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 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.

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

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

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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.

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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 ($aryl_2I^+$) 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).

cation it is necessary to heat the solutions for a short time. Conductivity measurements on a dimethyl sulfoxide solution of $[(C_6H_5)_2I]_2PtCl_4$ indicate very little change in electrolyte concentration in 3 weeks at room temperature; the conductivity drops rapidly at 150°, however. A color change (from orange to yellow) within the first hour at room temperature indicates that significant coordination of solvent occurs in this time. We conclude, then, that chloride ion and not chlorobenzene leaves the coordination sphere.

From dimethyl sulfoxide solutions we isolate $[Pt(DMSO)_2Cl_2]$. The infrared spectrum of this complex indicates it to be identical with the compound reported by Cotton, *et al.*[3]

The reaction in hot pyridine leads to the formation of the expected product, $[Pt(py)_4]Cl_2$, with no apparent contamination by $(C_6H_5)_2I^+$ salts. Heating $[(C_6H_5)_2I]_2PtCl_4$ in dimethylformamide gives an oil apparently containing coordinated solvent. The organic solubility of this substance makes it a promising intermediate for synthetic work.

Further work on these interesting salts is currently in progress in our laboratories.

Acknowledgment.—The author is indebted to Dr. Samuel J. Huang of this department for first bringing to his attention the reactivity of the diaryliodonium salts.

(3) F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).

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Photochemical Fluorinations of C_2N_2 and $R_fN{=}SF_2$ with N_2F_4[1]

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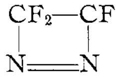
The properties of N_2F_4 and both isomers of N_2F_2 have been more than adequately described recently.[3] The main features of their properties that are applicable to this work are the facts that N_2F_4 is in equilibrium with the free radical NF_2 and that the K_p for the process at 25° is very small and that both N_2F_4 and *cis*-N_2F_2[4] absorb readily in the range between 2150 and 2250 Å. while NF_2 absorbs mainly at about 2600 ± 50 Å. A number of recent papers on the fluorination–difluoramination reaction in which the NF_2 radical is postulated as the main excited species have reportedly made use of low-pressure lamps which emit largely in the 2537 Å. range and not at all in the lower ranges, a factor that would favor activation of the free radical, NF_2.[5–7] The authors in the last paper also succeeded in preparing NF_2SF_5 in 30–35% yields from N_2F_4 and SF_4 and N_2F_4 and SF_5Cl as well as the most interesting $CF_3SF_4NF_2$ from CF_3SF_3 and N_2F_4. The difluoroaminosulfur pentafluoride was prepared previously *via* thermal free radical reactions using N_2F_4 and S_2F_{10}.[8,9]

Several fluorinations of cyanogen with different fluorinating agents are reported in the current chemical literature. Bigelow[10] has indicated that even under the most favorable conditions N–C–C–N chain retention, as $(NF_2CF_2)_2$, does not exceed 22% in the direct fluorination of cyanogen. Using AgF_2 as the fluorinating agent Emeléus and Hurst[11] found that, under optimum conditions, a 90% yield of the cyclic diazo compound,  $\begin{matrix} CF_2-CF_2 \\ | \quad\quad | \\ N{=}N \end{matrix}$, was obtained, while CoF_3 as the fluorinating agent tended to give the same products in kind and distribution as were obtained with free fluorine. There seems little doubt as to the ultimate free radical nature of the mechanisms for the reactions with these three fluorinating agents.

In the course of the work reported in this paper the ultraviolet spectra of all the substances used were obtained. It is of interest to note that each showed strong absorptions in the range of 2100–2300 Å., a region not incompatible with the source used in this work.

Initial studies involving the photoexposure of $R_fN{=}SF_2$ indicated little or no reaction was occurring without ultraviolet light over periods of time equal in extent to the reaction periods with N_2F_4 using ultraviolet light. In Table I are found data on the reaction conditions and final results of the photoreactions between the iminosulfur difluorides and N_2F_4 using a high-pres-

TABLE I

CONDITIONS AND RESULTS OF THE PHOTOREACTIONS INVOLVING $R_fN{=}SF_2$ AND N_2F_4

Reagent	Mole ratio N_2F_4/reagent	Moles of N_2F_4	Total initial press., mm.	Irradiation time, hr.	—Product yields,[a] %— NF_2SN_6	R_fF	N_2
$CF_3N{=}SF_2$	1.5	0.054	140	16.5	93	100	99
$C_2F_5N{=}SF_2$	1.5	0.048	130	31.0	65	100	98
$C_3F_7N{=}SF_2$	1.3	0.048	130	23.3	66	100	98

[a] Other identifiable products were SOF_2, SiF_4, SF_6, and *cis*-N_2F_2. Only SOF_2 was present in the final gas reaction products in excess of 3 mole % of the mixture. Main stoichiometry: $R_fN{=}SF_2 + {}^3/_2N_2F_4 \rightarrow R_fF + NF_2SF_5 + {}^3/_2N_2$.

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[2] Part of the material in this paper has been abstracted from the M.S. thesis of Miss Royal, graduate student in chemistry at the University of Florida.

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[4] The authors are grateful to Dr. Max Lustig, Rohm and Haas Co., Redstone Division, for a copy of the ultraviolet spectrum of this material.

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