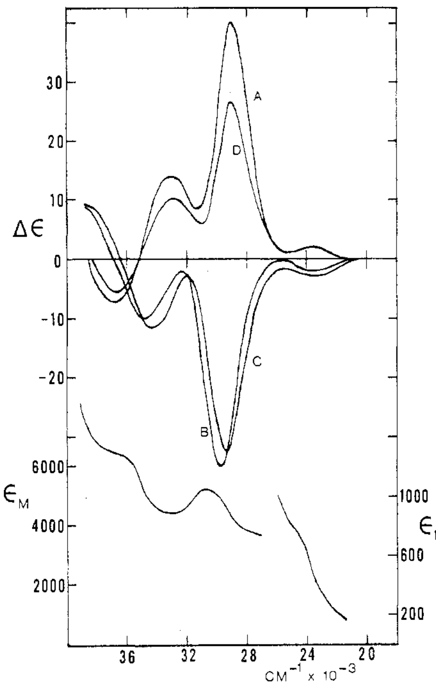

Figure 1. CD spectra of $Rh(atc)_3$ diastereomers in cyclohexane solution. Letters in the figure correspond to those in the text. The absorption spectrum of isomer B was done in cyclohexane solution.

Table I. X-Ray Powder Diffraction Data for $Rh((+)atc)_3$ Diastereomers

Isomer	Interplanar spacings, Å
A	12.31 vs, 9.48 mw, 8.29 s, 6.90 s, 6.52 s, 6.45 s, 5.87 m, 5.48 mw, 5.07 w, 4.77 w, 4.50 ms
B	12.23 vs, 10.09 ms, 8.99 ms, 8.34 s, 7.88 s, 7.39 w, 6.96 s, 6.55 m, 6.15 s, 5.68 mw, 5.47 ms, 5.14 w, 4.93 w, 4.72 w, 4.49 s
C	13.33 ms, 11.48 w, 9.50 s, 8.89 mw, 8.16 mw, 7.48 mw, 6.63 m, b, 5.94 s, 5.60 m, 5.32 m, 4.43 mw
D	15.56 w, 13.64 m, 12.20 vs, b, 11.38 m, 10.63 w, 9.70 ms, 8.66 s, b, 7.98 vs, b, 7.60 ms, 6.83 vs, b, 6.36 vs, 6.16 s, 5.80 ms, 5.56 ms, 5.30 w, 5.16 w, 4.83 ms, 4.65 ms

terns of isomer C and those of Λ-*cis*-$Co((+)atc)_3$ and Λ-*cis*-$Cr((+)atc)_3$ is found. If it can be assumed that isomorphous diastereomers have identical absolute configurations, then the following configurational assignments for the diastereomers of $Rh((+)atc)_3$ are consistent with the nmr, CD, and X-ray data: A, Δ-*trans*-$Rh((+)atc)_3$; B, Λ-*trans*-$Rh((+)atc)_3$; C, Λ-*cis*-$Rh((+)atc)_3$; D, Δ-*cis*-$Rh((+)atc)_3$. These assignments are in line with the observation discussed earlier[2] that the order of the tlc elution of diastereomers in the series $M((+)$-$atc)_3$ is Δ-trans > Λ-trans > Λ-cis > Δ-cis and is independent of the eluting solvents used.

Ligand field absorption bands are largely obscured in these Rh(III) diastereomers. The shoulder at *ca.* 25,000 cm^{-1} (Figure 1) may arise from a d-d transition, and a weak CD is associated with this band. CD bands in the ultraviolet region clearly show the relative helicities of the four diastereomers. In principle, absolute configurations could be deduced from signs of Cotton effects in this region using exciton theory;[7,8] however criteria[7] for use of this method do not appear to be satisfied for $Rh((+)atc)_3$. On an empirical basis the CD spectra shown in Figure 1 should serve as models to which CD spectra of other chiral tris(β-diketonato)rhodium(III) complexes may be compared for the purpose of making configurational assignments. For example, Dunlop, *et al.*,[9] obtained two of the four possible diastereomers of tris[(+)-hydroxymethylenecamphorato]rhodium(III). These were assigned the Δ-trans and Λ-trans configurations on the basis of pmr and steric arguments. The isomer assigned the Λ configuration shows a negative Cotton effect in the ORD spectrum around 28,000 cm^{-1}, in agreement with our results for Λ isomers of $Rh((+)atc)_3$. Also Fay, *et al.*,[10] observed a negative Cotton effect in the low-energy region of the ORD spectrum of the first eluted fraction during a partial resolution of tris(acetylacetonato)rhodium(III). The results presented in this paper indicate that the more abundant enantiomer in this first eluted fraction has the Λ configuration.

A recent report[11] on the reversible photoisomerization of $[(-)_{546}$-Rh^{III}-D-(−)-PDTA$]^-$ prompted us to test the photolability of $Rh((+)atc)_3$. Solutions of isomer A (10^{-3} *M*) in cyclohexane were irradiated for periods of 2-3.5 hr at 2537, 3000, and 3500 Å. No isomerization detectable by tlc occurred, however. Irradiation of isomer A by means of a high-intensity preparative photochemical reactor resulted in apparent decomposition of the complex. Also no thermal isomerization could be detected when toluene solutions of diastereomers A and D were maintained at 100-120° for periods up to 1 week.

Registry No. A, 42744-93-4; B, 42744-94-5; C, 42744-95-6; D, 42719-80-2.

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A Novel Vapor Pump Applied to the Synthesis of Diboron Tetrachloride

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To date the preferred preparation of B_2Cl_4 seems to be electrochemical wherein chlorine is excited from BCl_3 by means of an electrical discharge and scavenged by reaction with the electrode material resulting in the net reaction

$$2BCl_3 + M \leftrightarrows B_2Cl_4 + MCl_2$$

This preparation as originally described by Stock, Brandt, and Fischer[1] used zinc electrodes immersed in liquid BCl_3. It was then improved by Wartik, Moore, and Schlesinger,[2] who described a high-voltage ac discharge between mercury electrodes in the presence of BCl_3 vapor. The uses of micro-

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wave[3] and high-voltage dc discharge[4] have been reported as have alternate electrode materials such as copper.[5] Thus the effects of design, construction, and operating conditions for the discharge reactor have been fairly well investigated.

Since the products of the reaction (B_2Cl_4, B_4Cl_4, etc.) are considerably less volatile than BCl_3, it is reasonable to remove them *via* a low-temperature trap (usually −78°) and recirculate the BCl_3 in a closed system. Urry, Wartik, and Moore[6] contrived a Toepler type pump employing a moving piston of mercury to draw BCl_3 vapor back and forth through the discharge zone. Massey, Urch, and Holliday[7] later described a mercury diffusion pump to move the BCl_3 in a circular loop. While continuous operation with little attention is possible compared to trap-to-trap distillation of BCl_3 described elsewhere,[5] these do require specialized equipment, switches, and relays or sources of heating and cooling.

We report the design and use of a novel pump for the vapor of volatile liquids such as BCl_3, providing both circulation and fractionation and eliminating the need for auxiliary equipment except as required for the discharge cell.

Referring to Figure 1, the pump is constructed of four concentric tubes. Dimensions are given but are not considered critical. Operation is convenient at −78° where the vapor pressure of BCl_3 is 4 Torr. The long, slender design allows one to place a Dry Ice-alcohol bath around the pump.

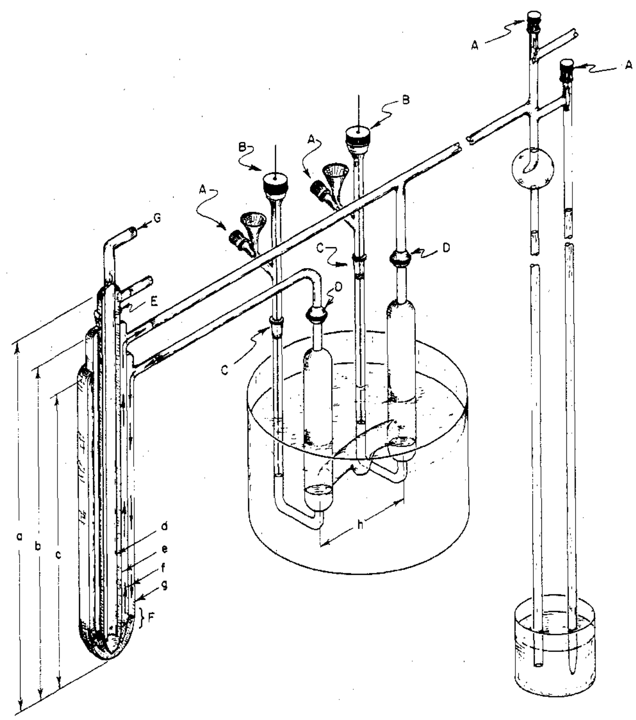

Figure 1. Diboron tetrachloride apparatus. The lower case letters correspond to dimensions (in mm) as follows: a, 370; b, 300; c, 240; d, 8; e, 16; f, 38; g, 50; h, 100. The stopcocks labeled A are Kontes No. 826600-0004. The valves are of Teflon. The electrode wire seals labeled B are Ace Glass Co. No. 5037-03. Joints D (standard taper 18/9) and E (standard taper 24/40) were sealed with wax (available from Fisher Scientific Co., Catalog No. 15-530). Joints C (standard taper 10/30) do not contact BCl_3 vapor and may be sealed with any vacuum grease.

Principle of Operation

By vaporizing BCl_3 from a liquid reservoir, condensing it in another, and then returning the liquid BCl_3 to the first, circulation of the vapor through a discharge reactor is maintained.

In this apparatus the reserviors are concentric. The outer well is kept at −78° by the cold bath. Liquid BCl_3 in the inner section is warmed by contact with a glass wall, warmed by passage of dry air *via* the fourth concentric tube G, thus locally increasing the vapor pressure. The liquid lock at F prevents equilibration except by forcing the BCl_3 vapor through the discharge zone to condense on the outermost wall along with the products from the reactor.

Experimental Section

The pump was tested using a modified mercury discharge cell (also shown in Figure 1) similar to that described by Massey,[7] *et al.* Commercial BCl_3 (10 ml), purified by pumping through a −78° trap and into a −196° trap, was transferred to the system. HCl was removed by pumping on BCl_3 at −78°. Occasional buildup of materials more volatile than BCl_3 necessitated venting the system to the vacuum line for 30–60 sec while the BCl_3 pump was held at −78°.

The cell was maintained at 20–30° by a water bath after discharge was initiated with a power supply delivering about 1 kV and about 0.4 mA. The rate of conversion as indicated by a typical experiment was 100–300 mg of B_2Cl_4/hr along with small amounts of B_4Cl_4. The B_2Cl_4 was purified by rapid fractionation through a −44° trap (trichloroethylene slush) and into a −78° (Dry Ice) trap and the purity was verified by infrared and mass spectra and vapor pressure (43 Torr (0°)).[5] In addition, B_4Cl_4 was recovered from the −44° trap and identified by its mass spectrum.

The driving pressure of the system, as indicated by the difference of level of BCl_3 between inner and outer reservoirs of the pump (see Figure 1 at the area marked F), is estimated to be 0.25 Torr.

Results and Discussion

The yield of B_2Cl_4 and production rate closely parallel those cited by Massey,[7] *et al.* With a suitable power supply, the improved production reported[5] for the multiple Cu-electrode cell should be possible using this pump instead of trap-to-trap distillation.

Most probably, vapors of other volatile liquids may be circulated by selection of appropriate baths in conjunction with this pump.

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Registry No. B_2Cl_4, 13701-67-2; BCl_3, 10294-34-5.

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Chemistry of the Polynuclear Metal Halides. XII. Preparation of Molybdenum and Tungsten $M_6X_8^{4+}$ Clusters by Reduction of Higher Halides in Molten Sodium Halide-Aluminum Halide Mixtures

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Although compounds containing the molybdenum and tungsten halide cluster units $M_6X_8^{4+}$ have been known for