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Dynamics of intramolecular hydrogen exchange in cyclic organohydroborate zirconocene complexes†

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ABSTRACT: Proton and ^{11}B NMR investigations of two zirconocene boracycloalkane derivatives **A** and **B**, as a function of temperature, identified two hydrogens bridged between boron and zirconium and a third attached only to zirconium. Observation of the ^{11}B decoupled proton NMR lineshape of **A** and **B** (toluene-d_8 solution) revealed a fast intramolecular mutual exchange of the two bridged hydrogens and a slower process which exchanges each of the latter with the single hydrogen bonded to zirconium alone. Comparison of the observed ^{11}B decoupled proton NMR spectra with calculated lineshapes which take account of the exchange processes yielded the corresponding rates and activation parameters. Proton NMR data for **A** and **B** (with ^{11}B coupled) indicate spin coupling between ^{11}B and the bridge hydrogens of *ca.* 55 Hz, subject to averaging by ^{11}B nuclear electric quadrupole induced relaxation; its rate increases with decreasing temperature. Thus, the coupling is averaged at the lower temperatures due to ^{11}B relaxation and on warming becomes obscured as a result of hydrogen exchange. Analysis of these latter lineshapes taking account of exchange dynamics, ^{11}B relaxation and the ^{11}B proton coupling constant provided dynamic parameters closely similar to those obtained from the ^{11}B decoupled proton NMR data. At elevated temperature (50 °C), broadening of the Cp proton resonance indicates that these protons undergo slow exchange with the three hydrido hydrogens. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{11}B NMR; hydrogen exchange; dynamic NMR; zirconocene; organohydroborate complexes

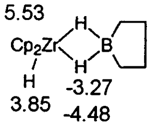
INTRODUCTION

Transition metal complexes with hydride ligands are of continuing interest,[1–3] in part because of their potential for dynamic behavior. Several types of intramolecular hydrogen exchange of metal hydride complexes have been observed.[4–13] One of the major categories of complexes examined is metal–tetrahydroborate complexes. In many of these complexes, terminal hydrides exchange with hydrogens that bridge metal and boron atoms.[4–7]

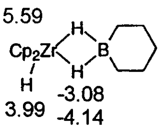
Until recently, little information had been reported on the preparation and dynamic character of metal–organohydroborate complexes. Hydrogen exchange between B—H, Zr—H—B and Cp hydrogens of $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ has been mentioned, but no details were given.[14] Recently, we prepared and structurally characterized two new cyclic organohydroborate–zirconocene complexes, $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ and $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$.[15] In these complexes the organohydroborate anions, $[H_2BC_4H_8]^-$ and $[H_2BC_5H_{10}]^-$, are bound to the zirconium atom through two Zr—H—B bridges. Single-crystal x-ray diffraction analyses and ^{1}H NMR spectroscopy confirmed the bidentate linkage of the Zr—H—B bond.

RESULTS AND DISCUSSION

Two compounds were prepared as described above, and from their method of preparation and other correlations, shown above, their structures are best represented by **A** and **B**.



A



B

At 0 °C, using toluene-d_8 solutions with ^{11}B decoupling, **B** gives rise to the proton NMR spectrum shown in Fig. 1. Shifts were assigned by analogy with published results and are given on the structures. In particular for **B** note the two single resonances at $\delta - 3.08$ and $\delta - 4.14$ assigned to the bridge hydrogens and that at δ 4.02 for Zr*H*. The bridge hydrogens cannot now be assigned individually. The corresponding shifts for **A** are very similar.

With increasing temperature above 0 °C, the proton resonances of **B**, ^{11}B decoupled, in toluene-d_8, assigned to H-1 and H-2 bridge begin to broaden and coalesce; by 20 °C the H-3 Zr resonance also starts to broaden (Fig. 1). Then, with further increases in temperature all three absorptions due to H-1, H-2 and H-3 begin to disappear into the baseline. This behavior is reversible with temperature; it does not appear to vary with the concentration of **B**. It is therefore best interpreted as due to the mutual intramolecular exchange of H-1 with H-2 being faster than that of either of these with H-3.

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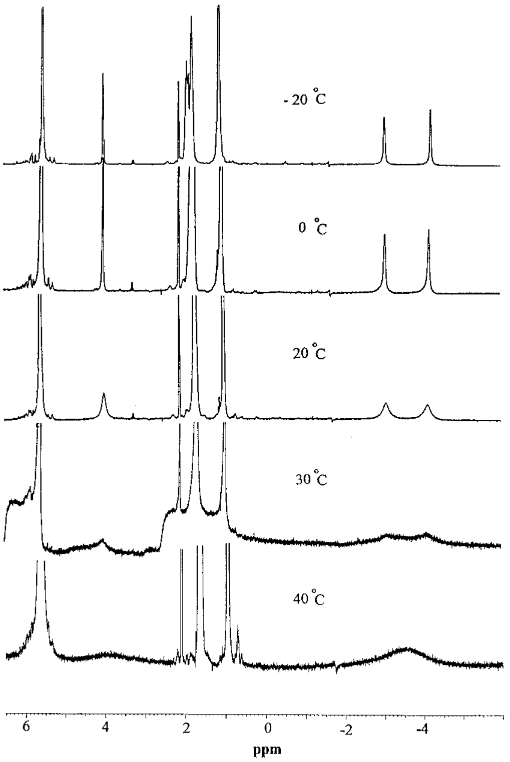

Figure 1. Proton NMR, 300 MHz, with ^{11}B decoupled, of **B** in toluene-d_8 solution at different temperatures.

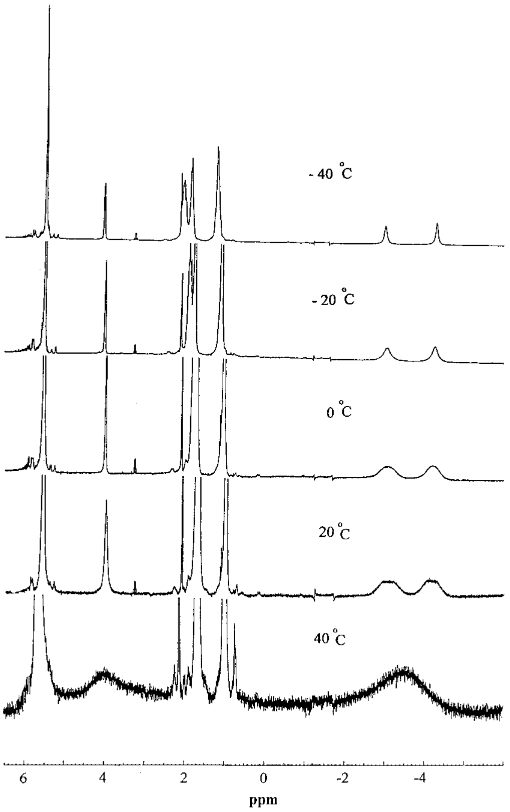

Figure 2. Proton NMR, 300 MHz, with ^{11}B coupled, of **B** in toluene-d_8 solution at different temperatures.

Below, it will be shown how NMR lineshape analysis[15] of the H-1, H-2 and H-3 resonance of **B**, obtained with ^{11}B decoupling, provides rate constants for the above exchange processes. Finally, at temperatures above 60 °C, the sharp single proton resonance for Cp on **B** begins to broaden, indicating that the Cp hydrogens exchange with H-1, H-2 and H-3 much more slowly than the rates at which these three exchange with each other.

Under conditions with ^{11}B coupled, the proton resonances of H-1 and H-2 in **B** are always broader than those in the ^{11}B decoupled spectrum (Fig. 2). The difference is small at −40 °C and becomes exacerbated with increasing temperature. By 20 °C the two resonances have flat tops, shapes indicative of some fine structure just missed due to relaxation processes. Further warming coalesces the H-1 and H-2 resonances to a broad line, so that by 40 °C the H-1 and H-2 absorptions, ^{11}B coupled and ^{11}B decoupled, have a very similar appearance.

These results implicate the operation of spin coupling, $^1J(^{11}\mathrm{B},^1\mathrm{H}\text{-}1)$ and $^1J(^{11}\mathrm{B},^1\mathrm{H}\text{-}2)$, in addition to a process which relaxes ^{11}B, most likely electric quadrupole induced relaxation.[16–18] The latter process speeds up with decreasing temperature, effectively decoupling ^{11}B from H-1 and H-2 at lower temperature (−40 °C). The effect has been described generically as relaxation of the second kind.[19] On the other hand, warming **B** increases the rates at which H-1, H-2 and H-3 mutually exchange, thus ultimately averaging the ^{11}B,H-1 and ^{11}B,H-2 coupling constants with the assumed zero or very small ^{11}B,H-3 coupling. This limiting splitting of $\frac{2}{3}$ $^1J(^{11}\mathrm{B},^1\mathrm{H})$ is not observed since the sample would not be thermally stable at the elevated temperatures required to average completely the resonances for H-1, H-2 and H-3. Note that because the rates of ^{11}B quadrupole induced relaxation and intramolecular proton exchange proceed in opposite directions with increasing temperature, effects due to ^{11}B,^{1}H coupling are barely observed within a narrow temperature window around 20–30 °C. The effect is more apparent in the ^{1}H NMR spectra of **A**, ^{11}B coupled, around 20 °C. Further, **A** in diethyl ether clearly shows in the ^{11}B NMR spectrum a 1 : 2 : 1 pattern due to ^{11}B coupling with the bridge hydrogens, 55 Hz. Similar values were successful in reproducing proton NMR of **A** and **B** in toluene-d_8 solution (see below). These results appear to be independent of the concentration of **A** and **B**, implying that the hydrogen exchange process is first order.

The NMR results for **A** in toluene-d_8 and their qualitative interpretation closely follow those given above for **B**, the difference being that ^{11}B,^{1}H coupling is more apparent among the **A** spectra.

It is now appropriate to consider lineshape analysis of the NMR data for **B**. In principle, the parameters required to reproduce the proton NMR lineshapes, ^{11}B coupled, for H-1, H-2 and H-3 of **A** and **B** are their chemical shifts, intrinsic linewidths at slow exchange, the two sets of rate constants H-1 $\rightleftharpoons$ H-2 and H-1 $\rightleftharpoons$ H-3 and H-2 $\rightleftharpoons$ H-3 (the last two being assumed to be identical but smaller than the first), the quadrupolar relaxation rate of ^{11}B and the ^{11}B,H-1,2 coupling constant.

Proton decoupled ^{11}B spectra for **B** in toluene were also obtained. The width of the ^{11}B resonance increased with decreasing temperature, as expected for quadrupole induced relaxation. These data provided the ^{11}B relaxation times. Then proton exchange rates obtained from the results of these treatments, allowed the analysis of the ^{11}B coupled proton NMR of **B**.

Proton decoupled ^{11}B lineshapes for **B** were simulated assuming that quadrupole induced relaxation, alone, was responsible for the linewidths. Boron-11 has I = 3/2. We depict the spin states, $\Phi_{m(z)}$ by their m_z values: $-3/2$, $-1/2$, $+1/2$, $+3/2$. Hence the required elements of the density matrix $\langle b|\rho|b'\rangle$ would be for b, b'; $-1/2$, $-3/2$; $+1/2$, $-1/2$; $+3/2$, $+1/2$, and are abbreviated ρ_1, ρ_2 and ρ_3. We then take the three elements of the density matrix equation

$$\langle \Phi_{m(z)} | i[\rho, \mathscr{H}] - \rho/T + R_q \rho | \Phi_{m(z-1)} \rangle = 0 \qquad (1)$$

where $R_q{}^{17,18}$ is the quadrupole relaxation operator applied at the extreme narrowing approximation:

$$R_q \rho = \sum J_\alpha [\mathscr{I}^\alpha, [\mathscr{I}^{-\alpha}, \rho]] \qquad (2)$$
$$\alpha = 0, \pm 1, \pm 2$$

where the Js are spectral densities and $\mathscr{I}$s the appropriate spin operator (see Table 1 for a list of terms). Under these conditions, the elements of R_q, ρ in J_0 are zero and all the other spectral densities J_α ($\alpha = \pm 1, \pm 2$) are identical.

The three elements of the density matrix equation [Eqn (1)] generate the three coupled first-order equations shown in matrix form in Eqn (3):

$$\begin{bmatrix} \begin{array}{c} i2\pi(v - v_B) \\ -(1/T) - 21.6r \end{array} & 0 & 7.2r \\ 0 & \begin{array}{c} i2\pi(v - v_B) \\ -(1/T) - 14r \end{array} & 0 \\ 7.2r & 0 & \begin{array}{c} i2\pi(v - v_B) \\ -(1/T) - 21.6r \end{array} \end{bmatrix} \begin{bmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{bmatrix} = iC \begin{bmatrix} \frac{\sqrt{3}}{2} \\ 2 \\ \frac{\sqrt{3}}{2} \end{bmatrix} \qquad (3)$$

The latter is solved for the ρ elements and the absorption summed as indicated in Eqn (4) (terms are defined in Table 2).

$$\text{Abs}\,(v) = -\,\text{Im}\,(\rho_1 + \rho_2 + \rho_3) \qquad (4)$$

Thus ^{11}B lineshapes are calculated as a function of the relaxation parameter, r, given in Eqn (5):

$$r = \left(\frac{e^2 qQ}{4I(2I - I)h} \right)^2 \tau \qquad I = 3/2 \qquad (5)$$

Hence comparison of the observed and calculated lineshapes provides experimental values for r.

Table 1. List of terms

v_A, v_B, v_C	Chemical shifts (Hz)
v	Frequency axis of NMR spectrum
$1/T$	Linewidth in the absence of exchange (rad s^{-1})
i	$\sqrt{-1}$
k_{AB}	Rate constant, first-order, exchange of H_A with H_B
C	Arbitrary constant set as 1
ρ^A	$\langle l|\rho^A|m\rangle$ element
R_q	Quadrupole relaxation operator
J_α	Spectral density
$\mathscr{I}$, $\mathscr{I}^*$	Spin operators for quadrupole induced relaxation
q	Electric field gradient
Q	Quadrupole moment
τ	Correlation time

Calculation of the H-1, H-2 and H-3, renamed H_A, H_B and H_C, lineshapes of the ^{11}B decoupled proton NMR of **B** in toluene-d_8 is handled as an equally populated, uncoupled, first-order, three-spin exhanging system. The required elements of the density matrix are written $<\alpha|\rho^i|\beta\rangle$ or ρ^A, ρ^B and ρ^C and the absorption is summed as in Eqn (6):

$$\text{Abs}\,(v) = -\,\text{Im}\,(\rho^A + \rho^B + \rho^C) \qquad (6)$$

One takes the corresponding elements of the density matrix equation:

$$\dot{\rho} = i[\rho, \mathscr{H}] - \rho/T + E\rho \qquad (7)$$

where E is the exchange operator which takes account of the following three exchange processes:

$$H_A \underset{}{\overset{k_{AB}}{\rightleftharpoons}} H_B \qquad (8a)$$

$$H_A \overset{k_{AC}}{\rightleftharpoons} H_C \qquad (8b)$$

$$H_B \overset{k_{BC}}{\rightleftharpoons} H_C \qquad (8c)$$

The term $E\rho$ takes the form

$$E\rho = k[\rho(\text{ae}) - \rho] \qquad (9)$$

where ae means 'after exchange,' with similar terms added for different exchange steps. An ρ(ae) element for

Table 2. Activation parameters for intramolecular hydrogen exchange in zirconocene boracycloalkane derivatives

	$\Delta H^{\neq}$(kcal mol^{-1})	$\Delta S^{\neq}$(eu)
$Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$	14[a]	−0.9[a]
Intra-bridge exchange	14[b]	−0.9[b]
Bridge ⇌ terminal	19.3[a]	15[a]
	21.8[b]	22[b]
$Cp_2ZrH\{\mu\text{-}H)_2BC_4H_8\}$		
Intra-bridge exchange	8.1[a]	−22[a]
Bridge ⇌ terminal	12.6[a]	−8[a]

[a] ^{11}B decoupled proton NMR.

[b] ^{11}B coupled proton NMR.

H_A involved in the $H_A \rightleftharpoons H_B$ exchange is given by Eqn (10):

$$\rho^{A}(\mathrm{ae})_{\alpha,\beta} = \rho^{B}_{\alpha,\beta} \qquad (10)$$

Thus the $E\rho$ element for H_A in exchanges (8a) and (8b) is given by Eqn (11), wherein the α,β states have been omitted:

$$(E\rho^{A})_{\alpha,\beta} = k_{AB}(\rho^{B} - \rho^{A}) + k_{AC}(\rho^{C} - \rho^{A}) \qquad (11)$$

The three coupled density matrix equations (12)–(14) are solved for ρ^A, ρ^B and ρ^C, using different sets of trial rate constants and the absorption obtained using Eqn (6):

$$[i2\pi(\nu - \nu_A) - 1/T - k_{AB} - k_{AC}]\rho^{A} + k_{AB}\rho^{B} + k_{AC}\rho^{C} = iC \qquad (12)$$

$$[i2\pi(\nu - \nu_B) - 1/T - k_{AB} - k_{BC}]\rho^{B} + k_{AB}\rho^{A} + k_{BC}\rho^{C} = iC \qquad (13)$$

$$[i2\pi(\nu - \nu_C) - 1/T - k_{AC} - k_{BC}]\rho^{C} + k_{AC}\rho^{A} + k_{BC}\rho^{B} = iC \qquad (14)$$

These results fit best using two sets of rate constants, the first one being for Eqn (8a), A,B exchange, the other A with C and B with C; observed and calculated spectra are shown in Fig. 3 and the observed Eyring plots in Fig. 4; activation parameters are listed in Table 2.

We now consider the ^{11}B coupled proton NMR of **B** in toluene. The parameters required to calculate the absorption due to H_A, H_B and H_C are, in addition to those used to calculate the ^{11}B decoupled spectrum, the ^{11}B,H-1 and ^{11}B,H-2 coupling constants and the ^{11}B nuclear electric quadrupole induced relaxation rates. The latter are estimated from the ^{11}B NMR while the coupling constants are likely to be close to 55 Hz, observed for **A**, in diethyl ether solution.

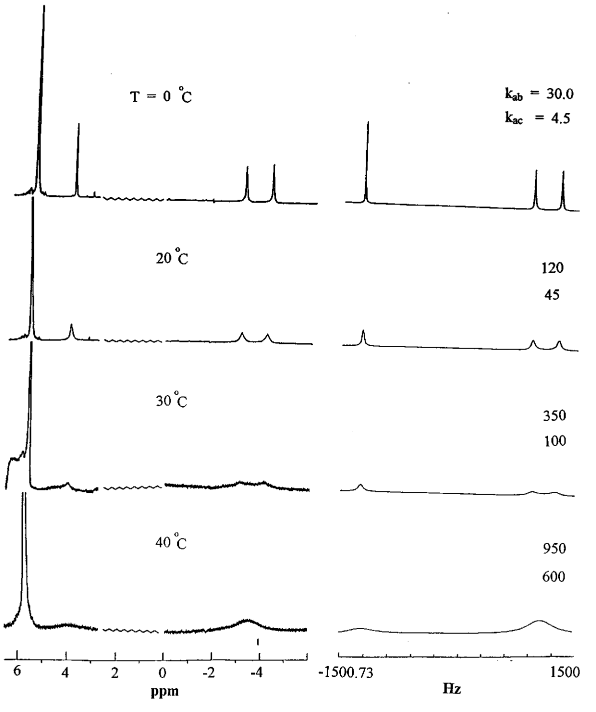

Figure 3. Proton NMR, with ^{11}B decoupled, of **B**, H_A, H_B and H_C parts. Left, observed, different temperatures; right, calculated to fit with rate constants.

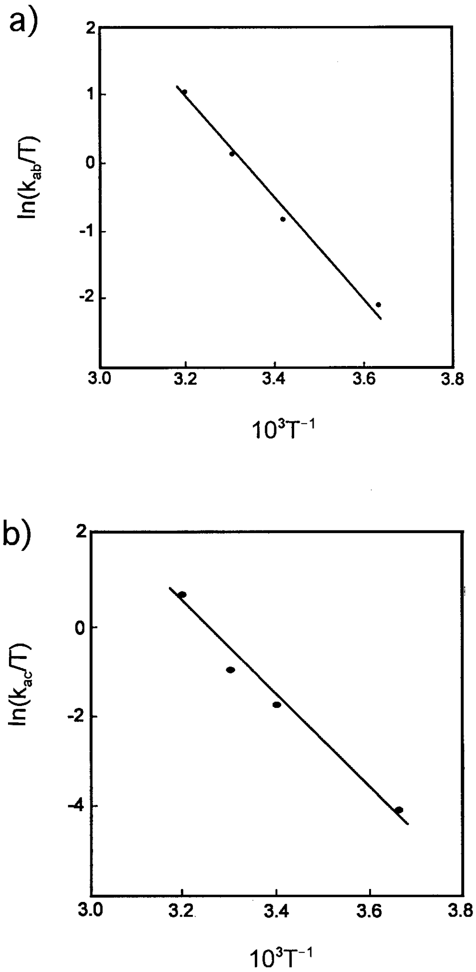

Figure 4. Eyring plots for mutual proton exchange among H_A, H_B and H_C in **B**, in toluene-d_8 solution. (a) A,B exchange; (b) A,C and B,C exchange.

The proton resonance of ^{11}B coupled **B** due to H_A, H_B, H_C and ^{11}B is treated as a four-spin system in the spin product representation as $\Phi_A\Phi_B\Phi_C\Phi_{B11}$. The required elements of the density matrix are diagonal in ^{11}B and in all but one of three protons, i.e. only first-order transitions are considered since the shifts are widely separated and there is no detectable spin coupling between the hydrogens. Hence the transitions are for H_A, $\alpha_A\Phi_B\Phi_C\Phi_{B11} \rightarrow \beta_A\Phi_B\Phi_C\Phi_{B11}$, H_B, $\Phi_A\alpha_B\Phi_C\Phi_{B11} \rightarrow \Phi_A\beta_B\Phi_C\Phi_{B11}$, and H_C, $\Phi_A\Phi_B\alpha_C\Phi_{B11} \rightarrow \Phi_A\Phi_B\beta_C\Phi_{B11}$, noting that there are four states for ^{11}B and four for two half spins. For brevity, the states of ^{11}B with m_z of $-3/2$, $-1/2$, $+1/2$, $+3/2$ are now labeled W, X, Y and Z, respectively. As before, we take all elements of the density matrix equation whose states differ by a first-order transition of H_A, H_B or H_C. An example of such an element is given as Eqn (15):

$$\langle \alpha\alpha\beta x \,|\, i[\rho, \mathscr{H}] - \rho/T + R_q\rho + E\rho \,|\, \beta\alpha\beta x \rangle = iC(1/32) \qquad (15)$$

Elements of $R_q \rho$ are given as in Eqn (2). Only the spin state of ^{11}B changes. The exchange process has the effect of permuting the spins within the spin product function but not the site labels; see, for example, Eqns (16) and (17):

$$\beta_A \alpha_B \beta_C X_{B11} \xrightarrow[H_A \rightleftharpoons H_B]{} \alpha_A \beta_B \beta_C X_{B11} \qquad (16)$$

$$\beta_A \alpha_B \beta_C X_{B11} \xrightarrow[H_B \rightleftharpoons H_C]{} \beta_A \beta_B \alpha_C X_{B11} \qquad (17)$$

Note also that since proton–proton spin coupling is not detected among the H_A, H_B and H_C resonances, proton exchange does not influence the spin state by ^{11}B. Hence the 48 elements of the density matrix are reduced to 12 by making the following substitutions:

$$\sum_{\Phi_B \Phi_C} \langle \alpha \Phi_B \Phi_C \Phi_{B11} | \rho | \beta \Phi_B \Phi_C \Phi_{B11} \rangle = A\Phi_{B11} \qquad (18)$$

$$\sum_{\Phi_A \Phi_C} \langle \Phi_A \alpha_B \Phi_C \Phi_{B11} | \rho | \Phi_A \beta_B \Phi_C \Phi_{B11} \rangle = B\Phi_{B11} \qquad (19)$$

$$\sum_{\Phi_A \Phi_B} \langle \Phi_A \Phi_B \alpha_C \Phi_{B11} | \rho | \Phi_A \Phi_B \beta_C \Phi_{B11} \rangle = C\Phi_{B11} \qquad (20)$$

noting that ^{11}B has four spin states. The resulting 12 coupled equations, Eqns (22)–(33), are solved for the composite elements and the latter summed as in Eqn (21) to give the absorption.

$$\text{Abs}\,(v) = -\text{Im} \sum (A\Phi_{B11} + B\Phi_{B11} + C\Phi_{B11}$$
$$\Phi_{B11} = W, X, Y, Z \qquad (21)$$

Since ^{11}B is not coupled to H_C, matrix elements of the density matrix equation involving a transition of H_C do not include $^1J(^{11}\text{B},^1\text{H})$ or ^{11}B quadrupolar relaxation terms.

$$[i2\pi(v - v_A - 3/2J) - 1/T - 48r - k_{ab} - k_{ac}]AW + k_{ab}(BW) + k_{ac}(CW) + 24r(AX + AY) = iC(1/8) \qquad (22)$$

$$[i2\pi(v - v_A - 1/2J) - 1/T - 48r - k_{ab} - k_{ac}]AX + k_{ab}(BX) + k_{ac}(CX) + 24r(AZ + AW) = iC(1/8) \qquad (23)$$

$$[i2\pi(v - v_A + 1/2J) - 1/T - 48r - k_{ab} - k_{ac}]AY + k_{ab}(BY) + k_{ac}(CY) + 24r(AW + AZ) = iC(1/8) \qquad (24)$$

$$[i2\pi(v - v_A + 3/2J) - 1/T - 48r - k_{ab} - k_{ac}]AZ + k_{ab}(BZ) + k_{ac}(CZ) + 24r(AY + AX) = iC(1/8) \qquad (25)$$

$$[i2\pi(v - v_B - 3/2J) - 1/T - 48r - k_{ab} - k_{bc}]BW + k_{ab}(AW) + k_{bc}(CW) + 24r(BX + BY) = iC(1/8) \qquad (26)$$

$$[i2\pi(v - v_B - 1/2J) - 1/T - 48r - k_{ab} - k_{bc}]BX + k_{ab}(AX) + k_{bc}(CX) + 24r(BW + BZ) = iC(1/8) \qquad (27)$$

$$[i2\pi(v - v_B + 1/2J) - 1/T - 48r - k_{ab} - k_{bc}]BY + k_{ab}(AY) + k_{bc}(CY) + 24r(BW + BZ) = iC(1/8) \qquad (28)$$

$$[i2\pi(v - v_B + 3/2J) - 1/T - 48r - k_{ab} - k_{bc}]BZ + k_{ab}(AZ) + k_{bc}(CZ) + 24r(BY + BX) = iC(1/8) \qquad (29)$$

$$[i2\pi(v - v_C) - 1/T - k_{ac} - k_{bc}]CW + k_{ac}(AW) + k_{bc}(BW) = iC(1/8) \qquad (30)$$

$$[i2\pi(v - v_C) - 1/T - k_{ac} - k_{bc}]CX + k_{ac}(AC) + k_{bc}(BX) = iC(1/8) \qquad (31)$$

$$[i2\pi(v - v_C) - 1/T - k_{ac} - k_{bc}]CY + k_{ac}(AY) + k_{bc}(BY) = iC(1/8) \qquad (32)$$

$$[i2\pi(v - v_C) - 1/T - k_{ac} - k_{bc}]CZ + k_{ac}(AZ) + k_{bc}(BZ) = iC(1/8) \qquad (33)$$

Rate constants for hydrogen exchange were taken from the analysis of the ^{11}B decoupled proton NMR of **B**. Estimates of the ^{11}B quadrupolar relaxation parameter, *r*, Eqn (5), first came from the proton decoupled ^{11}B NMR of **B** and were then iterated to fit the ^{11}B coupled proton NMR lineshape. Finally, values of 60 and 55.6 Hz were used for $^1J(^{11}\text{B,H})$ in **B** and **A**, respectively, and found to fit the ^{11}B coupled spectra best. The splitting is clearly seen in ^{11}B NMR of **A** in diethyl ether. Activation parameters are listed in Table 2.

The last dynamic process to be discussed involving **B** is evidenced by broadening of the cyclopentadienyl proton resonance by 60 °C indicating the onset of fast exchange of hydrogens between cyclopentadienyl and the H_A, H_B and H_C hydrogens. This process is significantly slower than exchange among H_A, H_B and H_C alone. Since by 60 °C the latter three resonances are already extremely broad, lineshape analysis involving the Cp hydrogen exchange is not possible. This last effect contrasts with results reported by Marks and Kolb for another compound.[7]

Analysis of the NMR lineshapes of **A** parallels that described above for **B**. Results are listed in Table 2.

The results reported here are necessarily approximate in that the influence of the ^{10}B isotopomer has been neglected. However, since the low-temperature ^{11}B decoupled proton NMR of our samples showed only sharp single lines for the A, B and C resonances, it appears that in the ^{10}B isotopomer these protons are effectively decoupled from ^{10}B due to fast ^{10}B quadrupole induced relaxation.

Acknowledgements

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