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A New Route for the Preparation of Transition-metal Hydride Derivatives

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WHILE several transition-metal hydride derivatives are known, no such compounds have been isolated for the Group IVA elements, although dimeric dicyclopentadienyltitanium(III) hydride has been reported¹ to occur as a reaction intermediate in ethereal solution. We have prepared the hydride derivatives $(\pi - C_5 H_5)_2 Zr(H) BH_4$, (I), and $[(\pi - C_5 H_5)_2 Zr H_2]_n$, (II), by the reaction of dicyclopentadienylzirconium diborohydride,2 $(\pi - C_5 H_5)_2 Zr(BH_4)_2$, with one or two moles of ligand molecules (e.g., trimethylamine) in benzene solution. The borane adduct, $H_3B \leftarrow L$, where L = ligand, is formed simultaneously. The diamagnetic hydride (I) is a white air-reactive solid which may be purified by sublimation in vacuo at 60°, and identified from its analysis, and its infrared (i.r.), (proton and ¹¹B) nuclear magnetic resonance and mass spectra. We have so far been unable to detect the single proton of the M-H bond in the n.m.r. spectrum, but its presence

is established both from the i.r. spectrum, giving a sharp band at 1945 cm. $^{-1}$ in addition to the bands associated with the borohydride group, and the mass spectrum which shows a cut-off at m/e = 236 corresponding to $(C_5H_5)_2^{90}Zr(H)^{11}BH_4^+$. The dihydride (II) precipitates as a white solid from benzene solution, and this affords a convenient method of isolation since the other product of reaction, $H_3B \leftarrow L$, remains in solution. The polymeric nature of (II) is suggested by its involatility, insolubility, and lack of reaction in air. The presence of a Zr-H-Zr bridging system may be inferred from the intense broad band at 1540 cm.⁻¹ in the i.r. spectrum. If the bonding scheme proposed by Ballhausen et al.3 for this class of compounds is accepted then the occurrence of hydrogen bridging in (II) may be due to the presence of a vacant orbital on the metal atom whereas in other similar derivatives (which are not polymeric) all the available orbitals are

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bonding of the borohydride group to the metal.

Thus the hafnium analogue, $(\pi - C_5 H_5)_2 Hf(BH_4)_2$,

and the metal borohydrides, $M(BH_4)_4$ where

M = Zr or Hf, react similarly producing hydride

species, but we have not yet been able to produce

hydrides from (π -C₅H₅)₂TiBH₄⁵ or (Ph₃P)₂CuBH₄⁶

suggesting that in these compounds the boro-

hydride group possesses considerably more ionic character, or possibly that the bonding is not as

it is usually represented, *i.e.*, through a double

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hydrogen bridge.

occupied, e.g., by hydrogen atoms $[(\pi - C_5H_5)_2TaH_3]$, or a lone pair of electrons $[(\pi - C_5 H_5)_2 Mo H_3]$. The empirical formulation of (II) is confirmed directly by analysis, and indirectly from the mode of preparation since the only other detectable product is $H_3B \leftarrow L$, two moles [per mole of (II)] being recovered.

The reaction illustrates the symmetrical cleavage

to that observed in other metal borohydrides,4 and offers a sensitive test of the nature of the

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