Contribution from the Department of Chemistry,
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Dicyclopentadienylzirconium Diborohydride

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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.

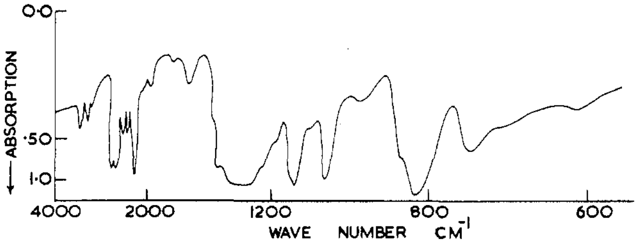

Fig. 1.—Infrared spectrum of $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$.

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.

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Contribution from Callery Chemical Company,
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Synthesis of Tetramethylammonium Superoxide

By A. D. McElroy and J. S. Hashman

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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.

Ammonium behaves chemically as an alkali metal, and the ammonium ion compares in size with alkali metal ions. Alkyl derivatives such as tetramethylammonium are similarly alkali metal-like, and the cations are generally more resistant to degradation than the ammonium ion. Stability was therefore predicted for tetraalkylammonium superoxides, and the results described below verify this prediction.

First attempts to prepare tetramethylammonium superoxide involved electrolyses of liquid ammonia solutions of tetramethylammonium chloride between a magnesium anode and an oxygen–platinum cathode. The expected electrode reactions were

$$\mathrm{Mg} + 2\mathrm{Cl}^- \longrightarrow \mathrm{MgCl_2} + 2\mathrm{e}^-$$

$$\mathrm{(CH_3)_4N^+} + \mathrm{e}^- + \mathrm{O_2} \longrightarrow \mathrm{(CH_3)_4NO_2}$$

Data obtained from a limited study indicated that these reactions did occur. Insoluble magnesium chloride was formed, and the ammonia solution became yellow during electrolysis. Evaporation of solvent yielded a residue containing superoxide oxygen. The studies indicated, however, that the superoxide ion was subject to cathodic reduction, possibly to peroxide, and yields of superoxide were as a consequence low. In any event this method was unsuitable for preparation of macro quantities of product.

Two methods were found suitable for production of tetramethylammonium superoxide in macro quantities. Potassium superoxide reacted in ammonia with tetramethylammonium fluoride, giving insoluble potassium fluoride and soluble tetramethylammonium superoxide. The solid extract was only about 70–80% pure, based on active oxygen content, with tetramethylammonium fluoride being the chief contaminant. Reaction of tetramethylammonium hydroxide pentahydrate with excess potassium superoxide yielded a product separable in high purity. The pentahydrate and potassium superoxide were tumbled under vacuum in a Rinco evaporator at room temperature for 3–4 days. The solid–solid reaction yielded potassium hydroxide, oxygen, and tetramethylammonium superoxide in accordance with the equation

$$11\mathrm{KO_2} + \mathrm{(CH_3)_4NOH\cdot 5H_2O} \longrightarrow \mathrm{(CH_3)_4NO_2} + 11\mathrm{KOH} + {}^{15}/{}_{2}\mathrm{O_2}$$

Rapid extractions with liquid ammonia (200 ml. of ammonia, $-33°$, 70 g. crude) gave 35–40% yields (based on $\mathrm{(CH_3)_4N^+}$) of pure tetramethylammonium superoxide. Exhaustive extractions resulted in 90% yields of 85–90% pure products. Analytical data of a high purity product [C, 44.5; H, 11.4; N, 13.0; $\mathrm{O_2}$ by acetic acid–diethyl phthalate[1] hydrolysis, 106 cc./g.; $\mathrm{O_2}$ by water–manganese dioxide hydrolysis, 158 cc./g.] compare favorably with theoretical values [C, 45.3; H, 11.4; N, 13.2; $\mathrm{O_2}$ by acetic acid–diethyl phthalate hydrolysis, 105 cc./g.; $\mathrm{O_2}$ by water–manganese dioxide hydrolysis, 157.5 cc./g.].

Good yields of tetramethylammonium superoxide were obtained only when potassium superoxide was charged in quantities equal to or in excess of that required by the above equation. The excess potassium superoxide converts water of hydration to hydroxide, which is unreactive with superoxide and insoluble in liquid ammonia.

Tetramethylammonium superoxide is a pale yellow crystalline solid. Its X-ray powder diffraction pattern indicates the absence of likely impurities. The density, as determined by displacement of *n*-decane, is 1.11 g./cc. The compound is quite hygroscopic and dissolves readily in water with evolution of oxygen. It melts sharply at 97° and decomposes at about 100°. It dissolves readily in ammonia and is qualitatively quite soluble; no quantitative solubility data are available.

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Iodyl Fluorosulfate

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Only a few inorganic compounds are known which contain the $\mathrm{IO_2}$ group. Muir[1] prepared an addition compound, $\mathrm{I_2O_5\cdot 2SO_3}$, which was later formulated as $\mathrm{(IO_2)_2S_2O_7}$[2] and presumed to contain the cation $\mathrm{IO_2^+}$. However, recent work of Gillespie and Senior[3] on solutions of $\mathrm{HIO_3}$ in $\mathrm{H_2SO_4}$ gave no evidence for $\mathrm{IO_2^+}$ cations. Conductometric and cryoscopic measurements indicated that $\mathrm{IO_2HSO_4}$ was present in a solvated and polymeric form. Iodyl fluoride[4,5] has been reported[6] not to combine with sulfur trioxide to form iodyl fluorosulfate.

Peroxydisulfuryl difluoride,[7] a substance known to be a good reagent for preparing fluorosulfates,[8,9] has now been used to prepare iodyl fluorosulfate from iodine pentoxide. The iodine pentoxide was first dried at 150°, pulverized, and placed in a flat-bottom reaction flask containing a Teflon-coated stirring bar. The flask had a side arm ending at a break-seal and a neck ending at a ground joint by which it could be attached to a vacuum

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