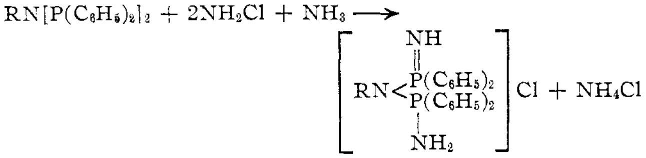
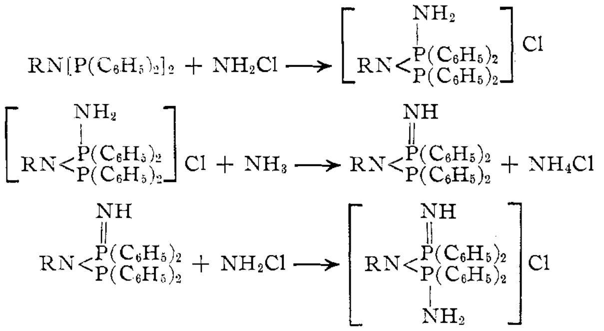
in the phosphonium salts relative to the starting material. This change in the chemical shift value is evidence that the environment of the phosphorus atom has changed considerably. If the chloramine had attacked the nitrogen atoms, the change in chemical shift values would probably have been small. Further, the infrared spectra of the chloramination products which contain P–phenyl bonds all exhibit the strong peak at about 1120 cm.$^{-1}$ which has been assigned to a tetracoordinate phosphorus atom having a P–phenyl bond.[1]

Analytical, n.m.r., and infrared data show clearly that the chloramination of compounds of the type $RN[P(C_6H_5)_2]_2$ results in the combination of the bisphosphinoamine with 2 moles of chloramine in accordance with the equation



$$RN[P(C_6H_5)_2]_2 + 2NH_2Cl + NH_3 \longrightarrow \left[RN{<}\begin{matrix}\overset{\overset{NH}{\|}}{P(C_6H_5)_2}\\ \underset{\underset{NH_2}{|}}{P(C_6H_5)_2}\end{matrix} \right] Cl + NH_4Cl$$

A reasonable rationalization of this result would involve the assumption that the initial monochloramination product undergoes dehydrohalogenation and thus remains in solution and available for the second chloramination step.



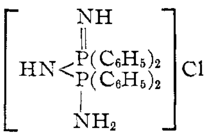
$$RN[P(C_6H_5)_2]_2 + NH_2Cl \longrightarrow \left[RN{<}\begin{matrix}\overset{\overset{NH_2}{|}}{P(C_6H_5)_2}\\ P(C_6H_5)_2\end{matrix} \right] Cl$$

$$\left[RN{<}\begin{matrix}\overset{\overset{NH_2}{|}}{P(C_6H_5)_2}\\ P(C_6H_5)_2\end{matrix} \right] Cl + NH_3 \longrightarrow RN{<}\begin{matrix}\overset{\overset{NH}{\|}}{P(C_6H_5)_2}\\ P(C_6H_5)_2\end{matrix} + NH_4Cl$$

$$RN{<}\begin{matrix}\overset{\overset{NH}{\|}}{P(C_6H_5)_2}\\ P(C_6H_5)_2\end{matrix} + NH_2Cl \longrightarrow \left[RN{<}\begin{matrix}\overset{\overset{NH}{\|}}{P(C_6H_5)_2}\\ \underset{\underset{NH_2}{|}}{P(C_6H_5)_2}\end{matrix} \right] Cl$$

This scheme is analogous to that previously postulated by our laboratory for the chloramination of 1,1-bisdiphenylphosphino-2,2-dimethylhydrazine, $[(C_6H_5)_2P]_2NN(CH_3)_2$.[2]

In the case of the compound $HN[P(C_6H_5)_2]_2$ the chloramination product obtainable according to this reaction scheme, *viz.*



$$\left[HN{<}\begin{matrix}\overset{\overset{NH}{\|}}{P(C_6H_5)_2}\\ \underset{\underset{NH_2}{|}}{P(C_6H_5)_2}\end{matrix} \right] Cl$$

is a tautomer of the previously prepared compound $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$[4] and would be expected to rearrange to yield that compound. Analytical, infrared, and n.m.r. data show that this is indeed the case and provide further evidence of the preference of the chloramine molecule for attack on the phosphorus rather than the nitrogen atom.

Acknowledgments.—The authors are pleased to acknowledge the support of much of this work by a grant from the Petroleum Research Fund administered by the American Chemical Society. We also wish to express our appreciation to Professor Wallace S. Brey, Jr., for his assistance in obtaining and interpreting the nuclear magnetic resonance data included in this paper.

CONTRIBUTION NO. 1291 FROM THE DEPARTMENT OF CHEMISTRY,
INDIANA UNIVERSITY, BLOOMINGTON, INDIANA

Synthesis of a New Deuterium-Labeled Tetraborane, μ-Deuteriotetraborane-10[1]

BY ARLAN D. NORMAN AND RILEY SCHAEFFER

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Isotopically labeled boranes are convenient compounds for studies of interconversion and other reaction mechanisms of boron hydrides; however, only two reports of specifically labeled tetraboranes have appeared. Schaeffer and Tebbe reported a reaction in which labeling of either the boron atom or the hydrogen atoms at the 2 position[2] could be effected.[3] Koski and co-workers have also presented some evidence for 1,3-dideuteriotetraborane-10 obtained during exchange reactions between tetraborane-10 and deuterated diborane.[4,5] Recently, by substituting deuterium oxide for water in the pentaborane-11 water reaction described by Boone and Burg,[6] we have prepared the first monodeuterium labeled tetraborane, μ-deuteriotetraborane-10.

Experimental

Preparation of Starting Materials.—All operations and manipulations performed in these investigations involve standard high-vacuum techniques described elsewhere.[7,8]

Pentaborane-11 used in these preparations was obtained by the pyrolysis of diborane in a hot–cold reactor in which the hot and cold surfaces were maintained at 155 ± 5° and −80°, respectively.[9] Carrying out the pyrolysis at a pressure of approximately 1 atm. for a 6- or 7-hr. period resulted in conversion of 30 to 40% of the diborane to tetraborane-10 and pentaborane-11. Final purification of pentaborane-11 was carried out by repeated fractionation at −98 to −101° using a low-temperature fractional distillation column.[10] Pentaborane-11 was obtained in 70 to 75% yield based on the amount of diborane converted.

Deuterium oxide (isotopic purity stated at >99.8%) obtained from the Atomic Energy Commission was used without further purification.

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(1) Studies of Boranes. XVIII. For paper XVII of this series see P. C. Keller, D. MacLean, and R. Schaeffer, *Chem. Commun.* (London), in press. Correspondence regarding this paper should be addressed to R. Schaeffer.

(2) The numbering system is that recommended for boron compounds by the Preliminary Report of the Advisory Committee on the Nomenclature of Organic Boron Compounds, available through *Chemical Abstracts.*

(3) R. Schaeffer and F. N. Tebbe, *J. Am. Chem. Soc.*, **84**, 3974 (1962); F. N. Tebbe, Ph.D. Thesis, Indiana University, 1963.

(4) J. E. Todd and W. S. Koski, *J. Am. Chem. Soc.*, **81**, 2319 (1959).

(5) T. P. Fehlner and W. S. Koski, *ibid.*, **85**, 1905 (1963).

(6) J. L. Boone and A. B. Burg, *ibid.*, **80**, 1519 (1958).

(7) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(8) R. T. Sanderson, "High Vacuum Manipulations of Volatile Compounds," John Wiley and Sons Inc., New York, N. Y., 1948.

(9) M. J. Klein, B. C. Harrison, and I. J. Solomon, *J. Am. Chem. Soc.*, **80**, 4149 (1958).

(10) J. Dobson and R. Schaeffer, "Studies of Boron–Nitrogen Compounds, X" to be published elsewhere.

μ-Deuteriotetraborane-10.—In a typical reaction 2.52 mmoles of pentaborane-11 and 4.0 ml. of deuterium oxide were allowed to react for 2 min. at 0° in a sealed tube. At the end of this time the reaction was quenched to −196° and noncondensable gases were removed. The product was crudely separated from deuterium oxide by passage through a −80° trap and finally purified by low-temperature fractional distillation. Pure μ-deuteriotetraborane-10 was collected from the column at −117 to −120°. In order to minimize unwanted scrambling of the deuterium atom, the vapor tension criterion of purity seemed undesirable; hence, the product was considered pure when no peaks attributable to other boron hydrides could be seen in its ^{11}B n.m.r. spectrum and when its mass spectrum was relatively free (<0.5%) of impurities. Yields were estimated on the basis of the amount of HD recovered from the reaction and ranged from 95 to 97%.

Spectroscopic Techniques.—^{11}B nuclear magnetic resonance spectra were obtained with a Varian Associates DP-60 spectrometer operating at 19.3 Mc./sec. equipped with standard Varian low-temperature probe accessories. Temperature uncertainty during these measurements was about ±1°. Chemical shifts and coupling constants were determined using the side-band technique. Infrared spectra were obtained on a Perkin-Elmer Model 137G spectrometer using gaseous samples at approximately 40 mm. pressure in a 5-cm. path length gas cell equipped with sodium chloride windows. The samples were kept frozen on the wall of the cell until scanning was begun to minimize isotope scrambling and decomposition.

Results and Discussion

The mass spectrum of the deuterated tetraborane is qualitatively that of a B_4 boron hydride. The peak of highest mass occurs at m/e 53 (intensity relative to m/e 50 = 4.2%) instead of m/e 52 ($^{11}B_4H_8^+$) as it does for normal B_4H_{10}.[11] The parent peak of normal B_4H_{10} at m/e 54 (attributable to the ion $^{11}B_4H_{10}^+$) has not been definitely observed. Fehlner and Koski[5] have measured a weak peak (0.4%) at m/e 53 which corresponds to the fragment $^{11}B_4H_9^+$; however, this fragment can only be observed on an instrument having high resolution and sensitivity. The m/e 53 peak which arises from the deuterated tetraborane is attributed to the ion fragment $^{11}B_4H_7D^+$. The molecular weight of the deuterated tetraborane is thus 55 and the formula can only be B_4H_9D.

The ^{11}B n.m.r. spectrum consists of a low-field triplet at δ +6.7 p.p.m., J = 124 c.p.s., and a high-field doublet at δ +40.8 p.p.m., J = 158 c.p.s. of equal relative intensities (chemical shift values measured relative to boron trifluoride diethyl etherate). The fine structure of the low-field triplet does not appear markedly changed from that observed in normal tetraborane-10; however, the secondary splitting of the high-field doublet is noticeably affected (Figure 1). Each line of the high-field doublet is further split into apparent doublets of J_A = 19.5 and J_B = 20.4 c.p.s. Additional fine structure appears evident but the lines are insufficiently resolved to be measured.

The over-all features of the ^{11}B spectra are readily interpreted as arising from a molecule having only hydrogen atoms in terminal 1 (3) or 2 (4) positions. It is apparent that the one deuterium atom of B_4H_9D is present in a bridging (μ) position. It is interesting to note the effect on the upfield doublet of replacing one hydrogen atom by a deuterium atom in a bridge; however, the complex coupling situation present in tetraborane-10 has been treated elsewhere[12] and is sufficiently complex so that no simple explanation of fine structure can be given here.

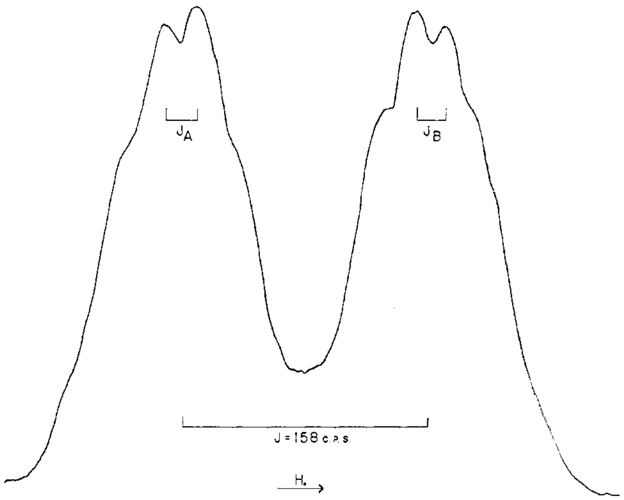

Figure 1.—Upfield doublet of the ^{11}B n.m.r. spectrum of μ-deuteriotetraborane-10. The spectrum was run at −53°.

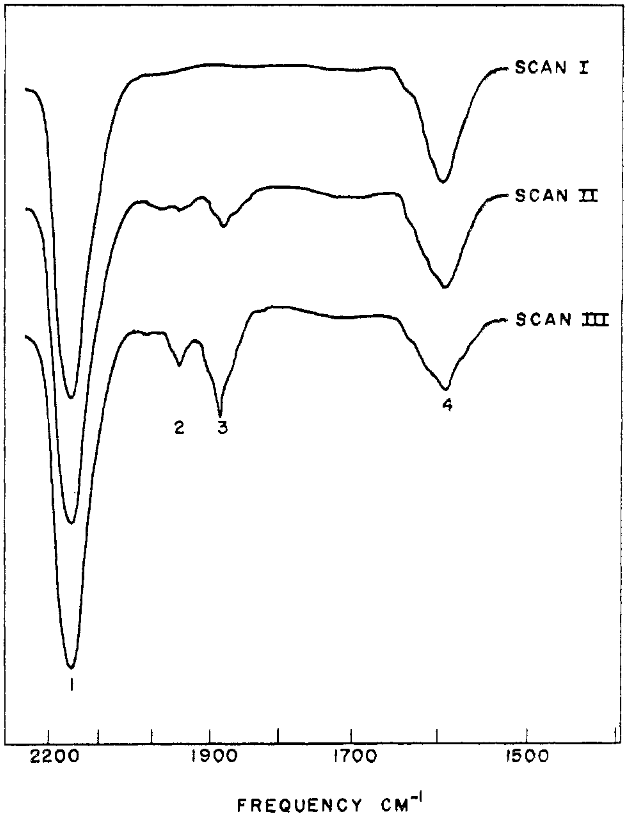

Figure 2.—The infrared spectrum of μ-deuteriotetraborane-10. The band numbers correspond to the following assignments: 1, B–H bridge; 2, 3, B–D terminal; 4, B–D bridge. Scans I, II, and III cover the time periods 0–3.3, 5.0–8.3, and 25.0–28.3 min., respectively.

Three scans of the significant region of the infrared spectrum (2250 to 1530 cm.$^{-1}$) of μ-deuteriotetraborane-

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[11] J. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehman in Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p. 127.

[12] J. D. Baldeschweiler, *et al.*, to be published.

10 are shown in Figure 2. Initially (I) two peaks occur at 2150 and 1583 cm.$^{-1}$ which may be assigned[13] to B–H and B–D bridge vibrational frequencies, respectively. During the second scan (II) the peak at 1583 cm.$^{-1}$ recedes and two new peaks at 1946 and 1875 cm.$^{-1}$ assignable to terminal B–D stretching frequencies begin to appear. After the third scan (III) the 1583 cm.$^{-1}$ peak decreases to 60% of its initial intensity and the peaks due to deuterium in terminal positions grow to the intensity shown. These data conclusively show that initially no detectable amount of deuterium resides in terminal positions in the μ-deuteriotetraborane molecule. Furthermore, they indicate that the molecule undergoes scrambling over a relatively short period of time, since at the end of approximately 0.5 hr. a significant loss of deuterium from the bridging (μ) position takes place.

The mechanism of formation of μ-deuteriotetraborane-10 has not been established experimentally. A relatively simple mechanism which partially rationalizes the product, involving the ionic intermediate $B_4H_9^-$, can be postulated (eq. 1). Support for the

$$B_5H_{11} + 2D_2O \longrightarrow B_4H_9^- + BH_2(D_2O)_2^+ \qquad (1)$$

$$B_4H_9^- + BH_2(D_2O)_2^+ + D_2O \longrightarrow B_4H_9D + B(OD)_3 + 2HD \qquad (2)$$

existence of an ionic intermediate in the cleavage of pentaborane-11 by a basic reagent may be drawn from the work of Schaeffer, *et al.*, which demonstrated the existence of $B_3H_8^-$ during cleavage of tetraborane-10 by strongly coordinating bases.[14] In the final step (2) a simple deuteron abstraction by $B_4H_9^-$ from deuterium oxide could lead to the observed product, μ-deuteriotetraborane-10. Further studies to elucidate the mechanism of the reaction are currently in progress and will be reported later.

Acknowledgment.—This work was in part supported by the National Science Foundation. A National Aeronautics Space Administration traineeship for A. N. is also gratefully acknowledged.

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[13] The B–H and B–D stretching frequencies observed for B_4H_9D agree with those reported by A. J. Dahl, Ph.D. Thesis, University of Michigan, 1963, for B_4H_{10} and B_4D_{10}. The combination band at 1826 cm. for B_4D_{10} occurs at 1875 cm.$^{-1}$ for B_4H_9D.

[14] R. Schaeffer, F. N. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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A New Reagent for the Synthesis of Platinum(II) Complexes

BY RONALD A. KRAUSE

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In recent years a number of workers have shown the diaryliodonium cations (aryl$_2$I$^+$) to be quite reactive.[1] Recent work in our laboratories indicates that many complex anions are precipitated from aqueous solution by the addition of diphenyliodonium chloride. These salts are then capable of undergoing a number of very interesting ligand reactions.

In this paper we report the synthesis of diphenyliodonium tetrachloroplatinum(II) ($[(C_6H_5)_2I]_2PtCl_4$) and its use as a general reagent for the synthesis of platinum(II) complexes in nonaqueous solvents.

Experimental

Preparation of Diphenyliodonium Chloride.—This compound was prepared in 52% yield (after recrystallization from methanol) using the procedure of Beringer, *et al.*[2]

Preparation of $[(C_6H_5)_2I]_2PtCl_4$.—$(C_6H_5)_2ICl$ (6.92 g.) was dissolved in 210 ml. of hot water (*ca.* 65°). To this was added 4.54 g. of K_2PtCl_4 in 100 ml. of water at the same temperature. The product precipitated immediately; after cooling it was isolated by filtration, washed with water and then with ethanol, and dried *in vacuo* over P_4O_{10} giving a tan solid; yield 8.32 g. (84.9%). *Anal.* Calcd. for $(C_{12}H_{10}I)_2PtCl_4$: C, 32.05; H, 2.24; Cl, 15.77. Found: C, 31.84; H, 2.29; Cl, 15.85.

Reaction of $[(C_6H_5)_2I]_2PtCl_4$ in Dimethyl Sulfoxide. Preparation of $[Pt(DMSO)_2Cl_2]$.—$[(C_6H_5)_2I]_2PtCl_4$ (2 g.) was dissolved in 35 ml. of dimethyl sulfoxide and heated for 1.5 hr. (*ca.* 160°). After treating with decolorizing charcoal the solution was evaporated (*in vacuo*, using a rotary evaporator) to an oil. On trituration with ether a yellow solid formed which was washed several times with ether and dried *in vacuo* over P_4O_{10}; yield 0.83 g. (88%). *Anal.* Calcd. for $Pt(C_2H_6SO)_2Cl_2$: C, 11.38; H, 2.86. Found: C, 11.48; H, 2.80.

Reaction of $[(C_6H_5)_2I]_2PtCl_4$ in Pyridine. Preparation of $[Pt(py)_4]Cl_2$.—$[(C_6H_5)_2I]_2PtCl_4$ (0.5 g.) was mixed with 15 ml. of pyridine and boiled for 30 min. Solid was present during the entire course of the reaction. On cooling to room temperature the white crystalline solid was isolated by filtration, washed with pyridine, and dried *in vacuo* over P_4O_{10}; yield 0.28 g. (88%). Infrared examination of this product indicated the absence of the $(C_6H_5)_2I^+$ ion and the presence of the (expected) ligand pyridine.

Reaction of $[(C_6H_5)_2I]_2PtCl_4$ with Dimethylformamide.—$[(C_6H_5)_2I]_2PtCl_4$ (2 g.) was dissolved in 35 ml. of dimethylformamide and boiled for 1 hr. After treating with decolorizing charcoal the solution was evaporated to a brown oil (*in vacuo*, using a rotary evaporator). Trituration with ether failed to crystallize this substance. However, the infrared spectrum indicates that it is probably a DMF complex (C=O stretch at 1650 cm.$^{-1}$); the $(C_6H_5)_2I^+$ ion appears to be absent. The solubility of this substance in a number of polar organic solvents (*e.g.*, acetonitrile, acetone, glyme) indicates it to be a potentially useful intermediate.

Discussion

The compound $[(C_6H_5)_2I]_2PtCl_4$ appears to be a versatile starting material for the synthesis of platinum(II) compounds. Heating $[(C_6H_5)_2I]_2PtCl_4$ in coordinating solvents leads to the formation of platinum(II) chloro–solvent (or solvent–chloride) complexes. The by-products of these reactions are not salts (as would be obtained from K_2PtCl_4) but are ultimately iodobenzene and chlorobenzene, facilitating purification of the complexes. Solutions of the salt in dimethylformamide or dimethyl sulfoxide could conceivably be treated with a new ligand when the salt is insoluble in the latter.

To effect complete decomposition of the $(C_6H_5)_2I^+$

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[1] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Am. Chem. Soc.*, **75**, 2708 (1953).

[2] F. M. Beringer, E. J. Heering, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).