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Bis(η^5-cyclopentadienyl)vanadium Tetrahydroborate. A Covalent Organotransition Metal Borohydride with Unusual Spectroscopic and Dynamic Properties

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Abstract: The synthesis and spectroscopic (vibrational, nmr) characterization of $(\eta^5\text{-}C_5H_5)_2VBH_4$ are described. In comparison to $(\eta^5\text{-}C_5H_5)_2TiBH_4$, both $(C_5H_5)_2VBH_4$ and $(C_5H_5)_2NbBH_4$, which also have bidentate MH_2BH_2 ligation, appear to be more covalent and show considerable weakening of B–H bridging bonds and possibly some strengthening of M–H bonds in the vibrational spectra. In addition, the free energy barrier to bridge–terminal hydrogen interchange is surprisingly high for the vanadium compound ($\Delta G^\ddagger \approx 7.6 \pm 0.3$ kcal/mol) and the fluxional behavior can be slowed on the nmr time scale. The permutation process is too rapid to slow in the niobium compound, and the reasons for the difference in rate are discussed in terms of the proposed rearrangement mechanism and the size of the metal ion.

It has been recently noted[3] that the tetrahydroborate ligand, BH_4,[4] appears to be in some ways electronically analogous to multihapto organometallic ligands such as η^3-allyl. The degree to which this might be so, and the fact that the structural and dynamic features of metal–BH_4 coordination may shed light on hydrogen transfer processes involving transition metals, has prompted our further exploration of this area. We report here the synthesis and some unusual spectroscopic and dynamic characteristics of the new compound $(\eta^5\text{-}C_5H_5)_2VBH_4$. Vanadium(III) formally possesses a d^2 electronic configuration and this new compound provides an especially informative comparison to the closely related, and structurally well-characterized, titanium(III) (d^1) complex $(\eta^5\text{-}C_5H_5)_2TiBH_4$.[5] Contrast is also made with the recently noted[6] compound $(\eta^5\text{-}C_5H_5)_2NbBH_4$. The results we present here further elaborate the electronic versatility of the tetrahydroborate functionality as a ligand, demonstrate that vibrational spectra can yield important information on bonding trends in such complexes, and provide the first evidence that differences in metal–ligand bonding can have an appreciable influence on the molecular dynamics.

Experimental Section

The synthesis and manipulation of all organometallics was necessarily carried out in an atmosphere of prepurified nitrogen or argon, with rigorous exclusion of air and moisture. Samples were handled by Schlenk methodology or in a glove box. All solvents were thoroughly dried in a manner appropriate to each and were distilled under nitrogen immediately prior to use. Melting points were determined in sealed, nitrogen-filled capillaries and are uncorrected. The reagent $(C_5H_5)_2VCl_2$ was prepared by the general method of Wilkinson and Birmingham[7] or was purchased from Pressure Chemical Co., Pittsburgh Pa.

Bis(η^5-cyclopentadienyl)tetrahydroboratovanadium(III). To 2.30 g (9.13 mmol) of $(C_5H_5)_2VCl_2$ in 200 ml of dimethoxyethane at −10° was added 1.03 g (27.2 mmol) of $NaBH_4$. The reaction mixture was stirred for 12 hr at −10°, during which time the color changed from dark green to dark violet. The reaction mixture was then suction filtered under nitrogen and the solvent removed under high vacuum. The residue was transferred to a sublimer and sublimation was begun at 55° (10^{-3} mm). Dark crystalline material soon began to collect on the cold finger. After 48 hr sublimation was complete, and the product could be collected in a glove box. Yields for a number of runs averaged about 25%. Bis(η^5-cyclopentadienyl)tetrahydroboratovanadium(III) is a pyrophoric, dark violet crystalline solid, mp >80° dec. It slowly (over a period of weeks) decomposes under nitrogen at room temperature to yield a gray solid. *Anal.* Calcd for $C_{10}H_{14}VB$: C, 61.28; H, 7.22; mol wt, 196. Found: C, 61.05; H, 7.69; mol wt, 235 (cryoscopic in benzene).

Bis(η^5-cyclopentadienyl)tetrahydroboratoniobium(III). This procedure appears to be similar to that outlined by Lucas and Green.[6] To 1.66 g (5.65 mmol) of $(C_5H_5)_2NbCl_2$, prepared by the method of Siegert and De Liefde Meyer,[8] in 150 ml of diethyl ether at 0°, was added 1.00 g (45.8 mmol) of $LiBH_4$. The mixture was stirred for 6 hr at 0°, then was suction filtered. Solvent was distilled from the green filtrate *in vacuo*, and the residue was sublimed at 55° (10^{-3} mm) for 48 hr, producing a green solid. Yields for several runs averaged about 10%. Bis(η^5-cyclopentadienyl)tetrahydroboratoniobium(III) is a green, microcystalline solid, mp > 80° dec. It oxidizes upon exposure to air and slowly decomposes at room temperature under nitrogen to a tan solid.

Anal. Calcd for $C_{10}H_{14}NbB$: C, 50.48; H, 5.93; mol. wt, 238. Found: C, 50.76; H, 5.96; mol. wt 238. (mass spectrometric[6]).

Spectroscopic Measurements. Infrared spectra were recorded on Beckman IR-5, IR-9, or Perkin-Elmer 267 spectrophotometers and were calibrated with polystyrene film. Nujol mulls were prepared in a nitrogen-filled glove box with dry, degassed Nujol. Solutions of compounds for infrared studies were prepared in Schlenk apparatus and were transferred *via* syringe to the sodium chloride infrared cell described previously[9] or to a vacuum-tight demountable cell with calcium fluoride windows and lead amalgam spacers. Results were identical. In all cases, samples were monitored for possible decomposition by observing whether changes took place in the spectrum during the course of several scans. Routinely, mulled samples were deliberately exposed to air, to ascertain the effect on spectra. Traces of air produced a rapid decay of the ν_{B-H} bands.

Raman spectra were obtained with a Spectra Physics Model 164 krypton (6471 Å, 0.30–0.40 W) laser and the detection apparatus described previously.[10] This particular excitation frequency was chosen to avoid resonance with the the strong absorption band which the vanadium compound exhibits at 4950 Å. Resonance studies will be discussed elsewhere. Samples were examined at *ca.* −100° in sealed Pyrex tubes, spinning at 1800 rpm.

Uv-visible spectra were obtained on benzene solutions in quartz cells fitted with Schlenk connections. A Cary 14 spectrophotometer was employed for measurements.

Proton magnetic resonance studies at 60 MHz were performed with a Perkin-Elmer Hitachi R20-B spectrometer. Spectra were calibrated with a Model TR-3824X frequency counter. Proton spectra at 90 MHz were recorded with a Bruker HFX-90 spectrometer, operating with 4- or 15-kHz field modulation. Spectra were calibrated with a Hewlett-Packard 5216A electronic counter, by measuring the frequency separation from the locking signal. Variable temperature studies were accomplished with the calibrated Bruker B-ST 100/700 temperature control unit. Heteronuclear boron-11 decoupling was performed with a Schomandl ND3OM frequency synthesizer, a Bruker B-SV2 broad-band power amplifier, and an appropriate matching preamplifier network. At each temperature, power, band width, and frequency were optimized for maximum decoupling. As can be seen in Figure 2, sufficient power was available to collapse the quadrupolar-broadened boron-coupled quartet ($J \approx 90$ Hz) to a sharp singlet. Continuous wave time-averaging (in the event of poor sample solubility) was performed with an interfaced Fabritek 1074 computer. Sample solutions were examined in tubes which had been sealed off on a vacuum line.

Results

The central focus of this work was to ascertain the effect on molecular properties of adding one electron on passing from $(C_5H_5)_2TiBH_4$ to $(C_5H_5)_2VBH_4$. Of secondary importance was comparison of the vanadium compound to its known congener $(C_5H_5)_2NbBH_4$,[6] the synthesis of which has been briefly noted,[6] without detailed discussion of spectral properties.

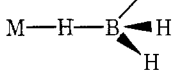
All three compounds can be prepared *via* reaction 1, and

$$(C_5H_5)_2MCl_2 \xrightarrow[\text{ether}]{M'BH_4} (C_5H_5)_2MBH_4 \qquad (1)$$

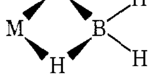
Ia, M = V M′ = Li or Na
Ib, M = Nb
Ic, M = Ti

purification is usually by vacuum sublimation. The vanadium compound readily sublimes at 55° (10^{-3} mm) and is thus markedly more volatile than the titanium analog, which requires temperatures of *ca.* 110°[3] to obtain comparable rates of sublimation. The volatility of the niobium compound is comparable to Ia. This behavior suggests (but by no means proves) considerably higher covalency for the vanadium and niobium species; *i.e.*, they are more like boron hydrides, less like $M^+BH_4^-$ compounds. Spectroscopic data bear this out (*vide infra*).

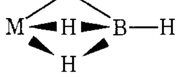
Structural Considerations. Vibrational spectroscopy is a useful tool for discerning the gross structural features of MBH_4 ligation,[3] *i.e.*, the choice between monodentate, A, bidentate, B, and tridentate, C, geometries. It has found



A

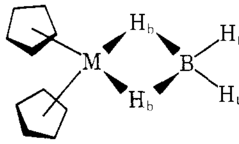


B



C

considerable utility since the tautomeric process which permutes bridge and terminal hydrogens in every tetrahydroborate complex studied to date[11] is rapid on the nmr time scale at all accessible temperatures in solution. Only in the case of a paramagnetic uranium borohydride has it been possible to observe slowing of the process,[12] and even then the slow exchange limit, necessary for structural information, could not be reached. The vibrational spectrum of $(C_5H_5)_2TiBH_4$ was discussed previously,[3] and our conclusion of a bidentate geometry has since been confirmed by X-ray diffraction,[5b] which indicates structure D.



D

Infrared spectra of Ia and Ib are presented in Figure 1; data are set out in Table I, along with assignments.[3] The spectra are in very good accord with structure D, with the exception of one striking anomaly. The bands assignable[3,13] to the symmetrically and antisymmetrically coupled B–H_b stretching vibrations, which normally[3] occur in the 2100–1960-cm^{-1} region, have been drastically displaced to lower frequency. The comparison is most meaningful between the titanium and vanadium compounds, where the oscillators have nearly identical masses. It can be seen that vibrations involving the terminal hydrogen portion (ν_{B-H_t} and δ_{BH_2}) are almost unchanged but that the perturbation is localized in the $M(H_b)_2B$ segment. Not only do the B–H_b bonds weaken, but the A_1 bridge stretch, which has considerable ν_{M-H} character,[3,13] increases in frequency from 1315 (Ic) to 1395 cm^{-1} (Ia). To further verify that ν_{B-H_b} of Ia had indeed shifted to the 1650–1750-cm^{-1} region, $(C_5H_5)_2VBD_4$ was synthesized from $(C_5H_5)_2VCl_2$ and $NaBD_4$. The resulting infrared spectrum is also shown in Figure 1. The spectrum is complicated by some scrambling of C_5H_5 protons with BD_4 deuterons[14] as indicated by a substantial ν_{B-H_t} band at 2405 cm^{-1} and a weak ν_{C-D} band at 2300 cm^{-1}.[15] However, it is still clear that the strong band at 1290 cm^{-1} is derived from the 1745-cm^{-1} band in the BH_4 compound ($\nu_H/\nu_D = 1.35$). Likewise, either the shoulder at

Table I. Infrared Vibrational Data ($\mathrm{cm^{-1}}$) for $(\eta^5\text{-}C_5H_5)_2MBH_4$ Compounds[a]

M	ν_{B-H_t}[b] A$_1$ and B$_1$	ν_{B-H_b} A$_1$ and B$_2$	Bridge expansion A$_1$	$\delta(BH_2)$ B$_2$	$\eta^5\text{-}C_5H_5$[c]
V[d]	2442 s, 2418 vs	1745 ms, 1650 m	1395 vs	1180 s	1020 ms, 855 m, 804 vs
V[e]	1820 m, 1760 s, 1720 m	1290 ms, 1230 w or 1180 w	1030 vs	860 s	
Ti	2438 s, 2400 vs	2050 m?, 1940 s	1315 vs	1155 s	1018 s, 818 vs
Nb	2460 s, 2423 vs	1745 m, 1628 s	1382 vs	1162 s	1000 ms, 900 m, 880 m, 838 s, 790 vs

[a] In $\mathrm{cm^{-1}}$: m = medium, s = strong, w = weak. All spectra recorded in dry, degassed Nujol unless otherwise noted. [b] In benzene solution. [c] Assignments derived from $(\eta^5\text{-}C_5H_5)_2MCl_2$ compounds, *cf.* F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 91, 7281 (1969). [d] Raman data: 2460 w, 2428 w, 2416 w, 2040 w, 1748 w, 1648 m, 1232 m, 1107 m, 1019 m, 480 w, 325 w, 255 w, 240 m $\mathrm{cm^{-1}}$. The bands at 1107 and 240 $\mathrm{cm^{-1}}$ are most likely C_5H_5 A$_1$ vibrations.[15] [e] $(C_5H_5)_2VBD_4$.

1230 or 1180 $\mathrm{cm^{-1}}$ may arise from the 1650-$\mathrm{cm^{-1}}$ band (ν_H/ν_D = 1.34 or 1.40). In the laser Raman spectrum (Kr$^+$, 6471 Å) weak bands are apparent for $(C_5H_5)_2VBH_4$ at 1648 and 1747 $\mathrm{cm^{-1}}$; the former is somewhat more intense. Data are compiled in Table I. The infrared spectrum of the niobium compound is similar to that of the vanadium (Figure 1). Assignments are given in Table I.

Stereochemical Dynamics. As already noted, the proton nmr spectra of covalent metal borohydrides invariably reveal the bridge and terminal BH_4 protons to be magnetically equivalent. It has been thought for some time[11,16] that this equivalency arose from dynamic intramolecular rearrangement, but variable temperature pmr studies have been complicated by unrelated boron quadrupolar relaxation effects,[11a] which depend upon the correlation time for molecular reorientation ("thermal decoupling" [11b]). In no case to date has the process been halted on the nmr time scale, and in only one case,[12] where the time scale was effectively expanded *via* isotropic shifts, could the approach of the coalescence point be observed.[12] The extreme rapidity of the fluxional process has been attributed to, among other factors, quantum mechanical tunneling, and the "unstoppability" of the process has virtually become dogma.[11b,16] The unusual vibrational spectra of Ia and Ib suggested that the potential energy surface connecting the bidentate configuration with other geometries might not be so "soft" in this case, and that a higher barrier to bridge-terminal hydrogen interchange might be present.

The room temperature pmr spectrum of Ia is shown in Figure 2. The chemical shift of the equivalent BH_4 protons is by the highest (τ 19.46) yet reported for a transition metal tetrahydroborate.[4] The magnitude of the shift no doubt arises from paramagnetic shielding[17,18] by the vanadium ion, which has a partially filled d shell. Broad-band decoupling of ^{11}B at 28.88-MHz (Figure 2) collapsed the BH_4 resonance to a singlet, and prevented the appearance in the pmr of the temperature-dependent, extraneous ^{11}B quadrupolar relaxation effects.[11a,12] The residual broadness of the proton singlet still apparently reflects coupling to ^{51}V ($I = 7/2$).[19] On lowering the temperature below *ca.* −20°, the BH_4 singlet broadens and finally collapses (Figure 2). Finally, below *ca.* −90°, a new resonance emerges at $\tau \approx 34$. This behavior is completely reversible, and identical down to −90° in pure toluene as the solvent. We attribute this behavior to slowing of the fluxional process and to freezing out of instantaneous structure D. The feature at $\tau \approx 34$ is logically assigned to the H_b resonance and integrates in a 1.9:10.0 ratio with respect to the C_5H_5 resonance. The H_t resonance is obscured by the solvent, but is calculated from the data at hand to be at $\tau \approx 5$ for a bidentate geometry. This is in close agreement with a value of $\tau \approx 6$ for the terminal protons of diborane.[20] Taking the frequency separation between exchanging sites to be 2500 Hz and the coalescence point to be −87 ± 7°, we calculate a free energy of activation[21] of 7.6 ± 0.3 kcal/mol. This barrier is somewhat larger than the 5.0 ± 0.6 kcal/mol barrier found for $(C_5H_5)_3UBH_4$,[12] which has tridentate ligation.[3]

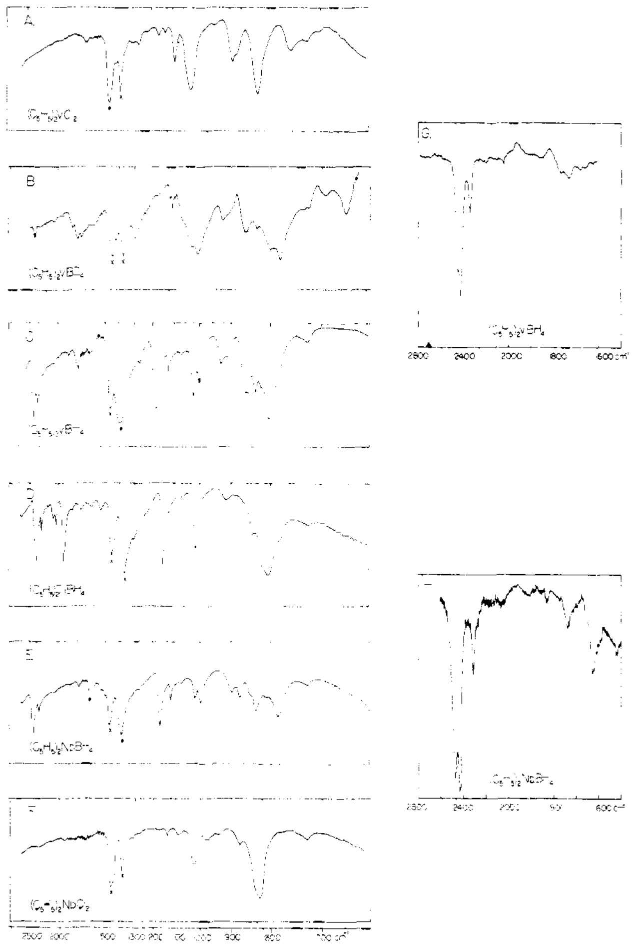


Figure 1. Infrared spectra of (A) $(\eta^5\text{-}C_5H_5)_2VCl_2$ in Nujol, (B) $(\eta^5\text{-}C_5H_5)_2VBD_4$ in Nujol, (C) $(\eta^5\text{-}C_5H_5)_2VBH_4$ in Nujol, (D) $(\eta^5\text{-}C_5H_5)_2TiBH_4$ in Nujol, (E) $(\eta^5\text{-}C_5H_5)_2NbBH_4$ in Nujol, (F) $(\eta^5\text{-}C_5H_5)_2NbCl_2$ in Nujol. Sharp bands marked × are due to Nujol. Infrared spectra of (G) $(\eta^5\text{-}C_5H_5)_2VBH_4$ in benzene, (H) $(\eta^5\text{-}C_5H_5)_2NbBH_4$ in benzene.

Proton nmr spectra of $(C_5H_5)_2NbBH_4$ are shown in Figure 3. At room temperature, the BH_4 resonance is an extremely broad multiplet with a line width of 800-1000 Hz even after ^{11}B decoupling. The C_5H_5 resonance (τ 4.93) is relatively sharp. On lowering the temperature, the BH_4 resonance narrows, and by −90° a singlet (line width ≈35 Hz) is observed at τ 26.2. This resonance integrates in a ratio of 4.1:10.0 with respect to the C_5H_5 protons, and as such represents all four BH_4 protons (calculated ratio, 4.0:10.0). Thus, in Ib, the bridge-terminal hydrogen exchange process is still rapid at these temperatures. No detectable broadening of this resonance was detected down to −120° in toluene-$(CH_3)_2O$. The spectral broadening observed on raising

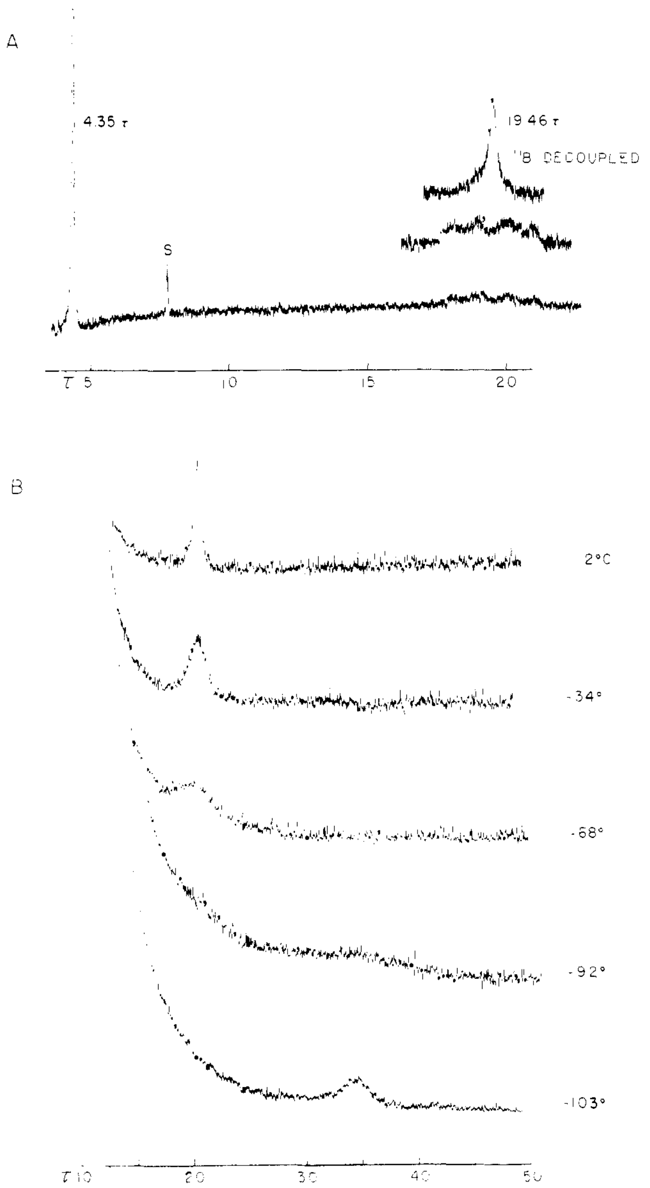


Figure 2. (A) Room temperature 90-MHz ^1H nmr spectrum of $(C_5H_5)_2VBH_4$ in toluene-d_8. S denotes solvent. (B) Variable temperature 90-MHz $^1H\text{-}\{^{11}B\}$ spectra of $(C_5H_5)_2VBH_4$ in 3:1 toluene-d_8:diethyl ether. Each spectrum is the result of three to six computer-averaged scans. Absorbance at the left is due to ether.

the temperature is most likely a manifestation of ^{93}Nb quadrupolar relaxation,[11a,19] which has been observed before[22] for niobium complexes. That the broadening of the proton resonance of the corresponding ^{51}V compound is considerably smaller, is not unexpected,[11a] since ^{93}Nb has a greater spin quantum number ($I = \frac{9}{2}$ vs. $\frac{7}{2}$) and quadrupole moment ($Q = -0.22$ vs. -0.05×10^{-24} cm^2).[23,24] The differences in observed line shapes will also be a function of the relative magnitudes of $J_{^{93}Nb-H}$ and $J_{^{51}V-H}$, as well as the rotational correlation times.[11a]

Discussion

The new compound $(C_5H_5)_2VBH_4$ represents the only case of a transition metal borohydride complex reported to date where the bridge-terminal hydrogen interchange process has possessed a sufficiently high free energy barrier, 7.6 ± 0.3 kcal/mol, to allow observation of the instantaneous structure in the low temperature pmr spectrum. In addition, this complex exhibits a unique vibrational spectrum. In comparison to the closely related complex $(C_5H_5)_2TiBH_4$, considerable weakening of the B–H_b bonds is observed. It is of interest to ask whether the kinetic and vibrational spectroscopic anomalies are at all connected. In the representation of M–BH_4 ligation dynamics in terms of a potential energy surface, the vibrational spectrum is descriptive of ground state (and relatively small excursions therefrom) bonding. The classical activation barrier represents the energy difference between the ground state potential well and the highest point on an allowed path across the surface, connecting one ground state well with an equivalent one (for a degenerate rearrangement). Hence, the observed activation energy can be altered either by changing the energy of the ground state configuration or that of the excited state. The minimum difference in barriers to hydrogen interchange between Ia and Ib can be estimated from the coalescence point data for Ia together with the physically reasonable assumption that $\log A = 13$ for both complexes, and that $\tau \leq 10^{-5}$ sec for Ib at 153°K. This yields $E_a \approx 7.9$ kcal/mol for Ia and $E_a \leq 5.6$ kcal/mol for Ib.

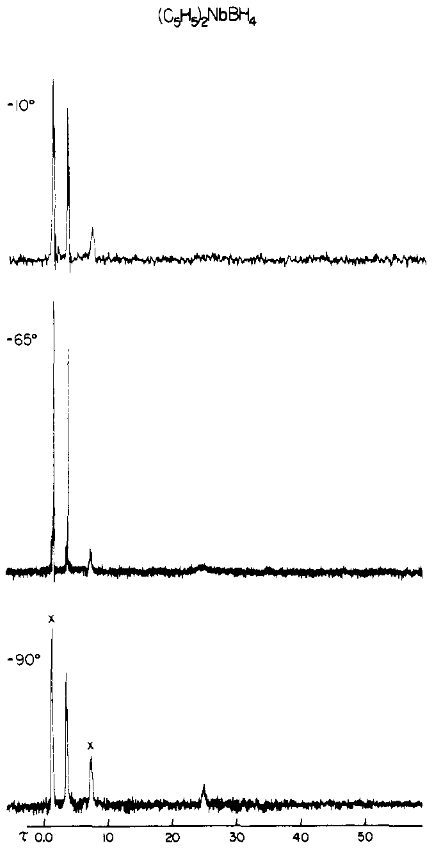


Figure 3. Variable temperature 60-MHz ^1H nmr spectra of $(C_5H_5)_2NbBH_4$. Resonances marked X are due to traces of benzene and toluene-d_7.

The differences in the vibrational spectrum of $(C_5H_5)_2VBH_4$ compared to other transition metal tetrahydroborates, especially $(C_5H_5)_2TiBH_4$, are explicable to a first approximation in terms of the degree of perturbation from an ionic $M^+BH_4^-$ valence bond hybrid. Flow of electron density from filled ligand molecular orbitals with considerable B–H bonding character (BH_4 A_1, B_1, and B_2 molecular orbitals[25] under C_{2v} local symmetry) into molecular orbitals with considerable metal–ligand bonding character[26] is, no doubt, general for all covalent tetrahydroborate complexes. The particular changes in force constants on proceeding from the Ti(III) d^1 system to the V(III) d^2 system suggests the additional electron is populating a molecular orbital with metal–ligand bonding character, and B–H antibonding character. Low-valent titanium and vanadium $(\eta^5\text{-}C_5H_5)_2M$ units can be shown both experimentally and theoretically to be electron rich;[30-32] it is conceivable, and orbitals of proper symmetry are available,[32b] that back-donation into predominantly B–H antibonding orbitals is also occurring. The effect such ground state changes in bonding will have on the tautomerism[33] is not quantitatively clear. We have previously suggested[3,12] that a bidentate $\rightleftharpoons$ tridentate ($B \rightleftharpoons C$) equilibrium provided a plausible pathway for hydrogen permutation. As the bonding deviates more from an ionic $M^+BH_4^-$ description, it may well be that small distortions in metal–ligand bond geometry will only take place at increasing costs in energy. However, the fact that $(C_5H_5)_2NbBH_4$ fluxional behavior is more rapid is not obvious from these ground state considerations alone.

As already noted, the vibrational spectrum of $(C_5H_5)_2NbBH_4$ was quite similar to that of Ia, and is also unlike that of other borohydride complexes. Though the increased mass of niobium renders exact comparison of Ia and Ib spectra difficult, it is clear from zirconium and hafnium tetrahydroborate data[3,34] that mass effects on BH_4-centered vibrations are not in excess of *ca.* 20–30 cm^{-1}, and that in $(C_5H_5)_2NbBH_4$ the ground state metal–ligand bonding is similar to $(C_5H_5)_2VBH_4$. Thus, it is likely that the excited state is also important in determining the barrier for hydrogen interchange. For a tridentate transition state this is highly plausible, since niobium has a larger ionic radius than vanadium[35] and more readily takes on high coordination numbers.[36] Most relevant to the present discussion are the $(\eta^5\text{-}C_5H_5)_2M(\text{allyl})$ compounds. The M = V compound is a η^1-allyl[37] while the M = Nb compound is a η^3-allyl.[8,38] Thus, the barrier to a bidentate → tridentate transition ($B \rightarrow C$) might be expected to be lower for the niobium complex.

Further synthetic, structural, and spectroscopic studies will be necessary to fully define the relationship of metal ion size and electronic configuration to tetrahydroborate ligation and stereochemical dynamics. This work indicates that there can be considerable fine structure and diversity to both.

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$$\frac{1}{T_1} = \frac{3}{40}\frac{2I+3}{I^2(2I-1)}(1+\eta^2/3)(e^2qQ/h)^2\tau_c$$

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