CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY, SHEFFIELD, ENGLAND

Dicyclopentadienylzirconium Diborohydride

BY R. K. NANDA AND M. G. H. WALLBRIDGE

Received June 29, 1964

The only reported examples of compounds in which both organic and borohydride groups are bonded to a transition metal are dicyclopentadienyltitanium(III) borohydride[1] and dicyclopentadienylniobium chloroborohydride,[2] $(\pi\text{-}C_5H_5)_2Nb(Cl)BH_4$. We have now prepared the title compound, $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$ (I), and for many studies it would appear to be more suitable than the titanium compound in that it is diamagnetic, not susceptible to oxidation, and only slowly hydrolyzed by moisture. The borohydride I may be prepared smoothly by stirring dicyclopentadienylzirconium dichloride (2.5 mmoles), prepared as described earlier,[3] with lithium borohydride (9.2 mmoles) for 8 hr. in ether under dry nitrogen. After filtering off the resulting lithium chloride, I is recovered from the filtrate as a white solid and can be purified by sublimation *in vacuo* at 110–115° to yield a very pale yellow solid, m.p. 155° dec. The solid was handled subsequently in a drybox. One atom of hydrogen is recoverable from each borohydride group, and is evolved as hydrogen, on treatment of I with trimethylamine hydrochloride in benzene at room temperature. *Anal.* Calcd. for $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$: C, 47.8; H, 7.21; Zr, 36.3; H (from $N(CH_3)_3$-HCl), 0.803. Found: C, 48.1; H, 7.13; Zr, 36.2; H, 0.786. If only a twofold molar excess of lithium borohydride is used in the preparation, then the chloroborohydride, $(\pi\text{-}C_5H_5)_2ZrCl(BH_4)$, is obtained, and it may be purified in the same way as the diborohydride.

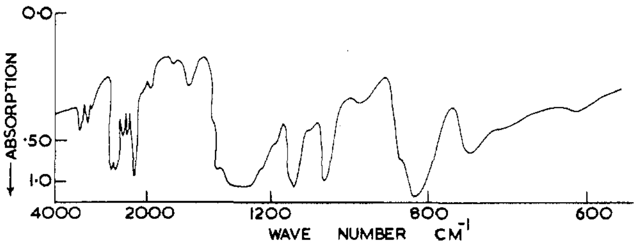

Fig. 1.—Infrared spectrum of $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$.

The infrared spectrum of I (Fig. 1) recorded over the range 4000–375 cm.$^{-1}$ (KBr disk) showed strong similarities to the specta of both other cyclopentadienyl derivatives of the transition metals[4] and typical covalent borohydrides, *e.g.*, aluminum borohydride,[5] with bands at (cm.$^{-1}$) 3109 m, 3095 sh, 2954 sh, 2929 m, 2857 w, 2440 s, 2386 s, 2296 m, 2225 m, 2149 s, 1965 w, 1785 vw, 1635 w, 1483 sh, 1447 sh, 1440–1290 vs (broad), 1240 sh, 1192 sh, 1132 sh, 1123 vs, 1075 w, 1025 vs, 940 w, 850 sh, 828 vs, 740 m, 690 sh, 613 w. Except for very small shifts in the bands at 2440, 2386, 2149, 1123, and 940 cm.$^{-1}$ and better resolution of the broad band at 1440–1290 cm.$^{-1}$ (into bands at 1303 s, 1370 m, 1400 sh, and 1447 m cm.$^{-1}$), the spectrum of I in benzene is similar considering the concomitant strong bands due to the solvent and the subsequent weak absorptions in these regions on compensation. We interpret these results as indicating that the bonding of the borohydride group is analogous to that postulated for other metal borohydrides.[5] It appears, therefore, to differ from the titanium compound, where it has been suggested, on the basis of the infrared spectrum, that a Ti–H bond and a coordinated BH_3 group are involved. While the presence of a Zr–H bond cannot be completely eliminated (although the weak and rather broad band at 1965 cm.$^{-1}$ does not have the usual characteristics of such a frequency, and the band at 2149 cm.$^{-1}$, together with the corresponding broad band at about 1400 cm.$^{-1}$, is very similar to that found in other borohydride compounds), the spectrum does indicate a significant difference from the titanium compound. Further, some asymmetry in the cyclopentadiene ligands is implied in view of the splitting in the spectrum of the C–H stretching frequency and other bands associated with the cyclopentadienyl groups. Such a conclusion is not unreasonable in view of the asymmetry recently reported for other compounds (in the crystalline phase), where a cyclopentadienyl group is bonded to a transition metal.[6] However, more information on similar systems is desirable before definite conclusions can be made.

Acknowledgments.—We thank the Commonwealth Scholarship Commission for a Scholarship (R. K. N.) and Miss M. A. KcKinnon for assistance with the analysis.

---

(1) R. Nöth and R. Hartwimmer, *Ber.*, **93**, 2238 (1960).

(2) R. B. King, *Z. Naturforsch.*, **18b**, 157 (1963).

(3) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **76**, 4281 (1954).

(4) E. R. Lippincott and R. D. Nelson, *ibid.*, **77**, 4990 (1955).

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

(6) M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason, *Nature*, **201**, 1318 (1964).

CONTRIBUTION FROM CALLERY CHEMICAL COMPANY,
CALLERY, PENNSYLVANIA

Synthesis of Tetramethylammonium Superoxide

BY A. D. MCELROY AND J. S. HASHMAN

Received July 24, 1964

Known or reported superoxides are almost without exception derivatives of the alkali and alkaline earth metals. Of those reported, only the superoxides of sodium and the heavier alkali metals are both available in high purity and stable at ambient or higher temperatures.