# Synthesis, Vibrational Spectra, and Proton Magnetic Resonance of Some Boron-Substituted Tris(cyclopentadienyl)uranium(IV) Tetrahydroborates[1]

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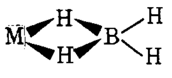
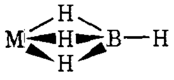
**Abstract:** The reaction of $(C_5H_5)_3UBH_4$ with $R_3B$ yields the corresponding $(C_5H_5)_3UH_3BR$ compound, $R = C_2H_5$, $C_6H_5$. Vibrational spectra indicate that the BR group is connected to uranium *via* a triple hydrogen bridge. The compounds $(C_5H_5)_3UNCBH_3$ and $(C_5H_5)_3UNCB(C_6H_5)_3$ were synthesized by the reaction of $(C_5H_5)_3UCl$ with the corresponding anionic borates. Vibrational spectra suggest the metal–borate linkage is of the type $\mathrm{UN{\equiv}CB}\!<$. Large isotropic shifts were observed in the pmr spectra of these paramagnetic U(IV) compounds. For the $(C_5H_5)_3UH_3BR$ system it was possible to separate contact and dipolar contributions; the mechanism of unpaired spin distribution involves negative spin density on the protons bound directly to uranium. The $^{11}B$-decoupled pmr spectrum of the fluxional molecule $(C_5H_5)_3UBH_4$ exhibits collapse of the $BH_4$ resonance at low temperatures. This indicates that the paramagnetism induces sufficient energy separation between exchanging sites (bridge and terminal hydrogens) to observe, for the first time in a metal tetrahydroborate, slowing of the dynamic intramolecular rearrangement process. At the estimated coalescence point ($-140 \pm 20°$) $\delta\omega$ = 15,000–36,000 Hz and $\Delta G^* \approx 5.0 \pm 0.6$ kcal/mol.

Interest in tetrakis(tetrahydroborato)uranium(IV) dates back to the Manhattan project.[3] Our interest in organometallic uranium derivatives of the $BH_4$ ligand[4] arose for two principal reasons. First, it has been pointed out that the tetrahydroborate ligand shares certain common features with the $\eta^3$-allyl ligand.[5] Thus, $BH_4$ offers the possibility for elaboration and functionalization of low coordination number organouranium chemistry. Secondly, the paramagnetic U(IV) ($5f^2$) ion is an excellent nuclear magnetic resonance probe.[6] Large pmr isotropic shifts are usually observed in conjunction with very narrow line widths. The attendant increased time resolution[1,6] appeared applicable to the identification of the rapid intramolecular rearrangement which is believed to permute bridge and terminal hydrogen atoms. In all reported cases of either bidentate (A) or tridentate (B) ground state geometry, it had not been possible to observe slowing of this dynamic process.[7,8] Also, analysis of hyperfine shifts in the $BH_4$ ligand would provide some insight into the electronic nature of the metal–ligand interaction and would represent the first contact shift data (both sign and magnitude) for a proton bonded directly to a metal ion in a paramagnetic complex. We present in this paper a full discussion of the synthesis, structures, and nmr spectroscopy of a series of $(C_5H_5)_3UH_3BR$ compounds, with the above considerations in mind.



A



B

## Experimental Section

The preparation and handling of all organoactinides was necessarily carried out in an atmosphere of prepurified nitrogen or argon, with rigorous exclusion of air and moisture. Sample manipulation was by Schlenk methods or 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 $(C_5H_5)_3UCl$ was prepared by our procedure,[9] while $(C_5H_5)_3UBH_4$ was synthesized according to the literature method.[10]

**Tris($\eta^5$-cyclopentadienyl)(ethyltrihydroborato)uranium(IV).** To 0.60 g (1.33 mmol) of $(C_5H_5)_3UBH_4$ in 25 ml of benzene was added 0.23 g (2.30 mmol) of triethylborane. The mixture was refluxed under nitrogen until infrared spectra indicated the absence of $\nu_{\text{B-H(terminal)}}$[5] (34 hr). The solvent was then removed *in vacuo* and the brown residue was pumped for 2 hr. Next, the residue was recrystallized twice from pentane (−78°) to yield 0.25 g (82%) of orange-brown needles of $(C_5H_5)_3UH_3BC_2H_5$, mp 220–232°. The compound burns fiercely on exposure to air.

*Anal.* Calcd for $C_{17}H_{23}UB$: C, 42.87; H, 4.88. Found: C, 42.12; H, 4.92.

**Tris($\eta^5$-cyclopentadienyl)(phenyltrihydroborato)uranium(IV).** To 3.76 g (8.4 mmol) of $(C_5H_5)_3UBH_4$ in 150 ml of benzene was added 3.67 g (15.1 mmol) of triphenylborane. The reaction mixture was then refluxed until pmr spectra indicated the reaction to be complete (2 days). Next, the solvent was removed under high vacuum to yield a red-brown solid. This was recrystallized from toluene–pentane (−40°) to yield 3.3 g (75%) of $(C_5H_5)_3UH_3BC_6H_5$ as dark red-brown crystals, mp 222–232°. The crystals begin to smoke upon exposure to air.

*Anal.* Calcd for $C_{21}H_{23}UB$: C, 48.13; H, 4.44. Found: C, 48.06; H, 4.78.

**Tris($\eta^5$-cyclopentadienyl)(cyanotrihydroborato)uranium(IV).** Under nitrogen, 2.24 g (4.8 mmol) of $(C_5H_5)_3UCl$ was combined with 0.91 g (14.4 mmol) of sodium cyanotrihydroborate, and 150 ml of tetrahydrofuran was added to the solids. The color of the solution immediately became a dark olive green and the reaction, monitored by pmr, was complete almost immediately. The mixture was allowed to react for an additional 24 hr and the solution then filtered to exclude the excess sodium cyanotrihydroborate and sodium chloride. The solvent was removed *in vacuo* and the green solid washed with *n*-pentane. Soxhlet extraction of the crude product with benzene yielded 1.45 g of green solid (72%), mp 237–242°. The compound immediately blackens and burns on exposure to air.

*Anal.* Calcd for $C_{16}H_{18}UBN$: C, 40.61; H, 3.83; N, 2.96. Found: C, 40.97; H, 3.90; N, 3.10. The mass spectrum (70 eV) exhibited a weak parent ion at *m/e* 473 and prominent fragments corresponding to $(C_5H_5)_3U^+$ and $(C_5H_5)_2U^+$.

**Tris($\eta^5$-cyclopentadienyl)(cyanotriphenylborato)uranium(IV).** To 1.80 g of $(C_5H_5)_3UCl$ (3.84 mmol) in a nitrogen filled flask was added 2.23 g (7.68 mmol) of sodium cyanotriphenylborate. Tetrahydrofuran (100 ml) was next added and the color of the reaction mixture turned to a light olive immediately. As in the case of the cyanotrihydroborate compound, the reaction was essentially instantaneous; however, it was allowed to proceed for 1 day to ensure completion. The solution was filtered and the tetrahydrofuran removed *in vacuo*. The light green compound was washed with pentane and then Soxhlet extracted with benzene. The light green crystals (1.30 g, 48% yield), mp 80–85°, turn yellow on exposure to air.

*Anal.* Calcd for $C_{34}H_{30}UBN{\cdot}C_6H_6$: C, 61.70; H, 4.65; N, 1.80.

Found: C, 62.14; H, 5.08; N, 2.04. The mass spectrum run at 10 eV exhibited a weak parent ion at *m/e* 701 and prominent ion fragments corresponding to successive loss of $C_5H_5$ and $C_6H_5$ with the strongest peak corresponding to a fragment of composition $(C_5H_5)_3UNC^+$.

**Spectroscopic Measurements.** Infrared spectra were recorded on Beckman IR-5 or IR-9 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 infrared cell described previously.[11] 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 $\nu_{B-H}$ bands[5] and appearance of the antisymmetric O=U=O stretch at *ca.* 925 $cm^{-1}$.[12]

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. Homonuclear decoupling was performed with a Model R-2015D decoupler, and continuous wave time averaging (and integration) with an interfaced ADS-VII computer. 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 ND30M 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[7] boron-coupled quartet ($J \approx 90$ Hz) to a sharp singlet. When necessary, continuous wave time averaging was performed with an interfaced Fabritek 1074 computer. In cases where resonance positions were greater than 12 KHz from the locking signal, spectra were recorded under unlocked, field-sweep (1.0 or 10.0 $\mu$G/sec) conditions. In such cases, time averaging was not possible. Sample solutions were examined under nitrogen in sample tubes capped with serum stoppers, or sealed off on a vacuum line. Solvents were rigorously dried and degassed.

Mass spectra were recorded on a CEC 21-104 at low ionizing voltage. Samples were introduced under inert atmosphere by the direct inlet technique. We thank Dr. L. A. Raphelian for assistance.

## Results and Discussion

**Synthesis.** The tetrahydroborate and substituted tetrahydroborate anions displace chloride from $(C_5H_5)_3UCl$ in either coordinating (tetrahydrofuran) or noncoordinating (benzene) solvents to produce the corresponding uranium(IV) complexes, **1a-c.** Equation 3 demonstrates that the presence of the B-H functionality is not essential. It has

$$(C_5H_5)_3UCl + NaBH_4 \longrightarrow \underset{\textbf{1a}}{(C_5H_5)_3UBH_4} + NaCl \quad (1)$$

$$(C_5H_5)_3UCl + NaBH_3CN \longrightarrow \underset{\textbf{1b}}{(C_5H_5)_3UBH_3CN} + NaCl \quad (2)$$

$$(C_5H_5)_3UCl + NaB(C_6H_5)_3CN \longrightarrow \underset{\textbf{1c}}{(C_5H_5)_3UB(C_6H_5)_3CN} + NaCl \quad (3)$$

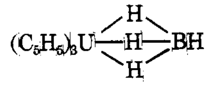
been reported [13] that $U(BH_4)_4$ can be alkylated with trialkyl boranes to produce the corresponding $U(BH_4)_n(BH_3R)_{4-n}$ species. We find this reaction generalizable to organouranium systems, eq 4. All compounds

$$(C_5H_5)_3UBH_4 + R_3B \longrightarrow (C_5H_5)_3UBH_3R + HBR_2 \quad (4)$$

$$\textbf{1d}, R = C_2H_5$$
$$\textbf{1e}, R = C_6H_5$$

prepared in this study are exceedingly air and moisture sensitive. Compounds **1a, d,** and **e** are red-brown in color, and **1d** and **e** are sufficiently soluble to be recrystallized from hydrocarbon solvents. Compounds **1b** and **c** are dark green in color and considerably less soluble. Purification was achieved *via* Soxhlet extraction. All compounds appear to be indefinitely stable at room temperature under nitrogen.

**Structural Considerations.** Vibrational spectroscopy has been shown[5] to be a useful tool for elucidating the gross structural features (*e.g.*, the choice between A and B) of organometallic tetrahydroborates. The presence in the infrared of a single ($A_1$) strong $B-H_{terminal}$ stretch at 2480 $cm^{-1}$ together with two ($A_1$, E) $B-H_{bridge}$ stretches at 2220 and 2160 $cm^{-1}$ and a bridge deformation (E) at 1160 $cm^{-1}$ was taken[5] as overwhelming evidence that $(C_5H_5)_3UBH_4$ possessed tridentate geometry, (C). The spectrum of $(C_5H_5)_3UCl$ was employed to identify bands arising from the $(\eta^5\text{-}C_5H_5)_3U$ moiety, *viz.*, $A_1$ and $E_1$ C-H out-of-plane wagging $\approx$800 $cm^{-1}$ (strong) and $E_1$ in-plane wagging $\approx$1010 $cm^{-1}$ (medium) under $C_{5v}$ local symmetry.



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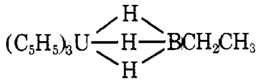


D

The infrared spectrum of **1d** is shown in Figure 1. The absence of a $\nu_{B-H(terminal)}$ band and the presence of two $\nu_{B-H(bridge)}$ bands at 2188 and 2118 $cm^{-1}$ (2187 and 2122 $cm^{-1}$ in benzene solution) is in good accord with structure D. It is unlikely that the presence of an alkyl group could lower the single $\nu_{B-H(terminal)}$ of a bidentate geometry to the 2100-$cm^{-1}$ region.[5,14] By analogy to the $(C_5H_5)_3UBH_4$ results, the strong band at 1219 $cm^{-1}$ is assigned to the E bridge deformation. The bands at 1276 and 1085 $cm^{-1}$ are associated with a $B\text{-}CH_2CH_3$ group,[15] the former probably being the $CH_2$ wag and the latter the $^{11}B\text{-}C$ stretch. In the region above 2000 $cm^{-1}$, the spectrum of **1e** is similar (Figure 1) to that of **1d**, ($\nu_{B-H(bridge)} \approx 2160$ and 2060 $cm^{-1}$) indicative also of a tridentate geometry. The region below 1500 $cm^{-1}$ is complicated by a number of bands common to phenyl organometallics.[16] The strong band at 1245 $cm^{-1}$ is most likely the $H_3B$ bridge deformation mode. Of the bands at 1160 and 1070 $cm^{-1}$, the former is probably a phenyl C-H out-of-plane bend,[16] and the latter the $^{11}B\text{-}C$ stretch.

The infrared spectra of the cyano derivatives **1b** and **1c** are also shown in Figure 1. These can be interpreted by reference to spectroscopic[17] and structural[18] data for other metal cyanoborates. For the $H_3BCN$ ligand, all known complexes which show no evidence for association are believed to be bonded through nitrogen as in E. These com-

$$M \longleftarrow N{\equiv}CBH_3$$

E

pounds exhibit $\nu_{C\equiv N}$ in the region *ca.* 2180-2210 $cm^{-1}$ and $\nu_{B-H}$ in the region 2280-2375 $cm^{-1}$. The B-H deformation mode is usually found at 1110-1130 $cm^{-1}$. The compound $[(C_6H_5)_3P]_2CuBH_3CN$[17c,18a] exhibits a more complex spectrum with the $\nu_{B-H}$ region at higher frequency and a new $\nu_{B-H}$ band appearing at 2207 $cm^{-1}$; the B-H deformation shifts to 1100 $cm^{-1}$ while $\nu_{C\equiv N}$ remains near 2190 $cm^{-1}$. The spectrum can be understood by consideration of the structure, F.[18a] The band at 2207 $cm^{-1}$ is in all probability a bridging $\nu_{B-H}$. The spectrum of $(C_5H_5)_3UBH_3CN$ in the solid state is most like the dimeric copper compound with $\nu_{B-H}$ at ($cm^{-1}$) 2462 w, 2360 m, 2240 ms, and $\nu_{C\equiv N}$ at 2178. The B-H deformation is found at 1104 $cm^{-1}$. This suggests a structure in the solid state which may be associated. The compound is insufficiently soluble in benzene to

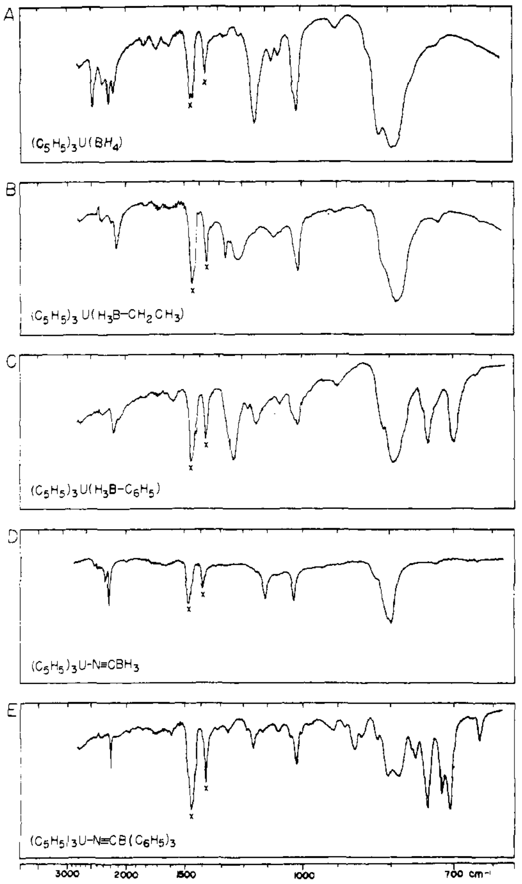
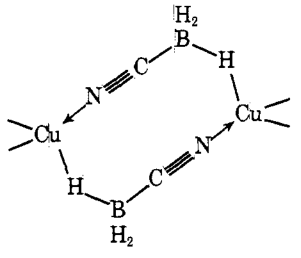
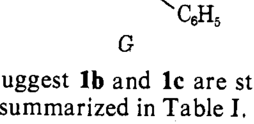


**Figure 1.** Infrared spectra of (A) ($\eta^5$-$C_5H_5)_3UBH_4$ in Nujol, (B) ($\eta^5$-$C_5H_5)_3UH_3BCH_2CH_3$ in Nujol, (C) ($\eta^5$-$C_5H_5)_3UH_3BC_6H_5$ in Nujol, (D) ($\eta^5$-$C_5H_5)_3UNCBH_3$ in Nujol, and (E) ($\eta^5$-$C_5H_5)_3UNCB(C_6H_5)_3$ in Nujol.



F

determine the molecular weight cryoscopically even with highly sensitive apparatus.[19] The low solubility has also hindered the recording of infrared spectra in solution. However, the pmr resonance positions in solution (*vide infra*) confirm that the structure is unlike C or D. The spectrum of the $(C_6H_5)_3BCN$ complex is also presented in Figure 1. The $\nu_{C\equiv N}$ band occurs at 2199 cm$^{-1}$ (literature values are in the range 2166–2206 cm$^{-1}$) and the complex is assigned structure G. In solution, the $C_5H_5$ pmr resonance frequencies (*vide infra*) suggest **1b** and **1c** are structurally similar. Infrared data are summarized in Table I.



$$(C_5H_5)_3UNCB(C_6H_5)_3$$

G

**Nmr Spectroscopy. Analysis of Isotropic Shifts.** As has previously been observed for $(C_5H_5)_3U^{IV}$ complexes,[1,6,20] the proton nmr line positions of the complexes synthesized for the present study are severely displaced from typical diamagnetic values (Table II). An example is shown in Figure 2. In general, the large isotropic chemical shifts reflect both contact (hyperfine) and dipolar (pseudocontact) contributions. The former term reflects the disposition of unpaired spin density (5f electron in the present case) through the ligand system. Under the practical assumption that $J$ is a good quantum number, it is possible to express the contact shift of the $i$th nucleus as[6,20]

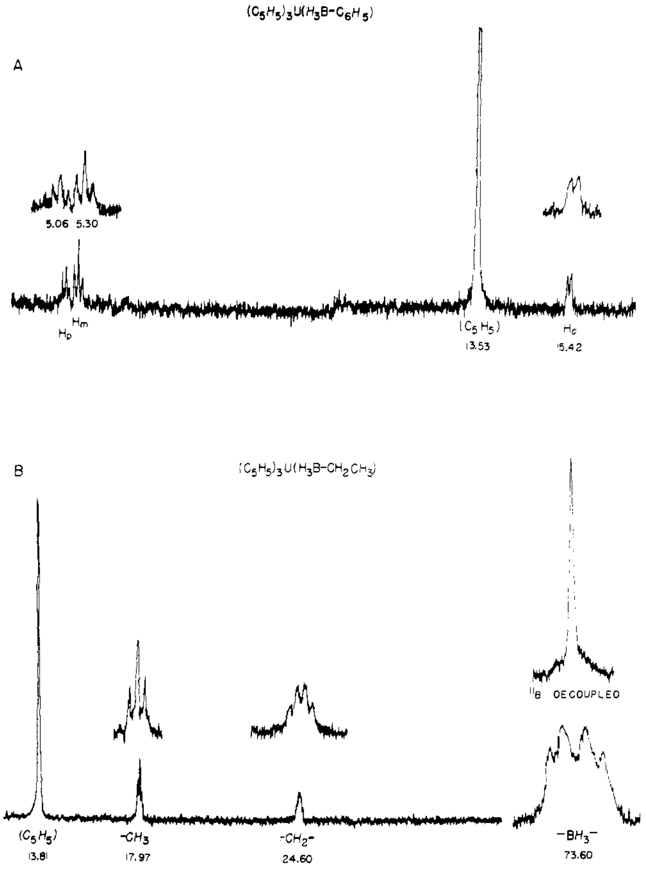


**Figure 2.** The 90-MHz proton magnetic resonance spectra of (A) ($\eta^5$-$C_5H_5)_3UH_3BC_6H_5$ in benzene and (B) ($\eta^5$-$C_5H_5)_3UH_3BCH_2CH_3$ in benzene. Chemical shifts are given under the peak positions in ppm from benzene lock signal. $^{11}B$ white noise decoupling is illustrated in (B) collapsing the $(H_3B)$ multiplet to a single resonance.

**Table I.** Infrared Spectroscopic Data for $(C_5H_5)_3UH_3BX$ Compounds[a,b]

| Compound | |
|---|---|
| $(C_5H_5)_3UBH_4$ | 2480 s, 2295 m, 2220 s, 2160 s, 1835 w, 1722 w, 1618 w, 1298 vw, 1235 vw, 1160 vs, 1105 m, 1080 m, 1020 s, 920 w, 825 s, sh, 797 vs |
| $(C_5H_5)_3UH_3BCH_2CH_2$ | 2290 w, 2188 w, 2118 s, 1276 s, 1215 s, br, 1085 w, br, 1010 s, 815 sh, 790 vs |
| $(C_5H_5)_3UHBC_6H_5$ | 2160 s, 2060 m, 1805 w, br, 1685 w, br, 1580 w, br, 1245 vs, 1181 vw, 1160 m, 1070 w, 1013 m, br, 910 w, br, 814 sh, 796 vs, 738 s, 699 s, 666 vw |
| $(C_5H_5)_3UNCBH_3$ | 2462 w, 2360 m, 2240 ms, 2178 s, 1975 vw, 1142 w, 1104 s, 1014 s, 823 sh, 794 vs, 730 w |
| $(C_5H_5)_3UNCB(C_6H_5)_3$ | 2199 s, 1960 vw, 1900 vw, 1825 vw, 1710 vw, 1594 vw, 1317 vw, 1266 vw, 1188 vw, 1160 m, 1126 w, 1075 w, 1033 vw, 1018 s, 1002 vw, 918 w, 892 w, 869 m, 859 w, 825 w, 805 s, 785 s, 764 vw, 758 w, 740 s, 718 m, 705 s, 664 m |

[a] In cm$^{-1}$. [b] Key: w = weak, m = medium, s = strong, sh = shoulder, br = broad, v = very.

Table II. Nuclear Magnetic Resonance Data for $(\eta^5\text{-}C_5H_5)_3UH_3BX$ Compounds[a]

| Compound | |
|---|---|
| $(C_5H_5)_3UBH_4$ | +13.37 (15 H, s), +67.2 (4 H, quart) |
| $(C_5H_5)_3UH_3BCH_2CH_3$ | +13.81 (15 H, s), +17.97 (3 H, trip), +24.60 (2 H, quart), +73.60 (3 H, quart) |
| $(C_5H_5)_3UH_3BC_6H_5$ | +13.53 (15 H, s), +5.06 (1 H, trip), +5.30 (2 H, trip), +15.42 (2 H, doub), +84.00 (3 H, quart) |
| $(C_5H_5)_3UNCBH_3$ | +9.71 (15 H, s), +30.10 (3 H, quart) |
| $(C_5H_6)_3UNCB(C_6H_5)_3$ | +8.67 (15 H, s), +0.38 (3 H, trip), +0.6 (6H), +0.7 (6 H) |

[a] Pmr data in ppm relative to internal benzene, + indicating shift to high field.

$$\frac{\Delta H_i^{\mathrm{con}}}{H} = -\frac{A_i(g_J - 1)\chi}{Ng_J\beta g_N\beta_N} \quad (5)$$

Here $A_i$ is the empirical electron–nuclear hyperfine coupling constant,[21] $\chi$ is the magnetic susceptibility, $g_J$ the Landé $g$ factor, and the other terms have their usual meaning. Under the reasonable (in the present case) assumption of axial symmetry, the dipolar contribution for the $i$th nucleus can be expressed as[6,20,22]

$$\frac{\Delta H_i^{\mathrm{dip}}}{H} = -\frac{1}{3N}[\chi^{\parallel} - \chi^{\perp}]\left\langle\frac{3\cos^2\theta_i - 1}{r_i^3}\right\rangle \quad (6).$$

where the symbols have their usual meaning.[6,20,22]

The relative contribution of $\Delta H^{\mathrm{con}}$ and $\Delta H^{\mathrm{dip}}$ to an observed chemical shift is of greatest interest. Magnetically anisotropic rare earth systems are commonly analyzed by assuming axial molecular symmetry and attempting to fit experimental shift ratios for various sites on the molecule to the calculated "geometric factor" ratios ($3\cos^2\theta - 1/r^3$) for these sites. In cases where dipolar shifts predominate, small deviations from exact agreement can be assigned to contact shifts. In one important case ($(C_5H_5)_3UR$, R = alkyl group[6]), we found contact shifts which were so large that this approach was not applicable.[6] However, by assuming that the contact shifts of nuclei in two positions in two selected molecules were proportional to electron-nuclear hyperfine interactions ($a_i$) in the corresponding R· free radicals, it was possible to set up simultaneous equations for separation of contact and dipolar shifts in the entire series.[6]

The analysis of isotropic shifts in $(C_5H_5)_3UH_3BR$ compounds began with the synthesis of the rigid compound where R = $C_6H_5$. Geometric factors were calculated with $UH_3B$ structural parameters derived from the neutron diffraction study of $U(BH_4)_4$.[23] Other distances and angles were taken from standard sources.[24] The results are presented in Table III, including results as a function of slight variations in the U–H distance. It can be seen that the isotropic shifts of the phenyl protons are predominantly if not exclusively dipolar in origin. Indeed, even the data for the geometrically less rigid R = $C_2H_5$ compound are also in agreement[25] with predominantly dipolar interactions. This allows calculation of the dipolar shift for the hydrogens bound directly to uranium. Subtraction of this value from the observed isotropic shift yields the contact (hyperfine) shift. These data are summarized inTable III. Values of the contact shifts for the protons bound directly to uranium fall in the range −36 to −61 ppm from the anticipated diamagnetic positions. This downfield shift is contrary to the result expected for direct delocalization of uranium spin density onto the hydrogen nuclei[26] and indicates delocalization instead of negative spin density. This result has been observed for other atoms (C, O, F, Al, P, etc.) bound directly to actinides and lanthanides with less than half-filled f shells.[6,20,27,28] The mechanism which is operative is believed to involve donation of ligand electron density ($RBH_3^-$ here) into (or polarization by) empty or partially filled metal orbitals (5f or 7s, 7p, 6d in the present case) with exchange interaction favoring transfer of spin density parallel to the spin already on U(IV), leaving unpaired spin density of the opposite sign remaining on the ligand.[6,27-29]

As already noted, the electron-nuclear hyperfine interaction constants, $a_i$ (derived from unrestricted Hartree-Fock INDO/2 SCF molecular orbital calculations[30]) for protons in R· and RO· predicted the sign and usually the magnitude of the proton contact shifts observed[6] in the corresponding $(C_5H_5)_3U$-complexes. For $\cdot H_3BC_2H_5$ we calculate an $a_i(H_3)$ of +53 G (observed $\Delta H^{\mathrm{con}}$ = −35 to −50 ppm) which roughly follows the opposition in signs of $a_i$ and $\Delta H^{\mathrm{con}}$ seen previously;[6] *i.e.*, $a_i(CH_3\cdot)$ = −9 G ($\Delta H^{\mathrm{con}}$ = +60 ppm) and $a_i(CH_3O\cdot)$ = +18 G ($\Delta H^{\mathrm{con}}$ = −28 ppm). The INDO/2 calculations also indicate some spin density on the ethyl group,[31] which we do not observe experimentally, and which is probably an artifact of assuming the spin density introduced *via* the localized metal-ligand interaction can be accurately simulated by the spin density distribution found in a relatively delocalized free radical.

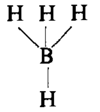
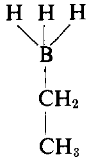
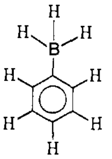
**Nmr Spectroscopy. Detection of Stereochemical Nonrigidity.** As mentioned in the introduction, the proton nmr spectra of covalent metal tetrahydroborates invariably show the bridge and terminal $BH_4$ protons to be magnetically equivalent. Though it has been thought for some time that this anomaly was due to rapid intramolecular rearrangement,[7,8,32] attempts at elucidation (or confirmation) have been deterred by extraneous quadrupolar relaxation processes[7] and the apparent extreme rapidity of the process. As illustrated in Figure 2 and by the work of other groups,[33] the former problem can be eliminated to varying degrees with white noise decoupling of $^{11}B$ from the proton spectrum. In some cases "thermal decoupling"[8,34] of $^{11}B$ has also been helpful. However, in no diamagnetic tetrahydroborate system to date have we or others been able, using these techniques, to observe slowing of the supposed dynamic process at low temperatures.[35]

The paramagnetic $5f^2$ system $(C_5H_5)_3UBH_4$ offered a number of distinct advantages. As already noted, the $(C_5H_5)_3U^{IV}$ moiety is known to induce large contact and dipolar shifts in the pmr spectra of appended groups while preserving narrow line widths.[1,6,20] This displaces the $BH_4$ resonances to spectral regions unmasked by any conceivable solvent, allowing greater flexibility in solvent choice.[36] More importantly, great amplification of the chemical shift difference between terminal and bridging hydrogens (the exchanging sites) is anticipated. This would increase the time resolution of the pmr experiment.[37] This can be seen by reference to the most relevant approximate solutions to the modified Bloch equations for an uncoupled, two-site exchange process,[38] given in eq 7 and 8, where $\tau$ = mean preexchange lifetime and $\delta\omega$ = site frequency separation in the absence of exchange. For $\tau$ constant in cases of reasonable frequency separations and spin-spin relaxation times in the absence of exchange ($T_2^0$), the line width is sensitive to change in $\delta\omega$ in the region of line narrowing above the coalescence point (fast exchange) and is also sensitive (though less so) near the coalescence point. Thus, expansion of $\delta\omega$ represents a valuable additional method of detecting rapid rate processes,[39] after temperature control and other variables have been pushed to the limit.

$$\frac{1}{\tau} = \frac{(\pi\delta\omega)^2}{4}\left[\frac{1}{T_2^{\mathrm{exch}}} - \frac{1}{T_2^0}\right]^{-1} \quad (7)$$

(fast exchange)

**Table III.** Isotropic Nmr Shift Data for $(\eta^5\text{-}C_5H_5)_3UH_3BX$ Compounds

| | Geometric factors U–B | | | Exptl.[a,b] $\Delta H^{con}$ + $\Delta H^{dip}$ | $\Delta H^{con}$ calcd.[c] | | | $\Delta H^{dip}$ calcd.[c] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $H_3BX$ | 2.37 Å | 2.52 Å | 2.67 Å | | 2.37 Å | 2.52 Å | 2.67 Å | 2.37 Å | 2.52 Å | 2.67 Å |
|  H H H | 0.1031 | 0.1010 | 0.0839 | | | | | +127.1 | +130.6 | +117.0 |
| H | 0.0425 | 0.037 | 0.0334 | | | | | +52.4 | +47.8 | +46.6 |
| $(BH_4)_{av}$ | 0.0880 | 0.085 | 0.0713 | +63.2 | −45.0 | −46.7 | −36.2 | +108.5 | +109.0 | +99.4 |
|  H H H | 0.1031 | 0.1010 | 0.0839 | +69.6 | −57.5 | −61.0 | −47.4 | +127.1 | +130.6 | +117.0 |
| $CH_2$ | 0.0219 | 0.0192 | 0.0182 | +18.4 | −8.6 | −6.4 | −7.0 | +27.0 | +24.8 | +25.4 |
| $CH_3$ | 0.010 | 0.0089 | 0.0080 | +11.8 | −0.5 | +1.5 | +0.6 | +12.3 | +10.3 | +11.2 |
|  H | 0.1031 | 0.1010 | 0.0839 | +80.0 | −47.1 | −50.6 | −37.0 | +127.1 | +130.6 | +117.0 |
| H | 0.0143 | 0.0133 | 0.0128 | +15.6 | −2.0 | −1.6 | −2.2 | +17.6 | +17.2 | +17.8 |
| H | 0.0053 | 0.0050 | 0.0043 | +5.5 | −1.0 | −1.0 | −0.5 | +6.5 | +6.5 | +6.0 |
| H | 0.0043 | 0.0041 | 0.0038 | +5.3 | 0 | 0 | 0 | +5.3 | +5.3 | +5.3 |

[a] In ppm from diamagnetic resonance position. [b] At probe temperature (28°). [c] Assuming $\Delta H^{exp}$ for para proton in $(\eta^5\text{-}C_5H_5)_3UH_3BC_6H_5$ is purely dipolar in origin. Assuming this for the meta or ortho protons gives essentially the same result.

$$\frac{1}{\tau} = \pi\delta\omega/\sqrt{2} \qquad (8)$$

(coalescence)

Figure 3 illustrates variable temperature pmr spectra of $(C_5H_5)_3UBH_4$ in the $BH_4$ region with white noise decoupling of $^{11}B$. The broadening and collapse pattern of the resonance, which we ascribe to slowing of the hydrogen exchange process, is identical in TMS–ether, toluene, and toluene–pentane solvents (which vary considerably in viscosity at low temperatures). Also, the $C_5H_5$ resonance broadens only slightly throughout the temperature range. Without $^{11}B$ irradiation, the broad signal begins to sharpen somewhat near −100° (due to "thermal decoupling") and then also completely collapses by −125°. The above observations rule out alternative nonexchange broadening mechanisms such as viscosity broadening (due to loss of field homogeneity or increase in dipolar relaxation with increasing rotational correlation times[40]) or artifacts in the decoupling procedure. Likewise, scalar relaxation of "the second kind" due to quadrupole-induced modulation of the $^{10}B$–H and $^{11}B$–H scalar interaction should not be important for anticipated $^{11}B$ spin–lattice relaxation times $(T_{1B})$;[7] *i.e.*, we are not in the region $T_{1B} \ll 1/2\pi J_{B\text{-}H}$,[41] and proton $T_2$'s should be increasing with decreasing $T_{1B}$. Hence, the only conceivable mechanism for the observed $BH_4$ resonance broadening other than slowing of chemical exchange is the paramagnetism of the U(IV) ion.

The mechanism by which nuclear resonances are broadened in paramagnetic complexes is well-understood.[40,42] Contributions to relaxation are both electron–nuclear hyperfine (contact) and electron–nuclear dipolar (pseudocontact) in origin, and the necessary time-dependent fluctuations arise either from molecular tumbling, electron spin relaxation, or both. For paramagnetic systems such as U(IV),[6,20] certain transition metal systems,[42a,b] and most lanthanides,[20,43] the sharpness of the lines observed is only compatible with rapid electron spin relaxation as the controlling fluctuation $(T_{1e} \approx 10^{-12}\text{–}10^{-13}$ sec). Those factors which determine $T_{1e}$ for f electron systems are not fully understood on a quantitative basis, especially in solution. However, it is likely that the large spin–orbit coupling and small separation between energy levels makes possible processes in which fluctuating electric fields produced by molecular vibrations and collisions couple with spin flips.[44] Orbach processes, *i.e.*, phonon-induced spin flips accompanied by simultaneous electronic excitation, are known[45] to be efficient for lanthanide complexes in the solid state. Similar processes appear likely in solution. For the case of $(C_5H_5)_3UBH_4$, the chemical shifts of the $C_5H_5$ and $BH_4$ protons exhibit approximate Curie–Weiss behavior throughout the temperature range studied (as is usually the case),[6] and this indicates there is no erratic change in contact and dipolar interactions below *ca.* −100°, which could cause the observed several orders of magnitude change in

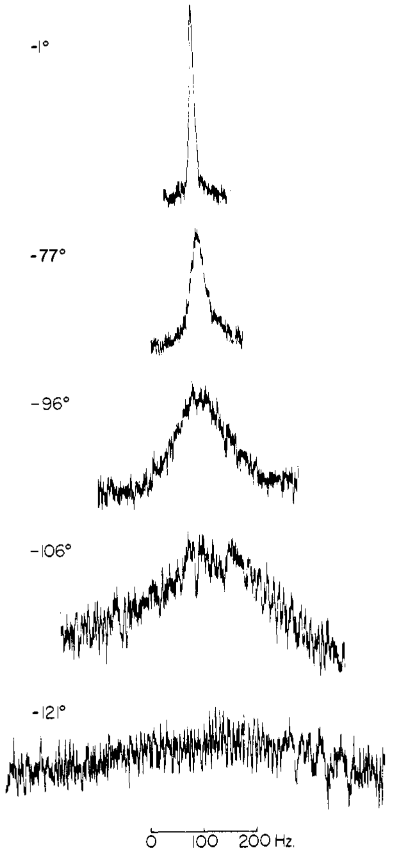


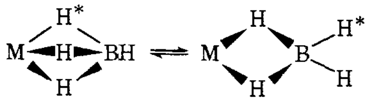
**Figure 3.** Variable temperature pmr (90 MHz) spectra for $(\eta^5\text{-}C_5H_5)_3UBH_4$ as a solution in 1:3 TMS:diethyl ether, with white noise decoupling of $^{11}B$.

$BH_4$ proton relaxation rates.[46] The functional dependence of $T_{1e}$ on temperature is not simple to predict; for the Orbach process the difficulty arises in calculating the temperature dependence of the correlation time for the electric field fluctuations in solution. Though it seems to us unlikely that this could cause $T_{1e}$ to remain relatively insensitive, then to change by several orders of magnitude over a relatively small temperature range, further arguments are necessary to rule out this final possibility.

Of the numerous U(IV) systems examined to date, none has exhibited anomalous line broadening at low temperatures which could not be associated with the slowing of a chemical exchange process. Furthermore, we have synthesized the complex $(C_5H_5)_3UH_3BC_2H_5$, which cannot undergo bridge-terminal hydrogen exchange, to rule out the relaxation mechanisms discussed in the preceding paragraph as major sources of the $BH_4$ broadening and collapse. The $^{11}B$-decoupled $H_3B$ resonance of **1d** was observed in a variety of solvents down to −125°. Though, as might be expected from the discussion in the preceding paragraph, slight broadening does occur at very low temperatures,[47] total collapse of the resonance does not occur. Thus, all evidence indicates that slowing of the dynamic hydrogen interchange process is being observed for the first time in a covalent tetrahydroborate complex.

Combining the chemical shift data for **1a** and **1d,** it is possible to estimate the chemical shifts of the bridging and terminal hydrogens in **1a,** since the data for **1a** give the weighted average shift position, and that for **1d** the position of the bridge hydrogens.[48] The value of $\delta\omega$ at any temperature can be obtained by extrapolation of shift *vs.* temperature plots. It is also possible to roughly estimate the coalescence temperature. This can be done by reference to the spectra of the related fluxional molecule $(C_5H_5)_3U(\eta^1\text{-allyl})$.[6] Here, the slow exchange limit could be reached so that it was possible to estimate the coalescence temperature, which was *ca.* 20–30° below the point at which the $A_4$ part of the $A_4X$ pattern had completely collapsed into the baseline. Since the chemical shift difference between exchanging sites will be seen to be of the same order of magnitude in both compounds, we feel that $-140 \pm 20°$ is a realistic estimate of the coalescence temperature for $(C_5H_5)_3UBH_4$. In this range, $\delta\omega$ = 15,000–36,000 Hz (*vs. ca.* 27,000 Hz for $(C_5H_5)_3U$(allyl) at −90°). Use of eq 8 yields $\tau \approx 22 \pm 8$ μsec, and $\Delta G_c{}^{*}$ [49] $\approx 5.0 \pm 0.6$ kcal/mol. The chemical shift separation of the exchanging sites is in such excess of the anticipated H–H coupling constant,[50] that we feel eq 8 is applicable at the present level of approximation.

The mechanistic nature of the dynamic process is most likely, as we have previously suggested,[7] a traversal of the potential energy surface which connects bidentate and tridentate geometries. Depending on which geometry represents a well on this surface and which a saddle point, the fluxional behavior for molecules with either tridentate or bidentate ground state geometries can be described. Our nmr results show that, neglecting tunneling, H and I can differ by no more in energy than *ca.* 5 kcal/mol (*i.e.*, the classical barrier for eq 9 is the upper limit to how much they can differ in energy). *Ab initio* SCF–CI calculations by Marynick and Lipscomb[51] on $Be(BH_4)_2$ also show the bidentate and tridentate geometries to differ little in energy. These results are in accord with some earlier suggestions we made,[5] derived from empirical electron counting, that bidentate and tridentate tetrahydroborate groups appeared to formally donate about the same number of electrons to transition metals.



(9)

H I

Thus, our results here further demonstrate that paramagnetic actinide probes can be useful in solving certain dynamic nmr problems by expanding the time resolution through isotropic shifts. We have, for the first time, observed slowing of the dynamic bridge-terminal hydrogen exchange process for a covalent tetrahydroborate complex in solution.[52] Incorporation of a covalently bound paramagnetic probe is an attractive alternative to adding lanthanide β-diketonates,[37a,b] since variable temperature spectra could be complicated by the slowing of intermolecular exchange processes[53] as well as by the sheer number of species in equilibrium.[54] Of course, in all such investigations care must be taken to minimize the effect of the probe on the rate of the processes being studied.

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# Electronic Structure of Octachlorodimolybdate(II)[1a]

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**Abstract:** An all-electron, first-principles SCF-X$\alpha$SW calculation of the electronic structure of $Mo_2Cl_8^{4-}$ is used to discuss the nature of Mo–Mo and Mo–Cl bonding in this ion and its electronic spectrum. The upper valence region of the energy-level diagram (−0.04 to −0.33 hartree) contains, in order of increasing energy, Mo–Cl bonding, Cl nonbonding, and Mo–Mo $\sigma$, $\pi$, and $\delta$ bonding levels. The $\delta$ level is the highest occupied; above it are empty $\delta^*$, two $d_{x^2-y^2}$, $\pi^*$, and $\sigma^*$ antibonding levels. The Mo and Cl character in the upper valence levels is made up almost entirely from 4d and 3p functions, respectively; eight nearly pure Cl 3s levels in the range −0.70 to −0.72 hartree complete the valence region, and no orbitals having large amounts of Mo 5s or 5p character are found. The d-like levels in $Mo_2Cl_8^{4-}$ and hypothetical $MoCl_4^{2-}$ are compared. The $\sigma_n$ levels postulated by Cotton to lie in the neighborhood of the $\delta^*$ level are not found; otherwise the ordering of metal–metal bonding and antibonding levels agrees completely with Cotton's qualitative proposals. Contour maps of the $\sigma$, $\pi$, and $\delta$ wave functions are presented, showing them to be essentially simple overlaps of $4d_{z^2}$, $4d_{xz,yz}$, and $4d_{xy}$ orbitals, respectively, on the metals. The predicted electronic spectrum is in good agreement with the experimental solid-state spectrum of $K_4Mo_2Cl_8 \cdot 2H_2O$. The two well-resolved peaks observed at 18.8 and 31.4 kcm$^{-1}$ are assigned to dipole-allowed $\delta \rightarrow \delta^*$ and $\pi \rightarrow d_{x^2-y^2}$ transitions, respectively. The strong unresolved absorption above 34 kcm$^{-1}$ is believed at least partially due to some combination of Cl $\rightarrow \delta^*$ charge-transfer and $\pi \rightarrow \pi^*$ transitions. The weak band at *ca.* 24 kcm$^{-1}$ is apparently due to one or both of the dipole-forbidden $\pi \rightarrow \delta^*$ and $\delta \rightarrow d_{x^2-y^2}$ transitions. The applicability of the energy-level diagram for $Mo_2Cl_8^{4-}$ to other dimeric complexes of $D_{4h}$ symmetry is discussed.

Metal–metal bond formation has become recognized as one of the most distinctive features in the chemistry of lower oxidation state transition metals. A large number of X-ray structural[2] and Raman spectral[3-5] investigations have shown that the strongest such interactions occur in Cr(II), Mo(II), and Re(III) compounds, with metal–metal distances up to 0.7 Å shorter than expected for single bonds. This agrees with the prediction of Cotton's qualitative molecular orbital treatment[6] that metal–metal bond order should maximize at four ($\sigma$-, $\pi$-, and $\delta$-type overlaps) for the d$^4$ electronic configuration. Although this treatment has also successfully rationalized trends in metal–metal dis-