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Spectroscopic Studies of Borohydride Derivatives of Zirconium and Hafnium

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The infrared (i.r.), proton and ¹¹B nuclear magnetic resonance (n.m.r.) spectra of zirconium and hafnium borohydrides have been investigated, together with the proton and ¹¹B n.m.r. spectra of dicyclopentadienyl zirconium diborohydride. The i.r. spectra indicate that the borohydride groups are bonded to the metal atom by bridging hydrogen atoms, but a rapid exchange process renders the bridge and terminal hydrogens indistinguishable in the n.m.r. spectra.

SEVERAL transition metal borohydrides, and derivatives thereof, have now been characterised.¹⁻⁶ However, the only studies relating to the structure and bonding of these compounds are those on derivatives of titanium,

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 $(\pi\text{-}C_5H_5)_2\text{TiBH}_4,^2$ zirconium, $(\pi\text{-}C_5H_5)_2Zr(\mathrm{BH}_4)_3,^3$ nickel, $[e.g.,~\mathrm{NiA}(\mathrm{BH}_4)_2,^4$ where A is a cyclic tetramine or a

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

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⁴ N. F. Curtis, J. Chem. Soc., 1965, 924.
⁵ J. M. Davidson, Chem. and Ind., 1964, 2021.
⁶ F. Cariati and L. Naldini, (a) Gazzetta, 1965, 95, 3; (b) *ibid.*, p. 201.

non-cyclic tetradentate ligand], copper, and silver, $(Ph_3P)_2MBH_4$,^{5,6} where M = Cu or Ag. In each case the presence of a borohydride group bonded to the metal atom by hydrogen bridges was deduced from the presence of a band at $\sim 2200-2000$ cm.⁻¹ in the i.r. spectrum. Since more information on similar systems is desirable, we now report the results of a study of the i.r. and n.m.r. spectra of the borohydrides of zirconium, $Zr(BH_4)_4$, and hafnium, $Hf(BH_4)_4$, together with the n.mr. spectrum of the dicyclopentadienyl zirconium derivative.

Zirconium and hafnium borohydrides are expected, from their physical properties 7 [Zr(BH₄)₄, m. p. 28.7°, v. p. $15.0 \text{ mm.}/25^{\circ}$; $\text{Hf}(\text{BH}_4)_4$, m. p. 29° , v. p. 14.9 mm./ 25°], to be intermediate in character between the ionic, e.g., Na⁺BH₄⁻, and covalent, e.g., Al(BH₄)₃, borohydrides. Although they decompose slowly, at 25°, evolving hydrogen, reliable gas-phase i.r. spectra may be obtained. Such spectra show only four major regions of absorption in the region 4000-400 cm.-1, and these may be interpreted in terms of a structure involving bridge hydrogen atoms, *i.e.*, $M < \begin{bmatrix} H \\ H \end{bmatrix}_4^H$, where M =Zr or Hf. Thus the bands near 2600 and 1200 cm.⁻¹ may be assigned to the stretching and deformation modes, respectively, of the terminal BH₂ group, and those near 500 cm.⁻¹ to the MB₄ asymmetric stretching modes, such assignments being similar to those made for the spectra of aluminium and beryllium borohydrides, $Al(BH_4)_3$ and $Be(BH_4)_2$ ^{8,9} The significant difference between the spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ on the one hand, and of aluminium and beryllium borohydrides on the other, is that the band near 1400 cm.⁻¹, assigned as a symmetric bridge stretching mode in the latter compounds, becomes inactive in the former. The small splitting (>10 cm.⁻¹) of the terminal BH₂ and MB₄ stretching modes suggests that such splitting is not due to the presence of asymmetric and symmetric modes, and the relative intensities do not appear to be compatible with an isotope effect. The bands in the 2200-2100 cm.⁻¹ region appear to be two distinct bridge stretching modes similar to those reported for aluminium borohydride.^{8,9} It seems more likely, therefore, that the molecules as a whole have D_{4d} (or D_{4h}) symmetry, which would lead to splitting of asymmetric modes and absence of the corresponding symmetric modes. The spectra are not consistent with dodecahedral (D_{2d}) symmetry. Such an argument further assumes the absence of any significant coupling between the various group vibrations. A comparison of the i.r. spectra is given in Table 1.

It is relevant that if the symmetry of zirconium borohydride is reduced, as in the dicyclopentadienyl derivative, then the symmetric bridge mode becomes active in the i.r. spectrum.³ While the zirconium and

7 H. R. Hoekstra and J. J. Katz, J. Amer. Chem. Soc., 1949, **71**, 2488.

¹⁰ J. K. Ruff, Inorg. Chem., 1963, 2, 515.

hafnium atoms are formally eight co-ordinate in $Zr(BH_4)_4$ and $Hf(BH_4)_4$, and zirconium ten co-ordinate in $(\pi - C_5 H_5)_2 Zr(BH_4)_2$, it is probable that the metal atom uses only one bonding orbital for each borohydride group, forming a multi-centre orbital similar to that postulated for aluminium borohydride.^{10,11}

TABLE	1
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Infrared spectra of borohydride derivatives

	Frequency (cm. ⁻¹)					
	B-H	BH_2	Bridge	Bridge		
	str.	deform-	str.	str.		
Compound	(asym.)	ation	(asym.)	(sym.)		
Zr(BH ₄) ₄	2584	1223	2198			
$Hf(BH_4)_4$	2581	1228	2207			
B ₂ H ₆ ^{<i>a</i>}	2614	1175	1850	1600		
$AI(BH_4)_a^b$	2549	1116	2154	1521		
$(\pi - C_5 H_5)_2 Zr(BH_4)_2^{c}$	2440	1123	2149	1440-1290		
$(Ph_3P)_2CuBH_4^d$	2420	1155	2010	g		
$(Ph_3P)_2AgBH_4^d$	2365	ſ	2010	g		
NaBH4	2290	1120				
"W. C. Price,	J. Chem.	Phys., 194	8, 16 , 89	4. ^b Ref. 8		
		J .				

^e Ref. 3. ^d Ref. 6. ^e T. C. Waddington, J. Chem. Soc., 1958, 4783. ^f Not recorded. ^g Obscured by bands due to Ph₃P.

Further information on the bonding may be obtained from the proton and ¹¹B n.m.r. spectra. Zr(BH₄)₄ and $Hf(BH_4)_4$ are both diamagnetic, and possess metal atoms whose predominant isotopes have nuclear spin quantum numbers of zero. Their proton spectra, and that of the derivative $(\pi-C_5H_5)_2Zr(BH_4)_2$, consist of a quartet (relative intensities 1:1:1:1), indicative of the equivalence of the borohydride protons. Such equivalence is confirmed by the ¹¹B spectra of $Hf(BH_{4})_{4}$ and $(\pi - C_5 H_5)_2 Zr BH_4)_2$, which both show a quintet (relative intensities 1:4:6:4:1). Similar results have been reported for the alkali metal borohydrides 12 and aluminium borohydride,¹³ in spite of their different physical properties; and from reports of the ¹¹B spectra of 1:1 adducts of beryllium borohydride,¹⁴ [e.g., $Me_{3}P_{4}Be(BH_{4})_{2}$, it is reasonable to expect a similar pattern for beryllium borohydride itself. The results are given in Table 2. It is noteworthy that diborane

TABLE 2

Proton and ¹¹B n.m.r. spectra of borohydride derivatives

	Protons			¹¹ Boron	
	1068	$J_{{}^{11}\mathrm{B-H}}$	$J_{10}_{\mathbf{B}^{-}\mathbf{H}}$	1068	$J_{{}^{11}\mathbf{B-H}}$
Compound	(p.p.m.)	(c./sec.)	(c./sec.)	(p.p.m.)	(c./sec.)
Zr(BH ₄) ₄	+5.65	90	29.8		
$Hf(BH_4)_4$	+4.38	89.3	29.6	+29.3	90
$(\pi - C_5H_5)_2Zr(BH_4)_2$	+6.4	85.7		+32.5	90
$Al(BH_4)_3^a$	+8.7	87		+55.1	86

Proton shifts relative to benzene, $^{11}\mathrm{B}$ shifts relative to trimethyl borate. " See ref. 13.

is the only "borohydride" so far reported for which distinct bridge and terminal hydrogen atoms have been observed in the n.m.r. spectra. The equivalence,

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 ¹² R. A. Ogg, J. Chem. Phys., 1954, 22, 1933.
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14 L. Banford and G. E. Coates, J. Chem. Soc., 1965, 5591.

 ⁸ W. C. Price, J. Chem. Phys., 1949, 17, 1044.
 ⁹ A. R. Emery and R. C. Taylor, Spectrochim. Acta, 1960, 16, 1455.

observed in all other metal borohydrides, would appear to be best explained by a rapid exchange process occurring through a single bridge atom species. A similar



rapid tautomerism has been discussed for aluminium borohydride, in preference to the tunnelling effect previously suggested.¹⁵

EXPERIMENTAL

Preparation of Zirconium and Hafnium Borohydrides.— The method of Reid et al.¹⁶ was used for zirconium borohydride, and adapted for the hafnium compound. The products were purified by sublimation in vacuo (Found: H, 10·4; B, 28·6; Zr, 62·0. Calc. for ZrB_4H_{16} : H, 10·7; B, 28·7; Zr, 60·6%. Found: H, 6·9; B, 18·1; Hf, 75·6. Calc. for HfB₄H₁₆: H, 6·8; B, 18·2; Hf, 75·0%). The compounds were analysed by hydrolysing, measuring the volume of hydrogen, titrating the boric acid in the resultant solution, and determining the zirconium gravimetrically as dioxide. Infrared and Nuclear Magnetic Resonance Spectra.— The i.r. spectra were recorded, from samples in the vapour phase, with a Unicam S.P. 100 spectrometer. The proton n.m.r. spectra were recorded with a Varian Associates model A60, and the ¹¹B spectra with an A.E.I. R.S.2 (at 20Mc./sec.) spectrometer, benzene being the solvent in both cases. In the proton spectra the solvent was used as the standard, and trimethyl borate used as an external standard for the ¹¹B spectra.

The complete i.r. spectra are given below:

Zr(BH₄)₄: 2584s, 2575s, 2568ssh, 2497w, 2435w, 2198s, 2135s, 1295vw, 1223vs, 1165vw, 1040vw, 509vs, 505ssh. Hf(BH₄)₄: 2588ssh, 2581s, 2509vw, 2447vw, 2207s, 2146s, 1300vw, 1228vs, 1140vw, 1020vw, 493ssh, 487vs.

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 ¹⁶ W. E. Reid, J. M. Bish, and A. Brenner, J. Electrochem. Soc.,

¹⁰ W. E. Reid, J. M. Bish, and A. Brenner, *J. Electrochem. Soc.*, 1957, **104**, 21.