4 scrambling process. The particular orientation of the BH_4 group showed that one of the Cu–H interactions can be considered as an 'incipient Cu–H bonding interaction'. Thus, although the hydrogen is definitely out of bonding range of Cu, it appears poised for coordination to the copper which could occur when one of the phosphine ligands dissociates). The hybridization model suggests that if the intermediate assumed a larger percentage of tridentate character, a lower energy intermediate would result, since the extent of electron donation should remain relatively constant [6]. If the intermediate assumed a larger percentage of monodentate character, a higher energy intermediate would result. Differences within similarly bonded complexes *e.g.* as with bidentate bonded species, should then depend on the steric interactions and the metallic radius and subsequent covalent character of the metal hydrogen bond. The observed $\Delta G^{\ddagger}$ for bridge–terminal hydrogen permutation in $(C_5H_5)_2NbBH_4$ is *much* lower (the exchange could not be slowed sufficiently on the NMR time scale to be observed) than for its vanadium counterpart, despite their very similar infrared spectra [2] (the IR indicate similar covalent M–H bond strength). The best explanation for this is that the larger radius of the Nb allows a significantly larger percentage of tridentate character.



(I)

The difference in $\Delta G^{\ddagger}$ for the bidentate copper complex (4.3 kcal/mol) and the bidentate vanadium complex (7.6 kcal/mol) would not be dependent on any significant differences in the geometry of the fluxional intermediate since crowding should not be a factor nor should a difference in metal covalent radii since the metals have comparable covalent radii. The difference then must be dependent on the greater covalency of the B–H–M bond in the vanadium complex. Infrared data show that the frequency difference between $B\text{–}H_t$ and $B\text{–}H_b$ vibrations is larger for V than Cu, indicating that the covalent interaction is larger with vanadium. It is reasonable, then, that this greater covalency is responsible for the higher $\Delta G^{\ddagger}$ for the vanadium complex compared to the copper complex.

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