tro enantiomer decayed to zero degrees with a half-life of one hour at 23°, which is the same half-life observed for the *levo* isomer. The lower specific rotation of the *dextro* isomer is due to the presence of some *levo* isomer in a relatively large quantity of *dextro* isomer.

Resolution of the complex cation D,L-$[Si(acac)_3]^+$ into its optical enantiomers indicates that the silicon(IV) is six-coördinate in this complex, and that the cation is octahedral. The possibility of seven-coördination (coördination by the chloride ion) is remote in view of the conductivity of the complex in anhydrous chloroform solution. Additional details of the resolution of this and other six-coördinate silicon(IV) complexes will appear in a forthcoming publication.

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DEPARTMENT OF CHEMISTRY S. K. DHAR
WAYNE STATE UNIVERSITY VERA DORON
DETROIT 2, MICHIGAN STANLEY KIRSCHNER

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DEUTERIUM EXCHANGE OF DECABORANE WITH DEUTERIUM OXIDE AND DEUTERIUM CHLORIDE

Sir:

We wish to report the results of a series of deuterium exchange experiments which illustrate the exchange of as many as eight hydrogen atoms of decaborane by deuterium and which further illustrate either the existence of two types of exchangeable hydrogens (bridge or terminal) or the dioxane catalyzed migration of bridge deuterium to terminal positions.

TABLE I

RESULTS OF D_2O–$B_{10}H_{14}$ EXCHANGE EXPERIMENTS IN DIOXANE SOLUTION AT ROOM TEMPERATURE

Equilibration time, hr.	Initial concn., mole/l. $B_{10}H_{14}$	D_2O	B–D infrared absorption	Deuterium/ mole
0.15	0.083	3.10	Bridge + extremely weak terminal	2.3
0.15	0.167	6.20	Bridge + very weak terminal	4.6
2.00	0.167	6.20	Bridge + weak terminal	5.2
36.0	0.083	3.10	Bridge + moderate terminal	6.2
72.0	0.120	1.55	Bridge + strong terminal	7.5

TABLE II

EXCHANGE OF $B_{10}H_{14}$ WITH DCl

Solvent	Exchange time, hr.	Initial quantities, moles DCl	$B_{10}H_{14}$	B–D infrared absorption	Deuterium/ mole
Dioxane	114	0.036	0.0024	Bridge + strong terminal	6.2
Dioxane	96	.032	.0016	Bridge + strong terminal	5.9
Methylene chloride	93	.0384	.0024	Identical with $B_{10}H_{14}$	0

Perdeuterodecaborane was prepared by the pyrolysis (100°) of perdeuterodiborane. This material gave B–D stretching absorptions in the infrared at 5.25 μ (terminal-d_{10}) and 7.30 μ (bridge-d_4). The latter absorption is characterized by a broad band and weak intensity. With normal decaborane the corresponding absorptions are found at 3.8 and 5.25 μ, respectively. All spectra were determined in carbon disulfide solution.

Partially deuterated samples of decaborane (prepared as described below) were sublimed, weighed and analyzed for hydrogen and deuterium by the quantitative pyrolytic decomposition of this material to boron and hydrogen–deuterium at 900° followed by mass spectrometric measurements of the H/D ratio.

Table I sets forth the infrared absorptions and deuterium analyses of several samples of decaborane which were equilibrated with deuterium oxide in dioxane solution for varying periods of time at room temperature.

As seen in Table I the first detectable deuterium which enters the decaborane molecule enters the bridge positions but longer equilibration times produce appreciable exchange at terminal positions. Furthermore the equilibration of a sample of $B_{10}H_{10}D_4$ (bridge-d_4) in pure dioxane produces after one day at room temperature appreciable amounts of absorption at 5.25 μ as a sharp band characteristic of terminal B–D bonds. Similar rearrangement of deuterium in $B_{10}H_{10}D_4$ (bridge-d_4) decaborane does not occur in methylene chloride solution under identical conditions of time and temperature.

Table II presents the results of three exchange experiments carried out with decaborane and deuterium chloride in sealed bulbs at room temperature. It is to be noted that methylene chloride solvent does not produce exchange.

These results clearly point to the fact that the four bridge hydrogens of decaborane are rapidly removed by bases (water, dioxane, etc.) and are easily replaced by acids (hydronium ion, hydrogen chloride, etc.). Furthermore, less rapid but appreciable exchange involving terminal positions appears to occur only in the presence of basic solvents such as dioxane or diethyl ether by what may be a base-catalyzed internal rearrangement of bridge deuterium to terminal positions or a base-catalyzed process involving another type of $B_{10}H_{13}^-$ anion formed by direct removal of a terminal proton. That this latter terminal hydrogen exchange process is not as rapid as bridge exchange is apparent from the above results.

REDSTONE ARSENAL RESEARCH
DIV. OF ROHM AND HAAS CO. M. FREDERICK HAWTHORNE
HUNTSVILLE, ALABAMA JOHN J. MILLER

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