cooled to −196° and warmed to 0° for 1 hr and then warmed to room temperature. Excess diborane (0.485 mmol) and a small amount of noncondensable gas were pumped from the reaction mixture. A white, crystalline solid, contaminated by a yellow solid, remained. The air-stable, crystalline solid was purified by dissolving in cyclohexane, filtering under vacuum, and stripping off the solvent. The ratio of Lewis base to diborane was 2.08:1.00 indicating formation of 2 mol of borane adduct. *Anal.* Calcd for $C_4H_{10}N_2PFBH_3$: C, 32.03; H, 8.76; B, 7.21; F, 12.67; N, 18.68; P, 20.65. Found: C, 32.06; H, 8.61; B, 7.13; F, 12.56; N, 18.65; P, 20.66. Ir (Kel-F, Nujol mulls) (cm^{-1}): Kel-F, ν(C–H) 2970 (vw), 2930 (m), 2890 (sh), 2860 (m), 2810 (w); ν(B–H) 2380 (s), 2330 (m), 2220 (w); $\delta^a(CH_3)$ 1475 (sh), 1465 (m), 1440 (w), 1415 (vw); $\delta^s(CH_3)$ 1370 (vw), 1345 (ms); Nujol, 1240 (s); 1200 (s); 1150 (s); 1140 (sh), 1135 (sh), 1120 (sh), 1072 (vw, sh), 1062 (w, sh), 1020 (s), 937 (s); 850 (w), 750 (vs, br); ν(P–F) (?) 670 (mw); 552 (m). The nmr spectra are as follows: ^1H (solvent $CHCl_3$), δ −3.25 ppm relative to TMS (complex multiplet, intensity 4, CH_2CH_2), δ −2.76 ppm (d, J_{HP} = 11 Hz, NCH_3, intensity 6), each member of the doublet being a doublet (J_{HF} = 2.4 Hz), δ −0.22 ppm (quartet, 1:1:1:1, J_{HB} = 98 cps, H_3B); ^{19}F (solvent $CHCl_3$), δ −21.2 ppm relative to TFA (d, J_{FP} = 1150 Hz, $FP(N)N$); ^{31}P (solvent $CHCl_3$), δ −129 ppm relative to 85% H_3PO_4 (d, J_{PF} = 1190 Hz, $FP(N)N$), signal greatly broadened due to splitting by boron; ^{11}B (solvent $CHCl_3$), δ +61.4 ppm relative to $B(OCH_3)_3$ (quintet, 1:4:6:4:1, $J_{BH} = J_{BP}$ = 100 Hz).

Preparation of $CH_3\overline{NCH_2CH_2(CH_3)N(BF_3)P}F$.—Trifluoroborane, 8.20 mmol, was condensed above a 0.7245-g (5.32-mmol) sample of I dissolved in toluene. The reaction mixture was warmed to 0° and then slowly to room temperature over a 1-hr period. The temperature of the exothermic reaction was moderated by external cooling with a 0° slush bath. The reaction vessel was then warmed to room temperature and the volatile components were fractionated through traps held at −30.6 and −196°. Trifluoroborane, 2.48 mmol, was recovered from the −196° trap. The ratio of Lewis acid to Lewis base consumed in the reaction was 1.07:1.00 indicating the formation of a 1:1 adduct.

Initially this adduct is a viscous, glassy liquid which crystallizes upon standing under vacuum for 1–2 days at room temperature. Sublimation of the white, crystalline solid by pumping on under vacuum in a sublimation tube chilled with liquid nitrogen yields an extremely hygroscopic compound of composition $C_4H_{10}N_2PFBF_3$. In every run a small amount of liquid did not crystallize. *Anal.* Calcd for $C_4H_{10}N_2PBF_4$: C, 23.56; H, 4.95; B, 5.30; F, 37.27; N, 13.74; P, 15.19. Found: C, 23.32; H, 4.81; B, by difference, 5.33; F, 37.11; N, 13.55; P, 14.88. Ir (Kel-F, Nujol mulls) (cm^{-1}): Kel-F, 3200 (w, br); ν(C–H) 2900 (m, br), 2820 (w, sh); δ^a(CH) 1490 (m), 1475 (m, sh), 1460 (m), 1440 (m); δ^s(CH) 1365 (w), 1355 (w); Nujol, 1270 (s); 1230 (s); ν(B–F) 1210 (sh), 1200 (sh), 1185 (sh), 1165 (s), 1140 (s), 1110 (s), 1080 (s, sh); 1030 (s); 1000 (m); 970 (m); 930 (sh), 890 (s); 835 (m); 765 (m, sh), 735 (s); 645 (mw); ν(P–F) (?) 605 (m); 540 (mw); 495 (m); 430 (w).

Nmr Titration.—In a typical titration run an 11.65-mmol sample of $C_4H_{10}N_2PF$ was condensed with a 4-ml sample of toluene in a reaction tube fitted with a magnetic stirrer and a series of nmr tubes. Consecutive samples of BF_3 were added to the reaction mixture, and aliquots of the resulting solutions were sealed in nmr tubes. Nmr data for the aliquots are reported in Table II.

Preparation of $[CH_3\overline{NCH_2CH_2(CH_3)NP}]^+[PF_6]^-$.—A 3.42-mmol sample of PF_5 was frozen in a reaction tube with a 3.00-mmol sample of I in 2 ml of CH_2Cl_2. The system was then warmed gradually to room temperature. After two such cycles of cooling and warming, excess PF_5 and solvent were stripped off at room temperature. A white, crystalline solid remained in the reaction tube. Due to the difficulty of separating the excess PF_5 from solvent, exact stoichiometry could not be obtained. The new compound owing to its slight sensitivity to moisture was handled in a drybox. It is slightly soluble in CH_2Cl_2 and soluble in 1,2-dichloroethane and CH_3CN. *Anal.* Calcd for $C_4H_{10}N_2P_2F_6$: C, 18.37; H, 3.85; F, 43.50; N, 10.69; P, 23.63. Found: C, 18.50; H, 4.07; F, 43.42, 43.59; N, 10.73; P, 23.65. Ir (Kel-F, Nujol mulls) (cm^{-1}): Kel-F, ν(C–H) 2915 (w), 2840 (w); 1780 (w) (962 + 825); $\delta^a(CH_3)$ 1480 (w), 1430 (w); $\delta^s(CH_3)$ 1375 (w), 1350 (w); Nujol, 1255 (m), 1220 (w), 1206 (w); 1190 (w); 1135 (ms); 1035 (mw), 1010 (w), 962 (mw); $\nu(PF_6^-)$ 825 (s, vbr); 720 (w); 587 (vw); $\delta(PF_6^-)$ 552 (s, sp). The nmr spectra are as follows: ^1H (solvent CD_3CN), δ −3.10 ppm (d, J_{HP} = 11 Hz, NCH_3, intensity 6), δ −3.83 (d, J_{HP} = 5 Hz, CH_2, intensity 4); ^{19}F (solvent 1,2-dichloroethane), δ −6.1 ppm (d, J_{F-P} = 710 Hz); ^{31}P (solvent 1,2-dichloroethane), δ +144.1 ppm (septet, J_{P-F} = 710 Hz); δ −264 ppm. (In CD_3CN the signal at −264 ppm broadens and is not detectable.)

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Structure and Dynamics in Metal Tetrahydroborates. II.[1] Vibrational Spectra and Structures of Some Transition Metal and Actinide Tetrahydroborates

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Vibrational spectroscopy allows a reasonably unambiguous distinction to be made between monodentate, bidentate, and tridentate hydrogen-bridged metal–BH_4 interactions for covalent organo–transition metal and –actinide tetrahydroborates. The following compounds have bidentate structures: $(h^5\text{-}C_5H_5)_2Ti(BH_4)$, $(h^5\text{-}C_5H_5)_2Zr(BH_4)_2$, and $(h^5\text{-}C_5H_5)_2Zr(H)(BH_4)$; the organoactinides $(h^5\text{-}C_5H_5)_3U(BH_4)$ and $(h^5\text{-}C_5H_5)_3Th(BH_4)$ have tridentate geometries. Data on these systems can be understood in terms of analogies with other organometallic systems (π-allyls). The synthesis of $(h^5\text{-}C_5H_5)_3Th(BH_4)$ is also reported.

Transition metal and actinide tetrahydroborates[3] are of current interest to inorganic and organometallic chemists for a number of reasons. Ideally, studies of any system of molecules should rest upon a firm structural foundation. For metal tetrahydroborates, one of the most significant structural questions concerns the mode by which the BH_4 group is attached

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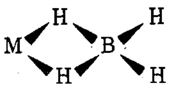
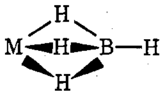
[1] Part I: T. J. Marks and L. A. Shimp, *J. Amer. Chem. Soc.*, **94**, 1542 (1972).

[2] (a) NDEA Predoctoral Fellow, 1970–present; (b) NSF Predoctoral Fellow, 1971–present.

[3] B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.*, **11**, 99 (1970).

to the metal, *i.e.*, bidentate (I)[4] or tridentate (II)[5]


I


II

structures are known. This question is frequently difficult to answer since X-ray diffraction methods are not particularly suitable for locating hydrogen atoms near heavy metals. In part I, we considered the nmr spectroscopy of covalent metal tetrahydroborates, which is replete with boron quadrupolar relaxation effects. Though electronic information about the metal–borohydride bond could be obtained, the intramolecular bridge–terminal exhange process was too rapid ($\tau \leq 10^{-4}$ sec) at all accessible temperatures to yield structural data. We wish to demonstrate here that vibrational spectroscopy, with a faster time scale, can provide useful structural data, the full potential of which has unfortunately gone unrealized in organo–transition metal and –actinide systems. Our results prompt a brief perspective discussion of molecular structure and valency in metal tetrahydroborates.

Experimental Section

All compounds employed in this study were prepared and handled in an atmosphere of prepurified nitrogen or *in vacuo*. All tetrahydroborates, as a precaution, were stored under prepurified nitrogen at −20° in the dark. Solvents were carefully dried in a manner appropriate to each and then distilled under nitrogen just prior to use.

The compounds $Zr(BH_4)_4$,[6] $Hf(BH_4)_4$,[6] $(h^5\text{-}C_5H_5)_2Ti(BH_4)$,[7] $(h^5\text{-}C_5H_5)_2Zr(BH_4)_2$,[8] $(h^5\text{-}C_5H_5)_2Zr(H)(BH_4)$,[9] and $(h^5\text{-}C_5H_5)_3\text{-}U(BH_4)$[10,11] were prepared by the literature procedures and were doubly sublimed. The synthesis of the thorium compound $(C_5H_5)_3Th(BH_4)$[12] was achieved by reaction of $(h^5\text{-}C_5H_5)_3ThCl$ and $NaBH_4$, as described below.

Synthesis of $(C_5H_5)_3Th(BH_4)$.—To 1.5 g (3.24 mmol) of $(C_5H_5)_3ThCl$[13] in 60 ml of freshly distilled tetrahydrofuran was added 0.30 g (8.00 mmol) $NaBH_4$. After stirring for 3 days, the reaction mixture was suction filtered and the filtration residue washed with two 10-ml portions of tetrahydrofuran. The combined filtrate was next evaporated under high vacuum. The white residue was transferred under nitrogen to a sublimer, and was sublimed at 120° (0.01 mm). The first small fraction of material to collect was discarded and the sublimation then continued for 3 days, to yield 0.60 g (42%) of white, microcrystalline solid, decomposition beginning slowly at 120° and becoming rapid by 230°. A slightly purer product can be obtained by resublimation. *Anal.* Calcd for $C_{15}H_{19}ThB$: C, 40.74; H, 4.34. Found: C, 40.20; H, 4.40. The pmr spectrum of this compound is similar to that reported previously[14] and as a toluene-d_8 solution consists of a sharp singlet, τ 3.95 (15 H), and a broadened quartet, τ 6.70 (4 H) with $J_{^{11}B-H} \approx 86$ Hz.

Spectroscopic Measurements.—Solutions of compounds for infrared studies were prepared in Schlenk apparatus and were transferred *via* syringe to the infrared cell described previously.[14] For $Zr(BH_4)_4$ and $Hf(BH_4)_4$, measurements were made on solutions in dry, degassed Nujol, between flat sodium chloride plates. In all cases, samples were monitored for possible decomposition by observing whether changes took place in the spectrum during the course of several scans. Where possible, solution spectra were taken at several different concentrations. Mulls were prepared in a nitrogen-filled glove bag employing dry, degassed Nujol or dry, degassed Fluorolube. Samples were again monitored for decomposition.

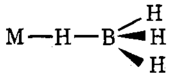
Raman spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ were recorded on melts (these compounds melt near room temperature) in sealed Pyrex capillaries containing, in addition, *ca.* 0.5 atm prepurified nitrogen. Again, repeated scans were employed to pinpoint any decomposition.

Infrared spectra were recorded on Beckman IR-5 and IR-9 spectrometers, and were calibrated with polystyrene film. Laser Raman studies were carried out using a Spex 1400-II double monochromator with either a Coherent Radiation Laboratories Model 52 argon ion laser source, operating at 514.5 nm with approximately 1 W output or a Spectra-Physics Model 125 He–Ne laser source operating at 632.8 nm with an output of approximately 50 mW. We are grateful to Professor D. F. Shriver for the use of this instrument, and to he and Miss A. Goya for helpful suggestions.

Results and Discussion

For the sake of generality, mention will also be made of two other conceivable MBH_4 geometries, besides (I) and (II). The ionic structure (III) is known for a number of alkali metal tetrahydroborates,[3] and the monodentate structure (IV), though not established

$M^+BH_4^-$
III


IV

for metal complexes, is analogous to the single-hydrogen-bridged structure proposed for $B_2H_7^-$[15a,b] and $(R_3B)_2H^-$[15] compounds.

A number of partial or complete vibrational analyses have been performed on B_2H_6,[16] $Al(BH_4)_3$,[17] $Zr(BH_4)_4$,[18] $Be(BH_4)_2$,[19] and BH_4^-[20] employing various combinations of infrared and Raman spectroscopy and isotopic substitution. Complementary structural data for B_2H_6 (gas-phase electron diffraction[21]) which has structure I, $Al(BH_4)_3$ (X-ray diffraction of the trimethylamine adduct,[4c] gas-phase electron diffraction[4b]) which has structure I, $Zr(BH_4)_4$(X-ray diffraction at −196°,[5a] gas-phase electron diffraction[5b]) which has structure II, and $Be(BH_4)_2$[4d] (X-ray diffraction) which is based upon structure I, are available. In all cases, the vi-

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(4) (a) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967); (b) A. Almenningen, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, **22**, 328 (1968); (c) N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Inorg. Chem.*, **7**, 1575 (1968); (d) D. S. Marynick and W. N. Lipscomb, *ibid.*, **11**, 820 (1972).

(5) (a) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 403 (1967); (b) V. Plato and K. Hedberg, *Inorg. Chem.*, **10**, 590 (1971).

(6) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *J. Chem. Soc. A*, 182 (1966).

(7) H. Nöth and R. Hartwimmer, *Chem. Ber.*, **93**, 2238 (1960).

(8) R. K. Nanda and M. G. H. Wallbridge, *Inorg. Chem.*, **3**, 1798 (1964).

(9) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *ibid.*, **6**, 1979 (1967).

(10) M. L. Anderson and L. R. Crisler, *J. Organometal. Chem.*, **17**, 345 (1969).

(11) Y. Hristidu, Ph.D. Dissertation, Ludwig-Maximilian University, Munich, 1962.

(12) This molecule has been mentioned previously, but no synthetic details or analytical data were reported: R. v. Ammon, B. Kanellakopoulos, R. D. Fischer, and P. Laubereau, *Inorg. Nucl. Chem. Lett.*, **5**, 219 (1969).

(13) G. L. Ter Haar and M. Dubeck, *Inorg. Chem.*, **3**, 1648 (1964).

(14) T. J. Marks, *J. Chem. Educ.*, **48**, 167 (1971).

(15) (a) Y. Matsui and R. C. Taylor, *J. Amer. Chem. Soc.*, **90**, 1363 (1968); (b) R. C. Taylor, private communication; (c) H. C. Brown and P. A. Tierney, *J. Amer. Chem. Soc.*, **80**, 1552 (1958); (d) A. Khuri, Ph.D. Thesis, Purdue University, 1960; *Diss. Abstr.*, **21**, 55 (1960).

(16) (a) R. C. Lord and E. Nielsen, *J. Chem. Phys.*, **19**, 1 (1949); (b) W. J. Lehmann, J. F. Ditter, and I. Shapiro, *ibid.*, **29**, 1248 (1958); (c) R. C. Taylor and A. R. Emery, *Spectrochim. Acta*, **10**, 419 (1958).

(17) (a) A. R. Emery and R. C. Taylor, *ibid.*, **16**, 1455 (1960); (b) W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1948).

(18) (a) N. Davies, D. Saunders, and M. G. H. Wallbridge, *J. Chem. Soc. A*, 2915 (1970); (b) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *ibid.*, 182 (1966); (c) a preliminary report of the Raman spectrum of $Zr(BH_4)_4$ has recently appeared: B. E. Smith and B. D. James, *Inorg. Nucl. Chem. Lett.*, **7**, 857 (1971).

(19) J. W. Nibler, D. F. Shriver, and T. H. Cook, *J. Chem. Phys.*, **54**, 5257 (1971); and references therein.

(20) (a) A. R. Emery and R. C. Taylor, *ibid.*, **28**, 1029 (1958); (b) V. V. Volkov, E. V. Sobelev, Z. A. Grankina, and I. S. Kalinina, *Russ. J. Inorg. Chem.*, **13**, 343 (1968).

(21) K. Hedberg and V. Schomaker, *J. Amer. Chem. Soc.*, **73**, 1482 (1951).

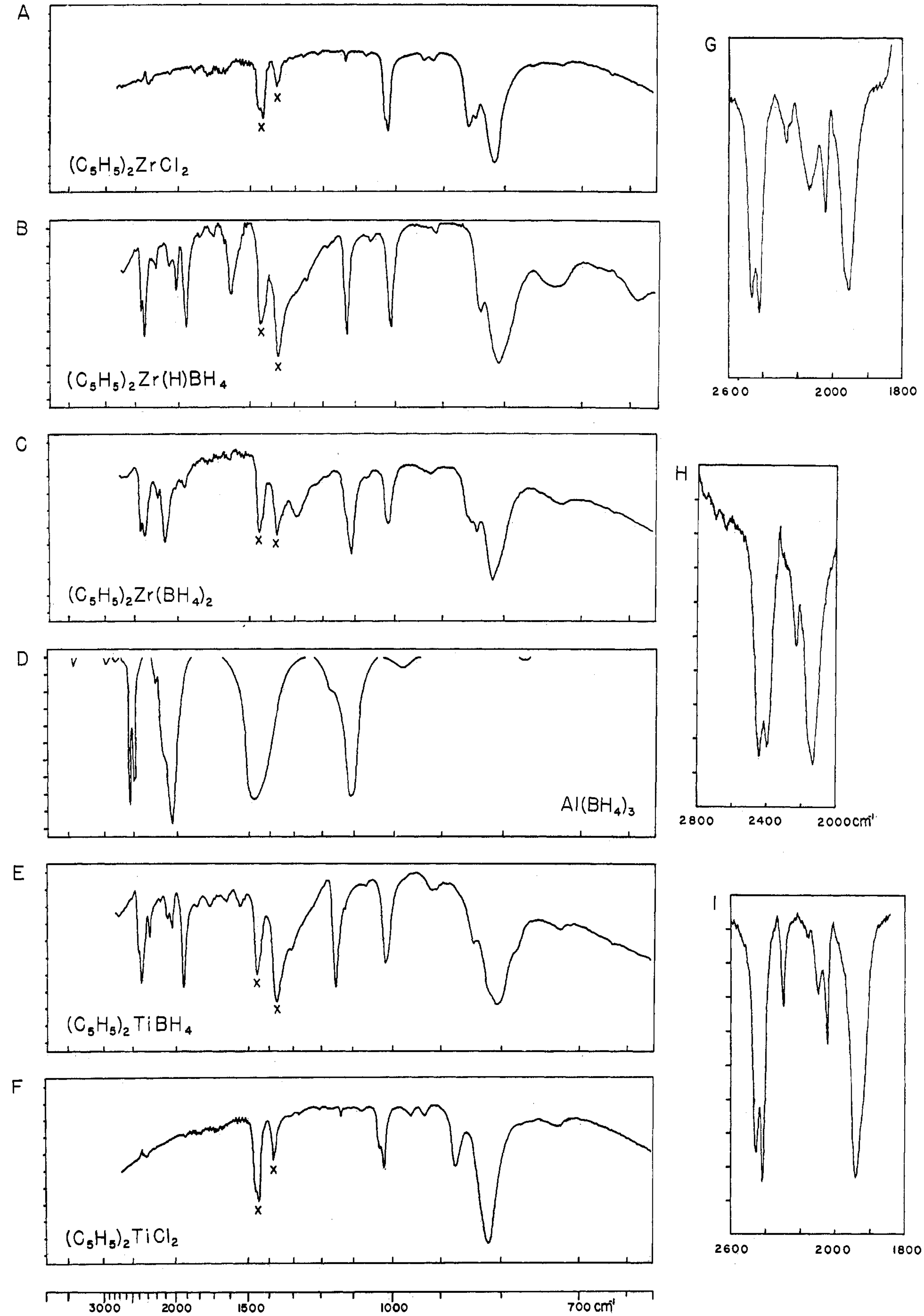

Figure 1.—Infrared spectra of (A) $(h^5\text{-}C_5H_5)_2ZrCl_2$ in Nujol, (B) $(h^5\text{-}C_5H_5)_2Zr(H)(BH_4)$ in Nujol, (C) $(h^5\text{-}C_5H_5)_2Zr(BH_4)_2$ in Nujol, (D) gas-phase, $Al(BH_4)_3$ reproduced from ref 17b, (E) $(h^5\text{-}C_5H_5)_2Ti(BH)_4$ in Nujol, (F) $(h^5\text{-}C_5H_5)_2TiCl_2$ in Nujol (sharp bands marked × are due to Nujol), (G) in the B–H stretching region of $(C_5H_5)_2Zr(H)(BH_4)$ in benzene, (H) $(C_5H_5)_2Zr(BH_4)_2$ in benzene, and (I) $(C_5H_5)_2Ti(BH_4)$ in benzene.

brational data can be shown to correlate well with the observed structures. We choose $Al(BH_4)_3$ and $Zr(BH_4)_4$, which have been subjected to the most extensive structural characterization and which have the heaviest metals, as model compounds. Principal attention will be focused on terminal B–H(ν_{B-H_t}) and to a lesser extent bridging B–H(ν_{B-H_b}) stretching vibrations. These vibrations are easily observed[16–20] and the former are expected to be relatively "pure."[22] Because of this and the relatively large number of intervening bonds, it is physically reasonable to assume that any interaction between these B–H vibrations centered on different BH_4 groups is small. Other normal modes involving deformations and various motions within the bridge are probably extensively mixed and may also interact to a larger extent with vibrations centered in other BH_4 groups. However, certain empirical generalizations can still be made about these modes for different bonding configurations. In all molecules examined, two boron isotopes are expected to be present in natural abundance, ^{10}B (18.8%) and ^{11}B (81.2%). Whether or not a smaller separate ^{10}B band is observed in addition to the main ^{11}B band will depend on how much boron movement is involved in that particular normal mode, and generally, a separate ^{10}B band is not completely resolved. We now consider vibrational spectra for structures I through IV.

Structure I.—A C_{2v} structure such as this has 12 normal modes of vibration, shown in Table I along with spectral activities. The characteristic symmetric and antisymmetric terminal B–H_t stretches usually appear in the infrared as a strong, sharp, doublet centered at 2400–2600 cm^{-1} with a splitting of 40–80 cm^{-1}.[19,21] The symmetric and antisymmetric bridging B–H_b stretches are usually seen as overlapped bands in the infrared near 2000 cm^{-1}. Two other strong bands in the ir, one at *ca.* 1400–1500 cm^{-1} (symmetric bridge stretch[18,19,21]) and one at *ca.* 1100–1200 cm^{-1} (BH_2 deformation[18,19,21]) are regularly observed. The infrared spectrum of the model compound $Al(BH_4)_3$, shown in Figure 1D, is in good accord with the above generalizations. Interaction between B–H_t vibrations on different BH_4 groups is as expected, small.[17,23]

TABLE I

NORMAL MODES AND SPECTRAL ACTIVITIES FOR VARIOUS MBH_4 CONFIGURATIONS

Structure	Normal Modes	Activity[a]	Structure	Normal modes	Activity[a]
I (C_{2v})	$5A_1$	Ir, R	III (T_d)	A_1	R
	A_2	R		E	R
	$3B_1$	Ir, R		$2T_2$	Ir, R
	$3B_2$	Ir, R	IV (C_{3v})	$4A_1$	Ir, R
II (C_{3v})	$4A_1$	Ir, R		4E	Ir, R
	4E	Ir, R			

[a] Ir = infrared active; R = Raman active.

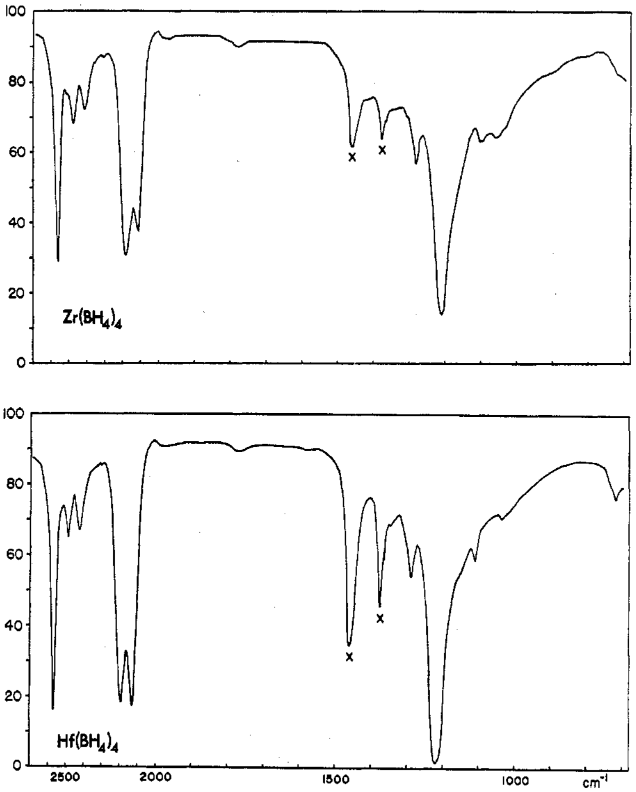

Figure 2.—Infrared spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ as solutions in Nujol. The sharp bands due to Nujol are marked ×.

Structure II.—A C_{3v} structure such as this gives rise to eight normal modes of vibration (Table I). The model compound is $Zr(BH_4)_4$, with additional reference to $Hf(BH_4)_4$. Infrared spectra of these compounds are shown in Figure 2. The great similarity of the spectra indicates that the molecules have very similar geometries and bonding, which should not be surprising in view of the numerous similarities in zirconium and hafnium chemistry,[24] and the pmr data.[1] This also indicates that the mass of the metal has an insignificant effect upon the structurally diagnostic vibrations. With the help of deuteration[20a] and Raman spectra,[18c] spectral assignments can be made (Table II). Structurally speaking, the most significant fea-

TABLE II

VIBRATIONAL DATA FOR $M(BH_4)_4$ MOLECULES[a]

$Zr(BH_4)_4$		$Hf(BH_4)_4$		
Ir	Raman (ρ)[c]	Ir	Raman (ρ)[c]	Assignment[b]
2560 s	2562 m (0.24)	2570 s	2572 m (0.38)	A_1B–H_t str
2472 w		2490 w		(1282 + 1210), (1290 + 1218)?
2413 w		2425 w		2 (1210), 2 (1218)?
	2210 sh		2223 sh	A_1^{10}B–H_b str?
2179 s	2178 m (0.12)	2197 s	2193 m (0.05)	A_1B–H_b str
2117 s	2127 sh	2128 s	2142 sh	E B–H_b str
1282 w	1284 m (0.28)	1290 w	1287 s (0.32)	A_1 bridge def
1210 s		1218 vs		E bridge def
1095 vw	1071 w (0.68)	1110 vw	1084 w	
1057 vw		1036 vw		
	576 sh			
	543 s (0.09)		551 s (0.10)	A_1
507 s		487 s	480 vvw	E
	219 s (0.72)		219 vs (0.66)	E

[a] Data in cm^{-1}; s = strong; m = medium; w = weak; v = very; sh = shoulder. [b] Assignment is based on an isolated MBH_4 moiety (see text). [c] Quantity in parentheses is the depolarization ratio; values are considered accurate to ±0.05. Absence of a value indicates the ratio could not be determined.

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[22] (a) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, Chapter I-18; (b) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, Chapter II, 4f.

[23] The exact degree of interaction is difficult to judge since published infrared data were obtained in the gas phase[17b] and Raman data in the condensed state.[17a,b] Price's data[17b] (ir and Raman) give a difference of 13 cm^{-1} between in-phase (ν_1) and out-of-phase (ν_{16})B–H_t symmetrical stretching vibrations, whereas the Raman data of Emery and Taylor[20a] indicate the value could be as large 20 cm^{-1}. In either case, the interaction is small.

[24] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Wiley-Interscience, New York, N. Y., 1966, p 913.

ture is the presence of a *single*, sharp $\mathrm{B{-}H_t}$ stretching vibration in the infrared at *ca.* 2560 $\mathrm{cm^{-1}}$. This readily distinguishes structures I and II. The near coincidence of this band with a single, strong, polarized band in the Raman indicates very small coupling between different $\mathrm{BH_4}$ groups, since these would correspond to different vibrations ($\mathrm{T_2}$ and $\mathrm{A_1}$) under T_d symmetry. Hence, we have treated these molecules as single $\mathrm{MBH_4}$ units; however, rigorous identification of several of the low-frequency bands requires an analysis of the entire system of 21 atoms and complete isotopic substitution data, which are not presently at hand.

The important point to be made here is that for structure II, the following diagnostic bands are expected in the infrared: one sharp band near 2500 $\mathrm{cm^{-1}}$, a doublet near 2100 $\mathrm{cm^{-1}}$, and an intense band near 1200 $\mathrm{cm^{-1}}$.

Structure III.—Solid-state effects may cause broadening or minor splitting of the bands,[19,20] but usually two strong bands are observed in the infrared: the triply degenerate antisymmetric B–H stretch, which is frequently seen as a broad, possibly split (due to solid-state effects[20a] and/or overtones[20b]) band at *ca.* 2250 $\mathrm{cm^{-1}}$, and the triply degenerate antisymmetric $\mathrm{BH_2}$ bend at *ca.* 1100 $\mathrm{cm^{-1}}$, which is usually sharper. In the presence of very strong solid-state effects, *e.g.*, $\mathrm{LiBH_4}$,[25] the Raman-active doubly degenerate symmetric $\mathrm{BH_2}$ bend becomes infrared active.[20a] Since all of the molecules examined here (*vide infra*) display marked covalent character, *e.g.*, volatility, solubility in nonpolar solvents, air and moisture sensitivity, it is not surprising that their vibrational spectra are grossly different from those of the alkali metal tetrahydroborates. However, it is worthwhile to comment on what influence ionic character will have on the vibrational spectra of structures A and B. First, the $\mathrm{B{-}H_t}$ vibrations should tend toward lower frequency (as in $\mathrm{BH_4^-}$).[17b,19] Also, the frequency difference between the $\mathrm{B{-}H_t}$ and $\mathrm{B{-}H_b}$ vibrations should decrease as the B–H force constants become more equal, and covalent interaction with the metal weakens.

Structure IV.—As in a type I structure, this molecule should exhibit two strong terminal B–H stretches ($\mathrm{A_1}$ and E) in the infrared. Unlike the bidentate molecule, only one bridging stretch is expected; however, since the $\mathrm{A_1}$ and $\mathrm{B_2}$ $\mathrm{B{-}H_b}$ modes are seldom resolved in the infrared spectra of the bidentate molecules, spectra of I and IV type molecules may be difficult to differentiate in this frequency region. One aid would be Raman depolarization studies which would ideally bring about a symmetric, polarized $\mathrm{B{-}H_b}$ band shape in (IV), but an asymmetric (due to the presence of two overlapping bands) polarized $\mathrm{B{-}H_b}$ band shape in (I). In the region below 2000 $\mathrm{cm^{-1}}$, the two types of metal–ligand geometry may be readily distinguished. Bidentate molecules are expected to show strong infrared absorptions at 1300–1500 $\mathrm{cm^{-1}}$ and 1100–1200 $\mathrm{cm^{-1}}$. In contrast, monodentate tetrahydroborates are expected to exhibit two bands ($\mathrm{A_1}$, E) in the $\mathrm{BH_3}$ deformation region, *ca.* 1150–1000 $\mathrm{cm^{-1}}$. In $\mathrm{B_2H_7^-}$ [15a,b,26] only the $\mathrm{A_1}$ band is observed in the infrared, at 1030 $\mathrm{cm^{-1}}$ (strong). In $\mathrm{(CH_3)_3N{-}BH_3}$,[27] both deformation bands are observed in the infrared (E, 1117; $\mathrm{A_1}$, 1166 $\mathrm{cm^{-1}}$) but the $\mathrm{A_1}$ mode is far more intense. Thus, infrared spectra of the IV type structure should not exhibit a strong band in the 1300–1500 $\mathrm{cm^{-1}}$ region but will show a strong absorption near 1000–1100 $\mathrm{cm^{-1}}$, and maybe a weaker one appearing as a shoulder.

We now consider the vibrational spectra of a variety of covalent metal tetrahydroborates and apply the structural criteria summarized in Table III.

TABLE III

INFRARED-ACTIVE FUNDAMENTAL VIBRATIONAL TRANSITIONS COMMONLY OBSERVED FOR $\mathrm{MBH_4}$ CONFIGURATIONS

Structure	Approx freq, $\mathrm{cm^{-1}}$	Type of internal coordinate change	Symmetry type	Comments
I	2400–2600	$\mathrm{B{-}H_t}$ str	$\mathrm{A_1}$, $\mathrm{B_1}$	strong doublet, 40–80 $\mathrm{cm^{-1}}$ splitting
	1950–2150	$\mathrm{B{-}H_b}$ str	$\mathrm{A_1}$, $\mathrm{B_2}$	strong band, possible shoulder
	1300–1500	Bridge str	$\mathrm{A_1}$	strong, broad
	1100–1200	$\mathrm{BH_2}$ def	$\mathrm{B_2}$	strong
II	2450–2600	$\mathrm{B{-}H_t}$ str	$\mathrm{A_1}$	strong singlet
	2100–2200	$\mathrm{B{-}H_b}$ str	$\mathrm{A_1}$, E	doublet, 50–80 $\mathrm{cm^{-1}}$ splitting
	1150–1250	Bridge def	E	strong
III	2200–2300	$\mathrm{B{-}H_t}$ str	$\mathrm{T_2}$	strong, broad
	1050–1150	$\mathrm{BH_2}$ def	$\mathrm{T_2}$	strong, broad
IV	2300–2450	$\mathrm{B{-}H_t}$ str	$\mathrm{A_1}$, E	strong, probably a doublet
	ca. 2000	$\mathrm{B{-}H_b}$ str	$\mathrm{A_1}$	strong
	1000–1150	$\mathrm{BH_3}$ def	$\mathrm{A_1}$, E	strong band, possibly with weaker one at slightly higher frequency

Actinide Molecules.—Figure 3 presents infrared spectra of $(h^5\text{-}\mathrm{C_5H_5})_3\mathrm{UBH_4}$ and $(h^5\text{-}\mathrm{C_5H_5})_3\mathrm{ThBH_4}$ as Nujol mulls and as benzene solutions. To identify the bands arising from the $(h^5\text{-}\mathrm{C_5H_5})_3\mathrm{M}$ moiety, the infrared spectra of $(h^5\text{-}\mathrm{C_5H_5})_3\mathrm{UCl}$ and $(h^5\text{-}\mathrm{C_5H_5})_3\mathrm{ThCl}$ are also given. The structure of $(h^5\text{-}\mathrm{C_5H_5})_3\mathrm{UCl}$ consists of a uranium atom in an approximately tetrahedral configuration, surrounded by three *pentahapto*-cyclopentadienyl rings and a chlorine.[28] From published correlations,[29] it is evident that both compounds under consideration have *pentahapto*cyclopentadienyl rings. Subtraction of these bands leaves the spectrum of the $\mathrm{MBH_4}$ moiety. Previous analyses of the infrared spectra[12,13] concluded that the uranium molecule had the bidentate structure I; however, it is clear from our spectra and correlations that the tridentate structure II prevails both in solution and in the solid state. The great similarity of the spectra indicates that the thorium and uranium compounds are very similar in structure and bonding.

$\mathbf{(C_5H_5)_2Zr(BH_4)_2}$.—Figure 1 presents mull and solution (a noncoordinating solvent) infrared spectra of this compound and also a mull spectrum of $(h^5\text{-}\mathrm{C_5H_5})_2\mathrm{ZrCl_2}$. Subtraction of the *pentahapto*cyclopentadienyl bands from the spectrum yields a pattern indicative of the bidentate structure I for both the solid state and solution structure. Our infrared and Raman re-

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[25] P. M. Harris and E. P. Meibohm, *J. Amer. Chem. Soc.*, **69**, 1231 (1947).

[26] R. C. Taylor, private communication.

[27] (a) R. C. Taylor, *Advan. Chem. Ser.*, **No. 42**, 59 (1964); (b) B. Rice, R. J. Galiano, and W. J. Lehmann, *J. Phys. Chem.*, **61**, 1222 (1957).

[28] C. H. Wong, T. M. Yen, and T. Y. Lee, *Acta Crystallogr.*, **18**, 340 (1965).

[29] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 7281 (1969).

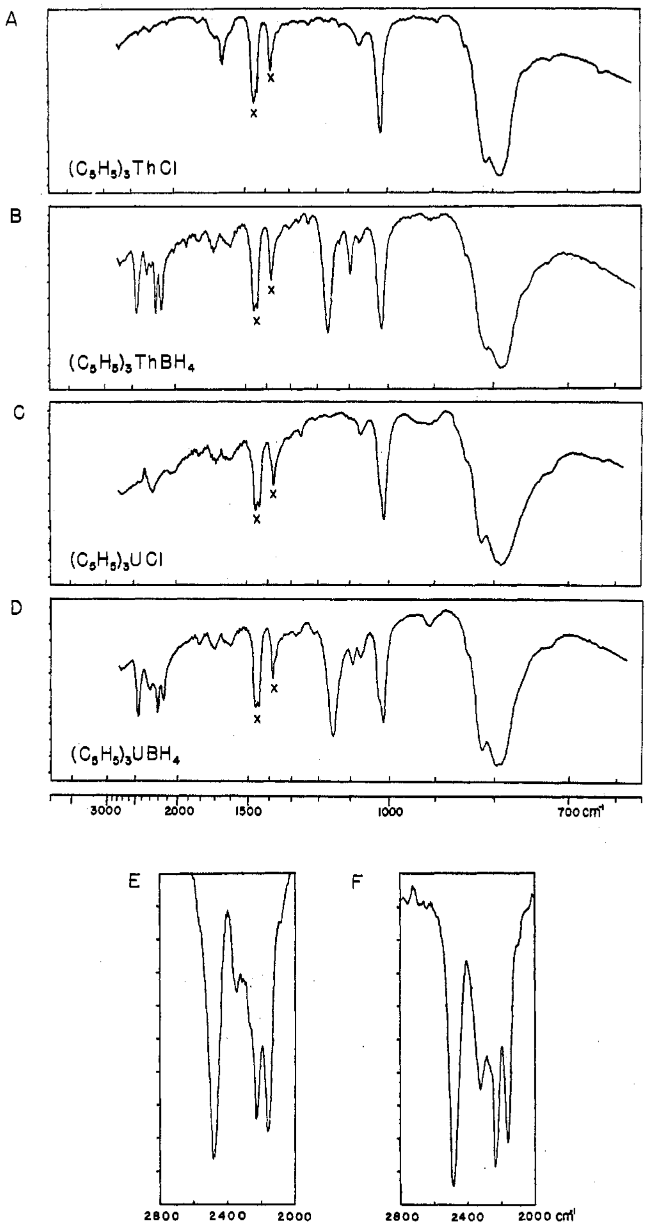

Figure 3.—Mull infrared spectra of (A) $(h^5\text{-}C_5H_5)_3ThCl$ in Nujol, (B) $(h^5\text{-}C_5H_5)_3Th(BH_4)$ in Nujol, (C) $(h^5\text{-}C_5H_5)_3UCl$ in Nujol, (D) $(h^5\text{-}C_5H_5)_3U(BH_4)$ in Nujol (sharp bands due to Nujol are marked ×), (E) $(h^5\text{-}C_5H_5)_3Th(BH_4)$ in the B–H stretching region in benzene solution; and (F) $(h^5\text{-}C_5H_5)_3U(BH_4)$ in benzene solution.

sults for the $M(BH_4)_4$ compounds discussed earlier show that the observed spectrum of $(C_5H_5)_2Zr(BH_4)_2$ cannot be explained in terms of two strongly coupled tridentate ligands. Likewise, the spectrum cannot be due to two grossly nonequivalent tridentate ligands. Earlier studies,[30] in the solid state, have reached essentially the same structural conclusion. The dissimilarity of spectra of this compound to those of other bidentate molecules is noteworthy (*vide infra*).

$(C_5H_5)_2Ti(BH_4)$.—Solution and mull spectra are shown in Figure 1 for this complex and also for $(h^5\text{-}C_5H_5)_2TiCl_2$. Again it is clear that the cyclopentadienyl rings are *pentahapto*.[29] Such a result is not necessarily that expected in view of recent findings[31] for other low-valent titanium systems. The solid-state spectrum strongly suggests a bidentate $TiBH_4$ structure, and the solution spectrum in the $B\text{–}H_t$ region confirms this. The exact assignment of the infrared-active band at 1945 cm^{-1} has been controversial in previous solid state examinations[7,30,32] of this compound. We believe this band, despite its relatively low frequency, to be the symmetric ν_{B-H_b} vibration rather than a terminal metal–hydrogen stretch[30] for two reasons. First, for the cyclic hydrogen bridged structure found in metal tetrahydroborate molecules it is to be expected that there will be extensive mixing of the various A_1 bridge stretching modes. This is true for diborane[16] and beryllium borohydride.[19] Also, these modes should be quite sensitive to the exact geometry and bonding in the metal–bridge system which should depend on the electronic requirements of the metal. Hence as expected, there is considerable fluctuation in frequencies for the ν_{B-H_b} and bridge stretching A_1 modes: $Al(BH_4)_3$, 2069 and 1495; $(C_5H_5)_2Ti(BH_4)$, 1945 and 1320; and $(C_5H_5)_2Zr(BH_4)_2$, 2145 and 1295 cm^{-1}. Further support for our assignment is derived from the H:D ratio (1.34[33]) observed for the 1945-cm^{-1} band in $(C_5H_5)_2Ti(BH_4)$ which is close to values observed for the A_1 ν_{B-H_b} vibration in $Al(BH_4)_3$, 1.38 and $(C_5H_5)_2Zr(BH_4)_2$, 1.37,[33] whereas a ratio of close to 1.41 is expected and observed for metal hydrides.[34] The weak doublet at *ca.* 2050 cm^{-1} may either be due to the antisymmetric ν_{B-H_b} vibration or to an overtone or combination band or to both. The infrared spectra of almost all metal tetrahydroborates exhibit weak, nonfundamental bands in this general region.

The possibility that this molecule possesses a BH_4-bridged dimeric structure similar to that proposed for $[(C_5H_5)_2TiCl]_2$[35] is unlikely. The molecule is monomeric in dioxane[7] and we find infrared spectra in the 1900–2600 cm^{-1} region to be identical in benzene and THF solutions.

$(C_5H_5)_2Zr(H)(BH_4)$.—This molecule is unique in that it is the only well-characterized transition metal hydride tetrahydroborate. In addition, it appears to be the only known zirconium hydride which is not polymeric.[36] High volatility, appreciable solubility in nonpolar solvents, and our cryoscopy studies in benzene indicate that $(C_5H_5)_2Zr(H)(BH_4)$ is monomeric. Solution and mull spectra are presented in Figure 1. The most striking feature of these spectra is their great similarity to spectra of $(C_5H_5)_2Ti(BH_4)$. This implies that the BH_4 group is bidentate and that the previous assignment[9] of the band at 1945 cm^{-1} to a terminal Zr–H stretch is unlikely. We assign the strong absorption at 1620 (mull), 1595 cm^{-1} (benzene solution) in the infrared, and that which is the strongest band in the Raman spectrum, to the terminal Zr–H stretch. Metal hydrides toward the left of the periodic table commonly exhibit such low ν_{M-H} frequencies.[34,37] Especially relevant are compounds which we believe

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[30] N. Davies, B. D. James, and M. G. H. Wallbridge, *J. Chem. Soc. A*, 2601 (1969).

[31] H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, **92**, 6182 (1970).

[32] F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968).

[33] Calculated from the data given in ref 30.

[34] D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968, Chapter 1.

[35] G. Natta, G. Dallastra, G. Mazzanti, U. Giannini, and S. Cesca, *Angew. Chem.*, **71**, 205 (1959).

[36] P. C. Wailes and H. Weigold, *J. Organometal. Chem.*, **24**, 405 (1970), and references therein.

[37] A. P. Ginsberg, *Transition Metal Chem.*, **1**, 111 (1965).

(*vide infra*) to be isoelectronic with $(C_5H_5)_2Zr(H)(BH_4)$, *e.g.*, $(C_5H_5)_2Nb(H)L$,[38] where $\nu_{M-H} = 1695$ (L = CO), 1650 ($L = P(C_6H_5)_3$), and 1635 cm^{-1} ($L = P(CH_3)_3$). The medium band at 720 cm^{-1} is conceivably an M–H deformation mode.[34] Various dynamic processes, which will be discussed elsewhere, have thwarted extensive deuteration studies.[39]

It is hoped that the criteria summarized in this paper will be of utility in the structural characterization of covalent metal tetrahydroborates. With data of this sort at hand, it is next of interest to begin placing MBH_4 compounds within the general scheme of low valent, especially organometallic molecules. Certain anomalies in the spectra will also become more understandable.

Structural Perspectives and Valence Considerations.—A curious relationship appears to exist between certain covalent metal tetrahydroborate and π-allyl[40-45] compounds (Table IV), which may be instructive in understanding the nature of the metal–tetrahydroborate interaction. All pairs of compounds have similar stoichiometry, molecularity, and volatility.[46] All evidence available indicates that the gross features of the coordination geometry about the metal are the same in corresponding pairs of compounds. Interestingly enough, where investigated, all molecules have also been found to be fluxional. Exactly how far the analogy between allyls and tetrahydroborates can be carried remains to be seen. Both ligands exist as stable anions, have a variable coordination geometry, and have somewhat similar steric requirements. Both ligands have several molecular orbitals of proper symmetry[47] for coordination to a metal.

TABLE IV

COMPARISON OF CORRESPONDING PAIRS OF ALLYL AND BH_4 COMPLEXES

Allyl	Ref	Nve[a]	Tetrahydroborate	Nve[a]
$Zr(h^3\text{-}C_3H_5)_4$	40	16 (3)	$Zr(BH_4)_4$	16 (3)
$Hf(h^3\text{-}C_3H_5)_4$	40	16 (3)	$Hf(BH_4)_4$	16 (3
$(h^5\text{-}C_5H_5)_2Ti(h^3\text{-}C_3H_5)$	41	17 (3)	$(h^5\text{-}C_5H_5)_2Ti(BH_4)$	17 (3)
$(h^5\text{-}C_5H_5)_2Zr(h^3\text{-}C_3H_5)\text{-}(h^1\text{-}C_3H_5)$	42	18 (3, 1), 16 (1, 1)[b]	$(h^5\text{-}C_5H_5)Zr(BH_4)_2$	18 (2), 16 (1)
			$(h^5\text{-}C_5H_5)Zr(H)(BH_4)$	18 (3), 16 (1)
$Th(h^3\text{-}C_3H_5)_4$	43	16 (3)	$Th(BH_4)_4$	
$U(h^3\text{-}C_3H_5)_4$	44	18 (3)	$U(BH_4)_4$	
$(h^5\text{-}C_5H_5)_3U(C_3H_5)$	45		$(h^5\text{-}C_5H_5)_3U(BH_4)$	

[a] Nve = number of valence electrons. The number in parentheses indicates the formal electron contribution from the neutral allyl or BH_4 group. [b] Nve = 16 if the structure is $(h^5\text{-}C_5H_5)_2Zr(h^1\text{-}C_3H_5)_2$.

Table IV tabulates the nve (number of valence electrons) each metal possesses, examining further the electronic consequences of the supposed analogy between tetrahydroborates and allyls. It is reasonable to assume that no transition metal will have an nve less than 16 or greater than 18,[48] with 18 being preferred if steric constraints permit. Two surprising observations emerge. First, in almost all cases, the neutral BH_4 ligand acts as a formal three electron donor.[49] Second, the mode of ligand–metal attachment (bidentate or tridentate) does not, to a first approximation, appear to affect the extent of electron donation. This latter flexibility may explain the very low barrier[1] to the fluxional process in covalent metal tetrahydroborates, since a bidentate $\rightleftharpoons$ tridentate transition[1] would not represent a large change in energy. More relevant to the present vibrational study, Table IV shows that the bidentate BH_4 group in $(C_5H_5)_2Zr(BH_4)_2$ experiences considerably different electronic demands than in both $(C_5H_5)_2Zr(H)(BH_4)$ and $(C_5H_5)_2Ti(BH_4)$, where electron donation (from predominantly $B\text{-}H_b$ bonding orbitals) is greater. This explains why the vibrational spectra of the latter two compounds are so similar, and yet different from the former. Counting of electrons also reveals that donation of three electrons by the BH_4 ligand in $[(C_6H_5)_3P]_2CuBH_4$,[4a] $(R_3P)_2M(H)BH_4$, M = Ni, Pd,[50] and $(R_3P)_2M'(CO)BH_4$, (M' = Rh, Ir)[51] allows the transition metal to attain an 18-electron valence system.[52] Further synthetic and spectroscopic studies are in progress to test some of these ideas.

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(38) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, **93**, 3793 (1971).

(39) T. J. Marks, J. R. Kolb, and L. A. Shimp, to be published.

(40) J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc. A*, 423 (1967). The low-temperature spectra are consistent with a *trihapto* structure for the allyl groups.

(41) H. A. Martin and F. Jellinek, *J. Organometal. Chem.*, **8**, 115 (1967). The infrared spectrum of this paramagnetic molecule has been interpreted in support of a *trihapto*allyl group. The X-ray structure of the 1,2-dimethylallyl analog supports this interpretation: R. B. Helmholdt, F. Jellinek, H. A. Martin, and A. Vos., *Recl. Trav. Chim. Pays-Bas*, **86**, 1263 (1967).

(42) H. A. Martin, P. J. Lemaire, and F. Jellinek, *J. Organometal. Chem.*, **14**, 149 (1968). The structure proposed was based upon infrared studies; exchange and fluxional behavior of the allyl groups is rapid at all accessible temperatures. Though the proposed structure is an 18 electron system, a 16 electron system (as in $(C_5H_5)_2ZrCl_2$) with two $h^1\text{-}C_3H_5$ groups could only be completely ruled out by X-ray data.

(43) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, **5**, 151 (1966). The pmr spectrum is consistent with four *trihapto*allyl groups.

(44) G. Lugli, W. Marconi, A. Mazzei, N. Paladino, and U. Pedretti, *Inorg. Chim. Acta*, **3**, 253 (1969). The proposed structure is based upon infrared data, and is supported by pmr data: N. Paladino, G. Lugli, U. Pedretti, M. Brunelli, and G. Giacemetti, *Chem. Phys. Lett.*, **5**, 15 (1970).

(45) T. J. Marks and A. M. Seyam, *J. Amer. Chem. Soc.*, in press. The low-temperature pmr spectrum of this fluxional molecule suggests a *monohapto*allyl geometry. Models indicate this may be a case where specific steric interactions destabilize the *trihapto* configuration, which has a larger "bite" than BH_4.

(46) $U(BH_4)_4$ is polymeric in the solid state: E. R. Bernstein, T. A. Keiderling, S. J. Lippard, and J. J. Mayerle, *J. Amer. Chem. Soc.*, **94**, 2552 (1972); however, it is monomeric in the gas phase: H. I. Schlessinger and H. C. Brown, *ibid.*, **75**, 219 (1953). The gas phase infrared spectrum is reported to be similar to that of $Zr(BH_4)_4$: B. D. James, Ph.D. Thesis, University of Sheffield, 1967.

(47) (a) M. L. H. Green, "Organometallic Compounds," Vol. II, Methuen, London, 1968, p 45; (b) R. A. Hegstrom, W. E. Palke, and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 920 (1967); (c) More detailed MO considerations will be discussed at a later date.

(48) C. A. Tolman, *Quart. Rev., Chem. Soc.*, in press. We thank Dr. Tolman for a preprint and a stimulating discussion.

(49) Alternatively, BH_4^- acts as a four electron donor. Formal charges are immaterial in such electron counting schemes.

(50) M. L. H. Green, H. Munakata, and T. Saito, *J. Chem. Soc. A*, 469 (1971).

(51) L. Vaska, W. V. Miller, and B. R. Flynn, *Chem. Commun.*, 1615 (1971).

(52) The low ν_{B-H_t} frequencies reported for several of these compounds implies an appreciable amount of ionic character, which is in accord with the reported insensitivities to protonic solvents.