

parently due to the partial formation of  $[(\text{CH}_3)_4\text{N}]_3\text{B}_{10}\text{Cl}_9\text{COH}\cdot\text{B}_{10}\text{Cl}_9\text{COOH}$ .

$(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{COHB}_{10}\text{H}_8\text{COOH}^{2-}$ .—A solution of  $(\text{CH}_3)_4\text{N}\cdot 1\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_3)_2^8$  (6.0 g, 23.7 mmoles) and  $1,10\text{-B}_{10}\text{H}_8(\text{CO})_2^3$  (4.0 g, 23.3 mmoles) was refluxed for 6 hr. Filtration gave 0.2 g (0.8 mmole) of recovered  $(\text{CH}_3)_4\text{N}\cdot 1\text{-B}_{10}\text{H}_9\text{S}(\text{CH}_3)_2$  and a light yellow filtrate which was concentrated until it became a viscous oil. This was stirred in water (80 ml), liberating 3.0 g of a yellow solid which was recrystallized from water and then from aqueous tetramethylammonium chloride to obtain  $[(\text{CH}_3)_4\text{N}]_2(\text{CH}_3)_2\text{-SB}_{10}\text{H}_8\text{COHB}_{10}\text{H}_8\text{COOH}\cdot\text{H}_2\text{O}$  (mp 162–164°). *Anal.* Calcd for  $[(\text{CH}_3)_4\text{N}]_2(\text{CH}_3)_2\text{SB}_{10}\text{H}_8\text{COHB}_{10}\text{H}_8\text{COOH}\cdot\text{H}_2\text{O}$ : C, 26.9; H,

9.4; N, 5.2; S, 6.0. Found: C, 27.2; H, 9.5; N, 5.2; S, 6.2. Ultraviolet  $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ : 365 ( $\epsilon$  27,600), 305 ( $\epsilon$  6800), 237 ( $\epsilon$  17,600).

$[(\text{CH}_3)_2\text{S}]_2\text{B}_{10}\text{H}_7\text{COHB}_{10}\text{Cl}_8\text{COOH}^-$ .—A solution of  $1,10\text{-B}_{10}\text{Cl}_8(\text{CO})_2^3$  (10.8 g, 23.1 mmoles) and  $1,10\text{-B}_{10}\text{H}_8[\text{S}(\text{CH}_3)_2]_2^8$  (10.8 g, 31.8 mmoles) in acetonitrile (125 ml) was refluxed in a nitrogen atmosphere for 3 hr. The acetonitrile was removed by evaporation. The residue was extracted with 1.6% aqueous sodium hydroxide (240 ml). The extracts were filtered and acidified with hydrochloric acid; the extract was initially colorless but became yellow during the acidification. A gummy solid separated after a considerable excess of hydrochloric acid had been added. This solid was recrystallized twice from dilute cesium chloride solution to obtain  $\text{Cs}[(\text{CH}_3)_2\text{S}]_2\text{B}_{10}\text{H}_7\text{COHB}_{10}\text{Cl}_8\text{COOH}\cdot\text{H}_2\text{O}$  as a yellow solid (2.4 g, 11%). *Anal.* Calcd for  $\text{Cs}[(\text{CH}_3)_2\text{S}]_2\text{B}_{10}\text{H}_7\text{COHB}_{10}\text{Cl}_8\text{COOH}\cdot\text{H}_2\text{O}$ : C, 8.4; H, 2.7; B, 25.3; S, 7.5. Found: C, 8.3; H, 2.8; B, 24.3; S, 7.4.

(8) W. H. Knoth, W. R. Hertler, and E. L. Muetterties, *Inorg. Chem.*, **4**, 280 (1965).

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## The Reactions of Lewis Bases with Tetrahydroborate Derivatives of the Group IVa Elements. The Preparation of New Zirconium Hydride Species

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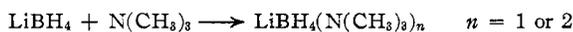
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Bis( $\pi$ -cyclopentadienyl)zirconium bistetrahydroborate,<sup>1</sup>  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{BH}_4)_2$ , reacts with 1 and 2 moles of trialkylamines to produce the new hydride species bis( $\pi$ -cyclopentadienyl)zirconium hydride tetrahydroborate,  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{H})\text{BH}_4$ , and bis( $\pi$ -cyclopentadienyl)zirconium dihydride,  $[(\text{C}_5\text{H}_5)_2\text{ZrH}_2]_n$ , respectively. The formation of these hydrides has been rationalized by postulating successive bridge cleavage reactions, and the physical and spectral properties of these compounds are discussed. The results of similar reactions attempted with bis( $\pi$ -cyclopentadienyl)titanium(III) tetrahydroborate,  $(\text{C}_5\text{H}_5)_2\text{-TiBH}_4$ , and bis(triphenylphosphine)copper(II) tetrahydroborate,  $((\text{C}_6\text{H}_5)_3\text{P})_2\text{CuBH}_4$ , are also reported.

### Introduction

While several transition metal hydride compounds are now known, no distinct hydride species has been isolated for the group IVa elements, although recently it has been suggested, as a result of an esr spectrum, that dimeric bis(cyclopentadienyl)titanium hydride,  $[(\text{C}_5\text{H}_5)_2\text{TiH}]_2$ , occurs as a reaction intermediate.<sup>2</sup>

In general, the two extremes of behavior of metal tetrahydroborates with ligand molecules (*e.g.*, trialkylamines) are (i) to form addition compounds with the ionic tetrahydroborates, probably by coordination with the metal cation,<sup>3</sup> *e.g.*



and (ii) to cleave the hydrogen bridge bonds in the covalent tetrahydroborates,<sup>4</sup> although this reaction may be preceded by coordination at the central metal atom if suitable vacant orbitals are available, *e.g.*

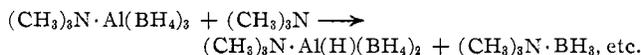


(1) We accept the suggestion of a referee that bistetrahydroborate is more suitable than the name of diborohydride since the latter has sometimes been used to designate the  $\text{B}_2\text{H}_7^-$  ion. Unfortunately no unambiguous name yet exists for differentiating between the presence of a discrete  $\text{BH}_4^-$  ion and a  $\text{BH}_4$  group bonded to a metal by hydrogen bridges as in this case.

(2) H. Brintzinger, *J. Am. Chem. Soc.*, **88**, 4305 (1966).

(3) G. W. Schaeffer and D. J. Hunt, Abstracts, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959, p 28M.

(4) P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc.*, 3923 (1965).



The latter reaction thus offers an alternative route to hydride derivatives of various metals. It was therefore of interest to compare the reactions of titanium, zirconium, hafnium, and copper tetrahydroborate compounds in the light of this reaction.

### Experimental Section

Solvents and ligands used were dried over lithium aluminum hydride or calcium hydride and distilled (in a vacuum line where appropriate) before use. Trimethylphosphine was prepared from a Grignard reagent, isolated as the silver iodide complex, and liberated from the latter by heating under vacuum.<sup>5</sup>

**Preparation of  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{BH}_4)_2$  and  $(\text{C}_5\text{H}_5)_2\text{Hf}(\text{BH}_4)_2$ .**—The method previously described for the zirconium compound<sup>6</sup> was used for both compounds, and the products were purified by sublimation under vacuum at 120°. The very pale yellow solids were subsequently handled in a nitrogen-filled glove box; yield, ~70% in each case.

**Preparation of  $(\text{C}_5\text{H}_5)_2\text{TiBH}_4$ .**—The method of Nöth, *et al.*,<sup>7</sup> was used, and the violet product was sublimed under vacuum at 110° prior to use. Rigorous precautions had to be taken to exclude any contact with oxygen, solutions proving especially sensitive to oxidation.

**Reaction of  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{BH}_4)_2$  with Trialkylamines.** (i) **Isola-**

(5) L. H. Long and J. F. Sackman, *Trans. Faraday Soc.*, **53**, 1606 (1957).

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

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

tion of  $(C_5H_5)_2Zr(H)BH_4$ .—A solution of  $(C_5H_5)_2Zr(BH_4)_2$  (1.2 g, 4.8 mmoles) in 50 ml of benzene was placed in a flask attached to the vacuum line. Trimethylamine (0.28 g, 4.8 mmoles) was slowly added, in several portions, to the solution which was cooled to near 0° and magnetically stirred during the reaction. After all of the ligand had been added, the stirring was continued for 30 min at 20°; no noncondensable gas was formed during this time. The solvent and trimethylamine borane (0.31 g, 4.25 mmoles), which was identified by comparison of its infrared spectrum with that of an authentic sample, were removed under vacuum leaving a white, solid residue. The discrepancy in the amount of  $(CH_3)_3NBH_3$  recovered (88.5% theoretical) is probably due to difficulty in affecting a quantitative separation from the benzene solvent since some of the solid always sublimed as the benzene was being removed.

The reaction product was purified by sublimation under vacuum at 60°; yield, 0.7 g; 60% theoretical. *Anal.* Calcd for  $(C_5H_5)_2Zr(H)BH_4$ : C, 50.6; H, 6.3; Zr, 38.5. Found: C, 51.1; H, 6.4; Zr, 39.2.

Very little further cleavage to the dihydride occurred during the reaction since only a trace of a white insoluble product was observed after all of the ligand had been added. The mass spectrum of the sample was recorded from a sample introduced directly into the source at 70°.

(ii) Isolation of  $[(C_5H_5)_2ZrH_2]_n$ .—A benzene solution of  $(C_5H_5)_2Zr(BH_4)_2$  (0.9 g, 3.6 mmoles) and triethylamine (0.73 g, 7.2 mmoles) was stirred for 12 hr. No noncondensable gas was detected and a white solid precipitated from the solution over this time. The deposit was filtered off under nitrogen, washed thoroughly with benzene, and dried under vacuum at 25°; yield, 0.62 g; 78% theoretical. *Anal.* Calcd for  $(C_5H_5)_2ZrH_2$ : C, 53.8; H, 5.4. Found: C, 53.4; H, 5.4.

The product was insoluble in a variety of hydrocarbon solvents and involatile up to 120° when decomposition occurred. Removal of the solvent from the filtrate left a residue of triethylamine borane (identified from its infrared spectrum), but in this case the product was not determined quantitatively. A similar reaction occurred with trimethylamine producing the dihydride and  $(CH_3)_3NBH_3$ .

**Reaction of  $(C_5H_5)_2TiBH_4$  with Various Ligands.**—The ligand  $N(CH_3)_3$ ,  $N(C_2H_5)_3$ ,  $P(CH_3)_3$ ,  $C_4H_8O$ , or  $C_5H_5N$  was condensed onto a known weight of powdered  $(C_5H_5)_2TiBH_4$ . After allowing the mixture to stand for several hours the excess ligand was pumped off at 20° and the  $(C_5H_5)_2TiBH_4$  reweighed. Only in the case of pyridine was any ligand retained, and the quantity here corresponded to that required for a 1:1 adduct. However, the weight of solid slowly reverted to its original weight on pumping for several hours, and the residue was identified as unchanged  $(C_5H_5)_2TiBH_4$  from its infrared spectrum.

**Reaction of  $((C_5H_5)_3P)_2CuBH_4$  with Ligands.**—An investigation similar to that used for the titanium derivative, with  $N(CH_3)_3$ ,  $C_4H_8O$ , and  $C_5H_5N$ , showed that no reaction occurred and that the starting materials could be recovered unchanged. The  $((C_5H_5)_3P)_2CuBH_4$  was prepared by the method of Davidson.<sup>8</sup>

**Spectroscopic Studies.**—The  $^1H$  nmr spectra were recorded from benzene solutions, using a Varian A60 spectrometer, up to  $\tau$  15 (the limit of the machine). Spectra at higher fields ( $\tau$  15–20) were recorded at 60 Mcps using a Perkin-Elmer R10 spectrometer, while the  $^{11}B$  spectrum was recorded at 19.25 Mcps using a similar machine.

The mass spectra were recorded using an AEI MS9 instrument at 70 ev, with source temperatures of 50–100°.

The infrared spectra were obtained from disks or mulls using a Unicam SP 100 spectrometer. The complete spectra ( $cm^{-1}$ ) were as follows:  $(C_5H_5)_2Zr(H)BH_4$  (Nujol): 3100 w, sh, 3087 w, [2929 w, 2865 vw (from KBr disk)], 2443 m, 2400 m, 2257 w, 2109 vw, 2034 m, 1955 s, sh, 1945 s, 1623 m, 1174 vw, 1132 s, 1066 vw, 1014 s, 919 vw, 841 s, 813 s, 755 m, sh, 725 w, sh, 645 m, 613 vw, 417 m.  $[(C_5H_5)_2ZrH_2]_n$  (KBr disk): 3121 w, 3071 m,

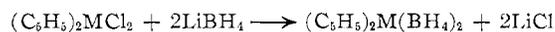
1540 s, 1445 s, 1375–1210 s, br, 1075 vw, 1029 s, 973 m, 919 w, sh, 902 m, 830 s, sh, 815 s, 745 s.

## Results and Discussion

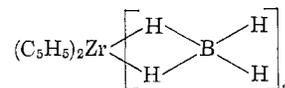
It is known<sup>7</sup> that bis(cyclopentadienyl)titanium(IV) dichloride reacts with an ethereal solution of lithium borohydride producing a tetrahydroborate derivative of Ti(III)



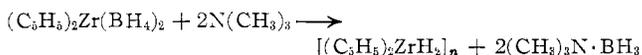
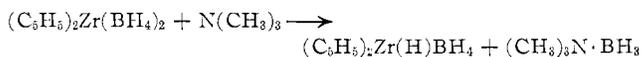
The analogous reaction with the zirconium and hafnium compounds does not result in reduction, and diamagnetic bistetrahydroborates are obtained<sup>6,9</sup>



where M = Zr or Hf. The bonding of the tetrahydroborate group to the metal atom in  $(C_5H_5)_2M(BH_4)_2$ , where M = Zr or Hf, is apparently different from that in  $(C_5H_5)_2TiBH_4$ . In the former compounds the bonding appears to be similar to that in aluminum tetrahydroborate<sup>10</sup> and to involve a double hydrogen bridge,<sup>6</sup> *i.e.*



whereas in the titanium compound a distinct Ti–H bond has been suggested to be present,<sup>7</sup> and the bonding of the remaining  $BH_3$  group has not yet been unequivocally determined. Although a hydrogen-bridged structure has been proposed for  $((C_5H_5)_3P)_2CuBH_4$ ,<sup>8,11</sup> the infrared spectrum resembles that of the titanium compound in the 2500–1500- $cm^{-1}$  region, and further studies are required before the bridged structure can be regarded as established. It is therefore not surprising that these types of compounds react differently with ligands. The zirconium compound,  $(C_5H_5)_2Zr(BH_4)_2$ , undergoes immediate reaction with trialkylamines, at room temperature, yielding the hydride derivatives as a result of bridge-cleavage reactions



Preliminary results show that the hafnium compound reacts similarly. In contrast, both  $(C_5H_5)_2TiBH_4$  and  $((C_5H_5)_3P)_2CuBH_4$  fail to react in this way and show no cleavage reactions at all with a range of ligand molecules. This may be attributed to the lack of a covalent hydrogen-bridge structure as discussed above.

The compounds  $(C_5H_5)_2Zr(H)BH_4$  and  $[(C_5H_5)_2ZrH_2]_n$  show interesting differences in their properties. Thus  $(C_5H_5)_2Zr(H)BH_4$  is volatile, slightly soluble in nonpolar solvents (benzene, ether, etc.), and air reactive in that it slowly hydrolyzes with loss of hydrogen. It therefore resembles  $(C_5H_5)_2Zr(BH_4)_2$  in its properties. In comparison,  $[(C_5H_5)_2ZrH_2]_n$  is more difficult to ob-

(9) N. Davies, B. D. James, and M. G. H. Wallbridge, unpublished work.

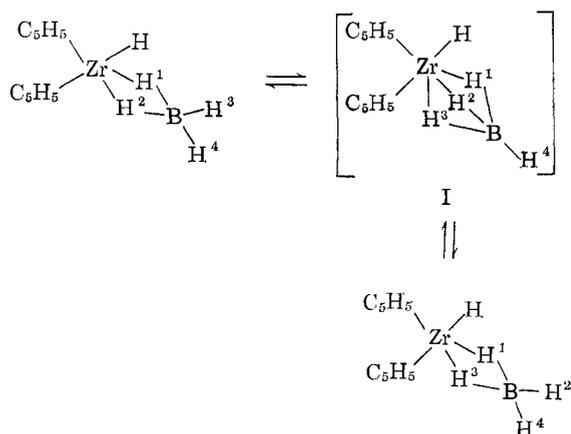
(10) W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).

(11) F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965).

(8) J. M. Davidson, *Chem. Ind. (London)*, 2021 (1964).

tain pure and behaves much like a polymeric material being involatile (decomposing above 120°) and insoluble in nonpolar solvents, and it apparently undergoes no reaction in air. In fact, the most convenient method for preparing a pure sample is to precipitate it from benzene solution using specially purified reactants. The formulation of  $(C_5H_5)_2Zr(H)BH_4$  as a hydride species has been deduced from both spectroscopic evidence and its method of preparation, but investigations of the product  $[(C_5H_5)_2ZrH_2]_n$  were limited by its physical properties, and only an infrared spectrum could be obtained.

The  $^1H$  nmr spectrum of  $(C_5H_5)_2Zr(H)BH_4$  shows three distinct sets of signals: (a) a sharp and intense signal, (b) a quartet whose relative intensities were 1:1:1:1, and (c) a weak signal to high field of (a) which was slightly broadened compared with that of (a). The appropriate values for these signals are given in Table I and compared with those for  $(C_5H_5)_2Zr(BH_4)_2$ .<sup>12</sup> The relative intensities given in the table indicate that the signal at  $-5.70$  ppm arises from the ten equivalent protons of the cyclopentadiene groups, and signals in other cyclopentadiene compounds occur in a similar region [e.g.,  $(C_5H_5)_2ZrCl_2$  at  $-6.50$  ppm, and  $(C_5H_5)_2TiCl_2$  at  $-6.61$  ppm,<sup>13</sup> both with TMS as reference]. The quartet (1:1:1:1) at  $+0.20$  ppm may be assigned to the four protons of the tetrahydroborate group, the signal arising from coupling with the  $^{11}B$  nucleus ( $I = 3/2$ ). This signal is interesting since from the infrared spectrum (discussed below) and comparisons with other metal tetrahydroborate systems there is little doubt that the boron is bonded to the zirconium atom by hydrogen-bridge bonds. Thus, while separate signals might be expected for the bridging and terminal protons, it has been shown that for a variety of metal tetrahydroborates these two sets of protons become equivalent in the nmr spectrum, and it is only in diborane itself that two distinct sets of signals may be observed. The exchange probably occurs through a rapid intramolecular process and may be represented as



Where the intermediate (I) could contain either a single or a triple hydrogen bridge. Similar exchange processes have been proposed for other metal tetra-

TABLE I  
PROTON NMR DATA FOR  $(C_5H_5)_2Zr(H)BH_4$

Compound	$\delta$ , ppm	$J_{11B-H}$ , cps	Relative integrated intensities
$(C_5H_5)_2Zr(H)BH_4$	$-5.70$	...	10
	$-4.53$	...	1
	$+0.20^a$	80	4
$(C_5H_5)_2Zr(BH_4)_2$	$-5.71$	...	10
	$-0.78^a$	85.7	8

<sup>a</sup> Quartet; the quoted value corresponds to the shift measured from the center of the quartet. All chemical shifts are relative to TMS, the positive and negative values representing high and low field shifts, respectively.

hydroborates,<sup>12,14</sup> and this type of exchange would leave all of the protons coupled to the boron and central metal atoms. However, since in this case the predominant zirconium isotopes ( $^{90}Zr$ , 51.5%;  $^{92}Zr$ , 17.1%;  $^{94}Zr$ , 17.4%) have spin quantum numbers of zero and it is only  $^{91}Zr$  (11.2%) which has  $I = 5/2$ , the signal is considerably simpler than that for other tetrahydroborates, e.g.,  $Al(BH_4)_3$ , where coupling with the  $^{27}Al$  ( $I = 5/2$ ) nucleus splits the quartet further into a 24-line multiplet. Thus by comparison of the proton nmr spectra of  $(C_5H_5)_2Zr(H)BH_4$  and other metal tetrahydroborates together with the results of integration and the expected  $J_{11B-H}$  values, there is little doubt that the quartet arises from the protons of the tetrahydroborate group. Attempts to obtain the  $^{11}B$  spectrum were not successful owing to the low solubility of the compound, and runs using a saturated solution in benzene resulted in only a very weak broad signal centered at  $\sim 30.5$  ppm to high field of  $B(OCH_3)_3$  used as a reference. No resolution of the signal could be obtained, and in this case therefore it was not possible to verify the existence of a 1:4:6:4:1 quintet as observed<sup>12</sup> in the  $^{11}B$  spectrum of  $(C_5H_5)_2Zr(BH_4)_2$  which represents the splitting of the boron signal by the four equivalent protons. It is relevant that for  $(C_5H_5)_2Zr(BH_4)_2$  the quintet is centered at 32.5 ppm to high field of  $B(OCH_3)_3$  and is thus in the same region as the signal observed for  $(C_5H_5)_2Zr(H)BH_4$ . The remaining signal at  $-4.53$  ppm may be assigned to the single proton bonded directly to the metal atom although such an assignment should be regarded as tentative until further information on other hydride derivatives of the group IVa metals is available. While the signal is weak it was reproducible, and integration confirmed the ratio shown in Table I, but attempts to increase the signal intensity were unsuccessful owing to low solubility in nonpolar solvents other than benzene (e.g., cyclohexane). The appearance of the signal at low field is surprising in view of the fact that other cyclopentadienylmetal hydrides [ $(C_5H_5)_2MoH_2$ , etc.] show the hydride signal at high field (5–30 ppm to high field of TMS).<sup>15</sup> A possible explanation is that the central metal has a  $d^0$  configuration, since it has been suggested that it is effects involving the d elec-

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

(13) E. Samuel, *Bull. Soc. Chim. France*, 3548 (1966).

(14) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

(15) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

trons which are responsible for enhancing the shielding of the proton attached to the metal atom.<sup>16,17</sup> A better analogy for the zirconium system might therefore be other d<sup>0</sup> metal hydride systems, *e.g.*, derivatives of Si, Ge, Sn, etc., and in these systems the proton signal is observed at low field ( $\sim 0$ –5 ppm to low field of TMS).<sup>18</sup> Occasionally the spectrum of  $(C_5H_5)_2Zr(BH_4)_2$  and  $(C_5H_5)_2Zr(H)BH_4$  showed an additional small sharp signal within  $\sim 15$  cps of the cyclopentadiene signal, and no satisfactory explanation can be offered to account for its presence. It does not apparently arise from a solution effect, since the signal could not be obtained consistently, and the solid could be recovered unchanged from solution. The most obvious cause is the presence of a volatile impurity introduced during sublimation of the solids in spite of the fact that analytical data for the samples were in close agreement with the calculated values.

The infrared spectra of many compounds containing cyclopentadiene groups  $\pi$ -bonded to metals are known, and the vibrations associated with the cyclopentadiene have been established.<sup>19</sup> The infrared spectra of the compounds  $(C_5H_5)_2Zr(BH_4)_2$ ,  $(C_5H_5)_2Zr(H)BH_4$ , and  $[(C_5H_5)_2ZrH_2]_n$  show such bands, *e.g.*, at 3100, 1014, and 813  $cm^{-1}$ , for  $(C_5H_5)_2Zr(H)BH_4$  (see Experimental Section). In other regions of the spectra the compounds show marked differences. Thus  $(C_5H_5)_2Zr(BH_4)_2$  shows bands at  $\sim 2500$  and  $\sim 1100$   $cm^{-1}$ , which may be associated with B–H stretching and  $BH_2$  deformation modes, respectively,<sup>6</sup> and bands at  $\sim 2100$  and  $\sim 1350$   $cm^{-1}$ , which correspond with similar bands observed for  $Al(BH_4)_3$ ,<sup>10</sup> such bands having been assigned to vibrations associated with the bridging hydrogen atoms. As expected, these bands also occur in the spectrum of  $(C_5H_5)_2Zr(H)BH_4$  and may be similarly assigned but are completely absent from  $[(C_5H_5)_2ZrH_2]_n$ . In addition to the bands associated with the cyclopentadiene and tetrahydroborate groups, both  $(C_5H_5)_2Zr(H)BH_4$  and  $[(C_5H_5)_2ZrH_2]_n$  show bands associated with the Zr–H bond, and these further bands do not appear in the spectrum of  $(C_5H_5)_2Zr(BH_4)_2$ . Thus  $(C_5H_5)_2Zr(H)BH_4$  shows a sharp and intense band at 1945  $cm^{-1}$  which may be assigned as the Zr–H stretching mode, while for  $[(C_5H_5)_2ZrH_2]_n$  the band at 1945  $cm^{-1}$  is replaced by a strong, broad ( $\sim 100$   $cm^{-1}$  at half-height) band at 1540  $cm^{-1}$ , and this may be reasonably assigned as the stretching mode of a [Zr–H–Zr] species, since it is known that in other polymeric hydrides the metal–hydrogen frequency appears as a broad band at lower frequencies than for the free M–H bond.<sup>20</sup> The infrared spectra therefore appear to be consistent with the formulation proposed above for the hydride compounds.

Further data on  $(C_5H_5)_2Zr(H)BH_4$  may be obtained from the mass spectrum which is shown in Figure 1. It is complicated by the fact that zirconium possesses

five isotopes [mass numbers 90 (51.5%), 91 (11.2%), 92 (17.1%), 94 (17.4%), and 96 (2.8%)] and boron possesses two [mass numbers 10 (18.8%) and 11 (81.2%)]. Thus the highest observable mass number would be 242 corresponding to  $(C_5H_5)_2Zr(H)^{11}BH_4^+$ , with further proportionate peaks at mass numbers 241, 240, 239, 238, 237, 236, and 235 [ $(C_5H_5)_2Zr(H)^{10}BH_4^+$ ], the most intense peak being expected at 236, from  $[(C_5H_5)_2Zr(H)^{90}BH_4^+]$ . It will be seen from Figure 1 that no peak is observed at 242, and the most intense peak occurs at 234. Both of these points suggest that fragmentation has occurred and that the predominant ions are of the type  $(C_5H_5)_2ZrBH_4^+$  which leads to  $(C_5H_5)_2ZrBH_3^+$  and eventually to  $(C_5H_5)_2Zr^+$ . The cracking pattern further suggests that the ion  $(C_5H_5)_2Zr^+$  is particularly stable, since a corresponding set of peaks is obtained at 110, 110.5, 111, etc., arising from  $(C_5H_5)_2Zr^{2+}$ , and no peaks corresponding to other fragments such as  $(C_5H_5)Zr^+$  or  $(C_5H_5)Zr(C_5H_4)^+$ , etc., are observed. We have obtained other evidence that related metal tetrahydroborates, *e.g.*,  $(C_5H_5)_2Zr(BH_4)_2$ ,  $Zr(BH_4)_4$ , and  $Hf(BH_4)_4$ , also do not show a strong parent ion, and the highest mass number corresponds to the loss either of protons or of boron-containing fragments from the molecule.<sup>21</sup> The only other major peaks were those at 66, 65, etc., arising from cyclopentadiene as previously reported,<sup>22</sup> and peaks at 28, 27, 26, etc., due to diborane which is probably formed from hydrolysis or thermal degradation of the sample in the source.

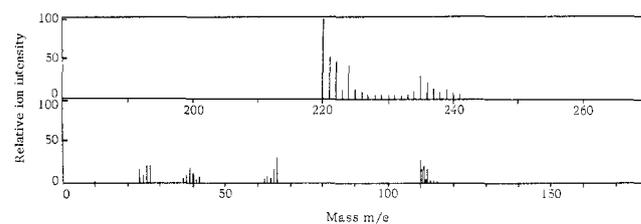


Figure 1.—Mass spectral cracking pattern of  $(C_5H_5)_2Zr(H)BH_4$ .

It is relevant at this point to speculate upon possible structures and bonding schemes adopted by this class of compounds in relation to earlier discussions on other cyclopentadienyl derivatives, *e.g.*,  $(C_5H_5)_2TiCl_2$ ,  $(C_5H_5)_2ZrCl_2$ ,  $(C_5H_5)_2MoH_2$ , etc. Only preliminary X-ray evidence has been published for  $(C_5H_5)_2TiCl_2$ <sup>23</sup> and  $(C_5H_5)_2ZrCl_2$ ,<sup>24</sup> but a complete determination of the structure of  $(C_5H_5)_2TiCl_2Al(C_5H_5)_2$ <sup>25</sup> shows that the cyclopentadiene rings are not parallel, and a similar angular arrangement of the rings is generally assumed for the halides themselves. The only cyclopentadiene metal hydride whose structure has been determined is  $(C_5H_5)_2MoH_2$ , and here also the rings are not parallel.<sup>26</sup> The bonding in this type of compound has been dis-

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(22) "Mass Spectral Data," Serial No. 1610, American Petrochemical Institute, April 1959.

(23) D. P. Schoemaker, unpublished observation. See G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 20 (1959).

(24) H. B. Bradley and L. C. Dowell, *Anal. Chem.*, **30**, 548 (1958).

(25) G. Natta, P. Corradini, and I. W. Bussi, *J. Am. Chem. Soc.*, **80**, 755 (1958).

(26) M. Gerloch and R. Mason, *J. Chem. Soc.*, 296 (1965).

(16) L. L. Lohr and W. N. Lipscomb, *Inorg. Chem.*, **3**, 22 (1964).

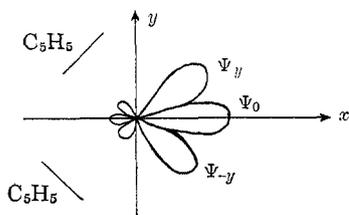
(17) A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 2747 (1964).

(18) N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, **85**, 1377 (1963).

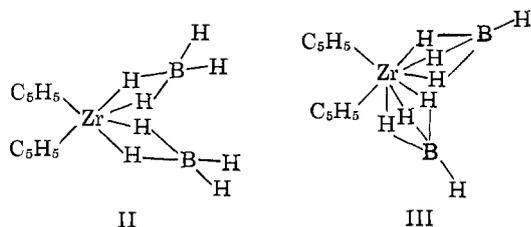
(19) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 240 (1964).

(20) L. Banford and G. E. Coates, *J. Chem. Soc.*, 5591 (1964).

cussed by Ballhausen and Dahl,<sup>27</sup> who suggest that, with the metal using all appropriate d, s, and p orbitals, after bonding the two cyclopentadienyl rings three hybrid orbitals remain available ( $\psi_y$ ,  $\psi_0$ ,  $\psi_{-y}$ )



They further suggest that the two Cl atoms in  $(C_5H_5)_2TiCl_2$  are bonded to  $\psi_y$  and  $\psi_{-y}$ . The bonding of the tetrahydroborate group in  $(C_5H_5)_2Zr(BH_4)_2$  may be discussed in terms of the model proposed for  $(C_5H_5)_2TiCl_2$  since, as has been previously discussed, it is possible for only one metal hybrid orbital to be involved for each  $BH_4$  group bonded by a double hydrogen bridge to the metal as in II.<sup>4,28</sup> Such a scheme would use the



$\psi_y$  and  $\psi_{-y}$  orbitals, and the essential difference between this type of bridge bond and that proposed for say diborane<sup>29</sup> is that of the four electrons associated with the  $Zr \begin{smallmatrix} H \\ < \\ H \end{smallmatrix} B$  bridge only *two* would be situated in a bonding molecular orbital, and two would necessarily be in a nonbonding orbital. Using this scheme it would be necessary to invoke the use of f orbitals on the metal atom for all of the four electrons to be in bonding orbitals. While it is possible to discuss the bonding in terms of a triple hydrogen bridge structure (III), the

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(28) J. K. Ruff, *Inorg. Chem.*, **2**, 515 (1963).

(29) For summary see H. C. Longuet-Higgins, *Quart. Rev. (London)*, **11**, 121 (1957).

infrared spectrum, by comparison with that of diborane,<sup>10</sup> suggests that a double hydrogen bridge is the more likely. The bonding in  $(C_5H_5)_2Zr(H)BH_4$  may then be considered to be similar to that for II, with one  $BH_4$  group replaced by a Zr-H bond. This scheme may be extended to  $[(C_5H_5)_2ZrH_2]_n$  following Ballhausen and Dahl's suggestion<sup>27</sup> that the hydride species formed for the group Va and VIa metals are determined by the number of electrons remaining on the metal atom in the  $\psi_y$ ,  $\psi_0$ , and  $\psi_{-y}$  hybrids. Thus, on going from group IIIa to VIIa the following hydrides would be predicted:  $(C_5H_5)_2YH$  (two vacant hybrid orbitals),  $(C_5H_5)_2ZrH_2$  (one vacant orbital),  $(C_5H_5)_2TaH_3$  (all orbitals filled),  $(C_5H_5)_2MoH_2$  (all orbitals filled, one lone pair), and  $(C_5H_5)_2ReH$  (all orbitals filled, two lone pairs), together with other intermediate hydrides of Ta, Mo, and Re proposed by Ballhausen and Dahl.<sup>27</sup> The polymeric nature of  $[(C_5H_5)_2ZrH_2]_n$ , in contrast with the monomeric  $(C_5H_5)_2TaH_3$ , may therefore be rationalized in terms of the occurrence of a vacant orbital on the metal atom, whereas all of the other hydrides of this type so far prepared have the three orbitals filled. Indeed, it might be argued that such polymerization would be favored since the 5s-4d-dp shell around the zirconium would be completed by the formation of a three-center Zr-H-Zr bond using the vacant hybrid orbital. This argument also suggests extensive polymerization would occur in the unreported  $(C_5H_5)_2YH$  derivative.

In summary, therefore, it would appear that if a metal tetrahydroborate or derivative has the tetrahydroborate group suitably bonded by bridging hydrogen atoms to the metal atom, then such species will react with ligands yielding eventually metal hydride compounds. Such a reaction offers an alternative and convenient route to hydride species which cannot be obtained by more conventional methods.

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