

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

By B. D. JAMES, R. K. NANDA, and M. G. H. WALLBRIDGE

(Department of Chemistry, The University, Sheffield)

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 $(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{H})\text{BH}_4$, (I), and $[(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2]_n$, (II), by the reaction of dicyclopentadienylzirconium diborohydride,² $(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{BH}_4)_2$, with one or two moles of ligand molecules (*e.g.*, trimethylamine) in benzene solution. The borane adduct, $\text{H}_3\text{B}\leftarrow\text{L}$, 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 $(\text{C}_5\text{H}_5)_2^{90}\text{Zr}(\text{H})^{11}\text{BH}_4^+$. 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, $\text{H}_3\text{B}\leftarrow\text{L}$, 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

occupied, *e.g.*, by hydrogen atoms $[(\pi\text{-C}_5\text{H}_5)_2\text{TaH}_3]$, or a lone pair of electrons $[(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2]$. The empirical formulation of (II) is confirmed directly by analysis, and indirectly from the mode of preparation since the only other detectable product is $\text{H}_3\text{B}\leftarrow\text{L}$, two moles [per mole of (II)] being recovered.

The reaction illustrates the symmetrical cleavage

of $\text{M} \begin{array}{c} \text{H} \\ \diagdown \quad \diagup \\ \text{B} \\ \diagup \quad \diagdown \\ \text{H} \end{array} \text{H}$ groups, where M = metal, similar to that observed in other metal borohydrides,⁴ and offers a sensitive test of the nature of the

bonding of the borohydride group to the metal. Thus the hafnium analogue, $(\pi\text{-C}_5\text{H}_5)_2\text{Hf}(\text{BH}_4)_2$, and the metal borohydrides, $\text{M}(\text{BH}_4)_4$ where M = Zr or Hf, react similarly producing hydride species, but we have not yet been able to produce hydrides from $(\pi\text{-C}_5\text{H}_5)_2\text{TiBH}_4$ ⁵ or $(\text{Ph}_3\text{P})_2\text{CuBH}_4$ ⁶ suggesting that in these compounds the borohydride group possesses considerably more ionic character, or possibly that the bonding is not as it is usually represented, *i.e.*, through a double hydrogen bridge.

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