shown by Pople, *et al.*[12] The slope of the Arrhenius plot (Fig. 3-B) gave $\Delta E = 8.6 \pm 1.5$ kcal. In this case, where the rate of exchange of borons between two environments is being observed, the observed and model[12] spectra are more easily correlated than in the case of diborane proton exchange, and the accuracy of the resulting activation energy is thus somewhat higher. The dissociation energy for gaseous diborane has been estimated to be 28.4 kcal.,[15] which corresponds to 14.2 kcal. for a single BHB bridge bond. The somewhat lower value obtained for the diborohydride ion–borohydride ion exchange suggests that the mechanism of exchange probably involves dissociation of the diborohydride ion into borane and borohydride ion, rather than direct exchange between the two negative ions.

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CONTRIBUTION NO. 1095 FROM THE DEPARTMENT OF CHEMISTRY,
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Convenient Preparations of Solutions Containing the Triborohydride Ion[1,2]

BY DONALD F. GAINES, RILEY SCHAEFFER, AND FRED TEBBE

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The triborohydride ion has been conveniently prepared either by hydroboration of the alkali metal addition compounds of naphthalene or triphenylboron with diborane in ether solutions, or by reaction of metal borohydrides with diborane in ether solutions at 100°. The diborane necessary in the second case may be easily prepared *in situ* by using a deficiency of boron trifluoride etherate in the conventional diborane preparation from borohydrides. Triborohydride ion may be isolated in high yield by conversion to the tetramethylammonium salt.

Relatively few studies of the chemistry of the triborohydride ion have been reported, at least in part as a result of the fact that no convenient synthesis of the material was available. Nevertheless, the material promised to be of considerable synthetic use if a relatively simple preparation could be developed. Triborohydride salts previously have been prepared from sodium amalgam and diborane[3] or pentaborane-11[4] and tetraborane and sodium hydride,[5] sodium borohydride,[6] sodium amalgam,[6] or ammonia,[7] and by the stepwise degradation of decaborane.[8] The long period required for the diborane–sodium amalgam reaction, even in the presence of solvent, and the instability and/or expense of the higher boron hydrides have made the isolation of large quantities of such salts impractical.

Preliminary studies carried out in these Laboratories some years ago suggested that the rate of reaction of diborane with sodium might be greatly enhanced by the presence of a sodium carrier. Other studies, with little success, concentrated on formal extraction of a proton from diborane *via* the postulated triborane-9 to produce the desired salts. Both types of reaction have now been demonstrated to be useful (although the mechanism of formation from diborane is unknown) and the second approach promises to make triborohydride ion in solution (and certain suitable derivatives) readily available laboratory reagents.

Tetrahydrofuran solutions of the alkali metal addition compounds of triphenylboron or naphthalene are deeply colored, but reaction to discharge the color occurs within a few seconds on addition of an equivalent amount of diborane, presumably according to the equation

$$2\ \text{M-carrier} + 2\text{B}_2\text{H}_6 \longrightarrow \text{MBH}_4 + \text{MB}_3\text{H}_8 + \text{carrier}$$

The resulting pale yellow or brown solutions contain the liberated triphenylboron or naphthalene and suspended metal borohydride and reasonable yields of tetramethylammonium triborohydride could be recovered following addition of tetramethylammonium hydroxide. The rapidity of this reaction compared with the 2-day diborane–sodium amalgam reaction suggests that the rate of formation of the triborohydride is primarily dependent upon the efficiency with which the alkali metal can be supplied to the diborane or intermediate species. The triborohydride salts were converted to the tetramethylammonium derivative since other salts are difficult to recover free of yellow impurities formed during the reactions and strongly retained solvent.

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(1) Interconversion of Boranes. VI. For part V see R. Schaeffer and F. Tebbe, *J. Am. Chem. Soc.*, **84**, 3974 (1962).

(2) The commonly used borohydride (BH_4^-), triborohydride (B_3H_8^-) nomenclature is employed rather than the American "hydroborate," "octahydrotriborate" recommendation in the Preliminary Report of the Advisory Committee on the Nomenclature of Organic Boron Compounds.

(3) W. V. Hough, L. J. Edwards, and A. D. McElroy, *J. Am. Chem. Soc.*, **80**, 1828 (1958).

(4) M. D. Ford, W. V. Hough, and L. J. Edwards, U. S. At. Energy Comm., *Nucl. Sci. Abstr.*, **11**, Abstr. No. 6233 (1957).

(5) R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

(6) W. V. Hough and L. J. Edwards in "Borax to Boranes," Advances in Chemistry Series, No. 32, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1961, pp. 189–190.

(7) G. Kodama and R. W. Parry, *J. Am. Chem. Soc.*, **82**, 6250 (1960).

(8) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *ibid.*, **83**, 2669 (1961).

Triborohydrides can be still more conveniently prepared by the novel reaction of diborane with metal borohydrides in suitable ethers, presumably according to the equation

$$B_2H_6 + MBH_4 \xrightarrow[100°]{\text{ethers}} MB_3H_8 + H_2$$

The required diborane can be easily generated *in situ* by reaction of boron trifluoride etherate and the metal borohydride. The over-all reaction is then

$$4BF_3 + 5MBH_4 \longrightarrow 3MBF_4 + 2MB_3H_8 + 2H_2$$

Preliminary experiments were carried out in sealed n.m.r. tubes so that the ^{11}B spectra could be used to follow the reactions. It was found that the reaction usually was complete after about 45 min. at 100°. When excess borohydride was present, no decomposition products were observed and the reaction appeared to be quantitative since no solids were precipitated and there were no extraneous peaks in the ^{11}B spectrum. The ^{11}B spectra showed that after 45 min. at 100° the only boron-containing substances were triborohydride ion and the reagent in excess for a variety of systems including diborane and: (1) potassium borohydride in ethylene glycol dimethyl ether (121), (2) sodium borohydride in either 121 or the dimethyl ether of diethylene glycol (141); and (3) lithium borohydride in diethyl ether. Sodium borohydride in diethyl ether did not lead to triborohydride formation even in the presence of lithium chloride, although it is possible that further study might uncover suitable conditions for this reaction. The only apparent requirement for the reaction is that both the diborane and the metal borohydride have some reasonable solubility in the solvent. In preparative scale experiments the glycol ethers proved very difficult, if not impossible, to separate from sodium triborohydride, so that it was most convenient to form the insoluble tetramethylammonium triborohydride[8] when isolation of solvent-free material was desired.

Experimental

The dimethyl ethers of ethylene glycol and diethylene glycol (Ansul Ethers 121 and 141) and tetrahydrofuran (Baker, reagent grade) were distilled from lithium aluminum hydride. Trimethylammonium tetraphenylborate was prepared from sodium tetraphenylborate (Baker, reagent grade) and was pyrolyzed in the reaction vessel to produce triphenylboron.[9] Sodium and potassium borohydrides (Metal Hydrides) and naphthalene (Schaar, technical grade) were used as supplied. Unless otherwise indicated, diborane was prepared by the reaction of sodium borohydride with polyphosphoric acid.[10]

Sodium and Diborane.—Triphenylboron in tetrahydrofuran solution was stirred under vacuum with sodium amalgam (6.2 g. of Na/ml. of Hg) to give a dark green or blue solution. After diborane addition the stirred solution quickly turned pale yellow at the reaction temperature, somewhat below 0°. Presence of sodium triborohydride in the filtered solution was shown by the ^{11}B n.m.r. spectrum.

A solution of 3.87 mmoles (0.496 g.) of naphthalene in about 10 ml. of THF was shaken under vacuum with 4.44 mmoles (0.102 g.) of sodium until the metal dissolved to give a homogeneous green solution. Diborane, 4.10 mmoles, was absorbed rapidly to produce a yellow solution which was filtered to remove sodium borohydride and treated with 4.4 mmoles (4 ml.) of a 10% aqueous solution of tetramethylammonium hydroxide. On addition of 50 ml. of anhydrous diethyl ether a white precipitate formed, which was filtered and washed in air with additional ether. The dried product, 0.96 mmole (0.11 g., 47% yield), was identified as tetramethylammonium triborohydride by the infrared spectrum. In larger preparations diborane, generated in molar quantities by the addition of boron trifluoride etherate to potassium borohydride,[11] was passed into tetrahydrofuran solutions of potassium– or sodium–potassium–naphthalene to produce the triborohydride ion using a normal hydroboration apparatus.[12] Satisfactory separation of products could no doubt be achieved but development did not appear desirable at the present time in view of the simpler system described below.

Sodium Borohydride and Diborane.—In a typical preparative scale reaction a reaction tube of 380 ml. volume (equipped with a constriction for sealing and a break-tip for opening) was flushed with nitrogen and charged with 1.49 g. (39.5 mmoles) of sodium borohydride and 15 ml. of 141. The tube and contents were cooled to −196° and 3.2 ml. (26 mmoles) of boron trifluoride etherate cooled to 0° was carefully added so that it formed a frozen ring above the other reactants. The tube then was evacuated, sealed, and slowly warmed to room temperature. The reaction tube was mounted horizontally and rotated for 2 hr. in a steam oven and an additional 6 hr. at room temperature. The tube again was cooled to −196° and opened into the vacuum line. A considerable hydrogen pressure was present but no diborane could be recovered.

The contents of the flask were filtered in air to remove sodium tetrafluoroborate and washed with several portions of ether. Thirty-five ml. (38 mmoles) of a 10% aqueous solution of tetramethylammonium hydroxide was added to the filtrate. Tetramethylammonium triborohydride precipitated and was filtered and washed with ether. The crude yield was 0.937 g. or 63% of theoretical based on boron trifluoride etherate used. The product was recrystallized from hot methanol.

The ^{11}B n.m.r. spectrum (obtained with a Varian Model 4300B high resolution spectrometer at 19.3 Mc.) of a dimethylformamide solution of tetramethylammonium triborohydride consisted of a symmetrical septet with $J = 33$ c.p.s. and $\delta = 29.8 \pm 0.5$ p.p.m. ($BF_3O(C_2H_5)_2 = 0$). These values are identical with those obtained for sodium triborohydride prepared in this Laboratory and are in reasonable agreement with the literature.[8,13]

The infrared spectrum of tetramethylammonium triborohydride in a potassium bromide pellet contains the prominent bands, 3.30 (m-sh), 3.38 (w-sh), 4.08 (s-b), 4.17 (s-b), 4.22 (sh), 4.31 (sh), 4.70 (m), 4.80 (m), 6.74 (s), 7.08 (m), 7.88 (w), 8.80 (s), 9.90 (s), and 10.55 (s)μ, in agreement with the less complete previously published spectrum.[8]

Discussion

Little evidence can be given at this stage to support a postulated mechanism for the reaction of diborane with borohydride ion to give triborohydride. The rationale behind the attempt, however, was that the triborohydride salts seemed to be salts of a relatively strong acid (from their behavior in aqueous solution) and that a logical preparation might be based on removal, by a suitable base, of a proton from the postulated but unob-

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(9) G. Wittig and P. Raff, *Ann. Chem.*, **573**, 195 (1951).

(10) R. O. Buttlar, Ph.D. thesis, Indiana University, 1962.

(11) (a) R. K. Pearson, L. L. Lewis, and L. J. Edwards, U. S. At. Energy Comm., *Nucl. Sci. Abstr.*, **12**, Abstr. No. 4069 (1958); (b) R. M. Adams in "Borax to Boranes," Advances in Chemistry Series, No. 32, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1961, pp. 60–68.

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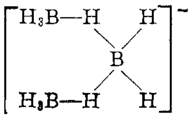
(13) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *ibid.*, **81**, 4496 (1959).

served triborane-9.[14] The borohydride ion reacts readily with strong acids (often with the acid only in the gas phase) to give a sodium salt and additional diborane. It therefore is uniquely non-interfering in the present reaction.

Another mechanism involves formation of diborohydride-7 ion followed by addition of a second borane to form the intermediate



which could lose hydrogen and form triborohydride ion directly.

Still a third possible mechanism which appears less probable involves formation of the diborohydride-7 ion, loss of hydrogen to form a diborohydride-5 ion, and addition of a borane group to give the observed product. Since reaction occurs readily between diborane and lithium borohydride in diethyl ether (a solvent in which diborohydride-7 apparently has low stability since it has not been detected), the third pathway seems less likely. A similar objection applies to the second mechanism. Further studies may well allow one to determine the correct mechanism.

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[14] R. E. Enrione and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **18**, 103 (1961).

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Organometallic Chemistry of the Transition Metals. III. Reactions between Sodium Cyclopentadienide and Certain Complex Transition Metal Halides[1]

BY R. B. KING[2]

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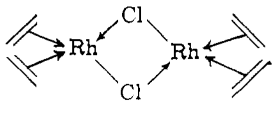
Reaction between $[(C_2H_4)_2RhCl]_2$ and sodium cyclopentadienide in tetrahydrofuran yields the novel ethylene complex $C_5H_5Rh(C_2H_4)_2$ as a yellow, volatile, crystalline solid. On the basis of n.m.r. data a novel structure is proposed for the complex $C_5H_5NiC_{13}H_{17}$ first reported by Criegee and Ludwig.[3] The orange volatile solid $C_{10}H_{12}OCH_3PdC_5H_5$ has been prepared from sodium cyclopentadienide and the palladium complex $[C_{10}H_{12}OCH_3PdCl]_2$ obtained from sodium tetrachloropalladate(II), dicyclopentadiene, and methanol.

Novel cyclopentadienyl derivatives of rhodium have been synthesized by the reaction between sodium cyclopentadienide and certain complex halides of rhodium. Thus sodium cyclopentadienide was found to react with the 1,5-cyclooctadiene complex $[C_8H_{12}RhCl]_2$ to give $C_5H_5RhC_8H_{12}$[4] and with the carbonyl halide $[(CO)_2RhCl]_2$ to give $C_5H_5Rh(CO)_2$.[5]

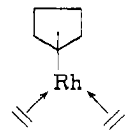
Recently the dimeric ethylene complex of rhodium of formula $[(C_2H_4)_2RhCl]_2$ (I) was described.[6] It seemed possible that this dimeric ethylene complex might react with sodium cyclopentadienide to form the monomeric ethylene complex $C_5H_5Rh(C_2H_4)_2$ analogous to the compounds $C_5H_5RhC_8H_{12}$ and $C_5H_5Rh(CO)_2$ mentioned above.

Reaction between I and sodium cyclopentadienide in tetrahydrofuran at 25 to 65° gave a mixture from which yellow crystals of the expected composition $C_5H_5Rh(C_2H_4)_2$ could be isolated by solvent removal followed by sublimation at 60° (0.1 mm.).

Cyclopentadienyldiethylene-rhodium is a yellow, volatile, air-stable solid soluble in organic solvents to give yellow solutions. The monomeric formulation is consistent with its high volatility and with isopiestic molecular weight determinations in dichloromethane. Indeed, $C_5H_5Rh(C_2H_4)_2$ appears to be the only known complex with two ethylenes bonded to a single metal atom which can be efficiently purified by vacuum sublimation. It is believed to have structure II, which is entirely analogous to the structure proposed for $C_5H_5RhC_8H_{12}$[4] but with two molecules of the monoölefin ethylene replacing one molecule of the chelating diolefin 1,5-cyclooctadiene.



I



II

The proton n.m.r. spectrum of $C_5H_5Rh(C_2H_4)_2$ shows a sharp peak at 5.08 p.p.m. due to the five cyclopentadienyl protons and two broad resonances at 2.75 and 1.00 p.p.m. due to the eight protons of the two ethylene

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[1] For Part II see R. B. King, *Z. Naturforsch.*, **18b**, 157 (1963).
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[3] R. Criegee and P. Ludwig, *Ber.*, **94**, 2038 (1961).
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[6] R. D. Cramer, *Inorg. Chem.*, **1**, 722 (1962).