the solvent molecule and these cations. Formation of solvates is common for catechol derivatives.[6] Loss of solvent has frequently made characterization of these complexes by analytical methods difficult. The THF solvates reported here (**1** and **5**) appear to be stable to loss of solvent.

## Conclusions

This work establishes that Cu(II)–DTBSQ complexes can be prepared and characterized analytically, spectroscopically, and structurally. Preparative methods and spectroscopic and structural features are similar to those of other metal–DTBSQ complexes.[6,7,13] Our complexes are stable to further reduction to Cu(I) ions and the *o*-benzoquinone in the absence of small molecules such as pyridine. However, exposure to dioxygen yields a Cu(II) species and *o*-benzoquinone. These results suggest that the formation of *o*-semiquinone species should be considered in the copper-catalyzed oxidation of catechols by copper complexes and dioxygen.[15]

**Acknowledgment.** The technical assistance of R. M. Swiatek and L. Lardear is gratefully acknowledged.

**Registry No.** **1**, 97467-47-5; **2**, 97467-49-7; **3**, 97467-51-1; **4**, 97467-53-3; **5**, 97467-55-5; $[Cu(NH(py)_2)(C_2H_4)]ClO_4$, 91128-06-2; $[Cu_2(NH(py)_2)(OCH_3)_2](ClO_4)_2$, 97486-05-0; $[Cu(TMEN)(C_2H_4)]ClO_4$, 93757-51-8; $[Cu(TMEN)_2(OH)(OCH_3)](ClO_4)_2$, 97467-57-7; $[Cu(TEEN)(C_2H_4)]ClO_4$, 93757-58-5; $[Cu(bpy)(C_2H_4)]ClO_4$, 93757-62-1; $[Cu_2(bpy)_2(OH)(OCH_3)](ClO_4)_2$, 97467-59-9; $[Cu(OP)(C_2H_4)]ClO_4$, 93757-69-8; $[Cu_2(OP)_2(OCH_3)_2](ClO_4)_2$, 97467-61-3.

**Supplementary Material Available:** General temperature factors (Table III), calculated hydrogen atom positions (Table IV), structure factor amplitudes (Table V), and complete bond distances and angles (Table VI) (16 pages). Ordering information is given on any current masthead page.

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(15) (a) All of the compounds reported here, including the Cu(I)–ethylene complexes and the Cu(II)–DTBSQ complexes, are catalytically active in the oxidation of DTBC in DTBBQ, as determined by literature procedures.[5a,15b] (b) Oishi, N.; Nishida, Y.; Ida, K.; Kida, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2847-2850.

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Contribution from the Departments of Chemistry, The Ohio State University, Columbus, Ohio 43210,
Brookhaven National Laboratory, Upton, New York 11973, Indiana University, Bloomington, Indiana 47450,
and University of Southern California, Los Angeles, California 90089

# Preparation and X-ray and Neutron Diffraction Structure Determination of the Chlorotrihydroborate Ion, $[BH_3Cl]^-$

STEVEN H. LAWRENCE,[†] SHELDON G. SHORE,[*,†] THOMAS F. KOETZLE,[*,‡] JOHN C. HUFFMAN,[*,§]
CHIAU-YU WEI,[∥] and ROBERT BAU[*,∥]

*Received January 28, 1985*

In the course of attempts to grow a single crystal of the [PPN]$^+$ salt of the heptahydrodiborate anion, $[(Ph_3P)_2N]^+[B_2H_7]^-$, for X-ray and neutron diffraction analysis, prolonged exposure of $[B_2H_7]^-$ to the mother liquor $[CH_2Cl_2/(C_2H_5)_2O]$ yielded colorless crystals containing a new anion, $[(Ph_3P)_2N]^+[BH_3Cl]^-\cdot CH_2Cl_2$. An improved synthetic procedure for $[BH_3Cl]^-$ was subsequently developed, and spectroscopic and structural analyses of $[(Ph_3P)_2N]^+[BH_3Cl]^-\cdot CH_2Cl_2$ were completed. The compound crystallizes in space group $P\bar{1}$ with the following cell parameters at 90 K: $a = 9.514$ (1) Å, $b = 10.495$ (3) Å, $c = 16.982$ (9) Å, $\alpha = 90.74$ (4)°, $\beta = 93.89$ (5)°, $\gamma = 94.44$ (2)°, $V = 1686$ (2) Å$^3$, $Z = 2$. The structure was refined to yield the following agreement factors: for the X-ray analysis (carried out at 105 K), $R_F = 0.075$ and $R_{wF} = 0.095$ for 5588 reflections with $I > 3\sigma(I)$; for the neutron analysis (carried out at 90 K), $R_F = 0.071$ and $R_{wF} = 0.069$ for 2917 reflections with $I > 3\sigma(I)$. The $[BH_3Cl]^-$ anion has an approximately tetrahedral geometry in which the B–Cl bond, however, is unusually long [2.003 (8) Å], due to the fact that $[PPN]^+[BH_3Cl]^-$ is cocrystallized with a small amount (12–19%) of its precursor, $[PPN]^+[B_2H_7]^-$.

## Introduction

A number of adducts formed by anions with $BH_3$ are known, the most familiar being $[BH_4]^-$ ($BH_3 + H^-$). Among other such adducts, the best known is the cyanotrihydroborate(1–) anion, $[H_3BCN]^-$,[1-4] the first reported example of an adduct between $BH_3$ and a pseudohalide;[5] other known pseudohalide adducts of $BH_3$ are $[H_3BNC]^-$,[4] $[H_3BSCN]^-$,[3,6] $[H_3BNCS]^-$,[3] and $[H_3BN_3]^-$.[7] Attempts to prepare isolable salts of the corresponding halide adducts have been less successful. The only such adduct isolated prior to this study was $[H_3BF]^-$,[6] although $[H_3BCl]^-$ and $[H_3BBr]^-$ were reported by other investigators to be present in solution in the presence of other hydroborate anions.[8,9]

During attempts to grow crystals of $[PPN]^+[B_2H_7]^-$ [$PPN^+ = (Ph_3P)_2N^+$] from dichloromethane solutions,[10] one solution that had been allowed to stand for an extended period of time yielded crystals found to be isostructural with the $[B_2H_7]^-$ salt but to have the composition $[PPN]^+[H_3BCl]^-\cdot CH_2Cl_2$. This outcome was apparently the result of prolonged contact between the $[B_2H_7]^-$ anion and the solvent, resulting in the replacement of some of the $[BH_4]^-$ of $[B_2H_7]^-$ with $[Cl]^-$. We subsequently learned that other workers had reported a similar observation but had not isolated the products from reaction mixtures.[11] This encouraged us to develop a practical synthesis for the chlorotrihydroborate(1–) anion and to study the properties of some of its salts, as well as to investigate the possibility of preparing and isolating the corresponding bromide and iodide derivatives.

## Results and Discussion

**Preparation of $[PPN]^+[H_3BCl]^-$, $[Bu_4N]^+[H_3BCl]^-$, and $[Et_4N]^+[H_3BCl]^-$.** Tensimetric titrations of $[PPN]^+Cl^-$,

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[†] The Ohio State University.

[‡] Brookhaven National Laboratory.

[§] Indiana University.

[∥] University of Southern California.

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$[Bu_4N]^+Cl^-$, and $[Et_4N]^+Cl^-$ with $B_2H_6$ in dichloromethane at −78 °C indicated the reaction stoichiometry

$$[E]^+Cl^- + {}^1/_2B_2H_6 \rightleftarrows [E]^+[H_3BCl]^- \qquad [E]^+ = [PPN]^+, [Bu_4N]^+, [Et_4N]^+ \tag{1}$$

In each case, a plot of vapor pressure vs. the mole ratio of $B_2H_6$ to $[E]^+Cl^-$ gave a break in the curve at (mmol of $B_2H_6$)/(mmol of $[E]^+Cl^-$) = 0.5. Both $[PPN]^+[H_3BCl]^-$ and $[Bu_4N]^+[H_3BCl]^-$ precipitated out of solution as colorless solids, while $[Et_4N]^+[H_3BCl]^-$ remained in solution. The corresponding tensimetric titrations of $[Me_4N]^+Cl^-$, $[PPN]^+Br^-$, $[Bu_4N]^+Br^-$, and $[PPN]^+I^-$ with diborane showed no evidence for reaction.

Solutions of $[H_3BCl]^-$ salts were generally handled at lower temperatures to avoid anion dissociation (i.e., the reverse of eq 1) and disproportionation (vide infra). Solid salts of $[H_3BCl]^-$ were isolated by the removal of volatiles at −63 °C. When $[PPN]^+[H_3BCl]^-$ isolated in this manner was reacted with methanol, 95% of the hydrogen expected on the basis of pure product was obtained, which, in conjunction with spectroscopic data, indicated the isolation of a relatively pure $[H_3BCl]^-$ salt. The presence of a trace quantity of $B_2H_6$ in the recovered volatiles indicated a small degree of anion dissociation in dichloromethane solutions of $[PPN]^+[H_3BCl]^-$, a phenomenon more pronounced for dichloromethane solutions of the more soluble $[Bu_4N]^+$ and $[Et_4N]^+$ salts of $[H_3BCl]^-$.

The infrared spectrum in the B–H stretching region (2200–2600 $cm^{-1}$) of the Nujol mull of each of the isolated products exhibits absorptions at 2210 (m), 2299 (s), and 2340 (s) $cm^{-1}$ (±5 $cm^{-1}$ for all values). As solids, the $[H_3BCl]^-$ salts reported here are stable under inert atmosphere at room temperature but decompose rapidly upon exposure to air. Heating $[PPN]^+[H_3BCl]^-$ to 200 °C with continuous removal of volatiles resulted in the recovery of $CH_2Cl_2$, $B_2H_6$, and a small amount of hydrogen. The remaining solid was found to be $[PPN]^+Cl^-$. The behavior of dichloromethane solutions of $[H_3BCl]^-$ salts varies with temperature, with higher temperatures promoting both anion disproportionation and diborane evolution.

**NMR Studies.** Boron-11 and proton NMR spectra, not reported previously for $[H_3BCl]^-$, were recorded for $[PPN]^+[H_3BCl]^-$ in $CD_2Cl_2$. At −80 °C, the $^{11}B$ NMR spectrum showed a broad single peak at −14.6 ppm, which resolved into a quartet (1:3:3:1) at 25 °C, $J(^{11}B-^1H) = 104 \pm 1$ Hz. A small amount of $B_2H_6$ was also observed at −80 °C. The $^1H$ NMR spectrum, recorded in $CD_2Cl_2$ at −80 °C, exhibited a signal at 1.8 ppm, which resolved into a quartet (1:1:1:1) at 25 °C, $J(^1H-^{11}B) = 104 \pm 2$ Hz.

The disproportionation of $[H_3BCl]^-$ in solution at higher temperatures was observed by $^{11}B$ NMR spectroscopy. At 25 °C, in addition to signals observed for unreacted $[H_3BCl]^-$ and $[B_2H_7]^-$, a triplet (1:2:1) was observed at −2.8 ppm, $J(^{11}B-^1H) = 131 \pm 1$ Hz, and assigned to the $[H_2BCl_2]^-$ anion. In the $^1H$ NMR spectrum, also recorded at 25 °C, $[H_2BCl_2]^-$ exhibited a quartet (1:1:1:1) at 3.4 ppm, $J(^1H-^{11}B) = 130 \pm 2$ Hz. Like $[H_3BCl]^-$, $[H_2BCl_2]^-$ was reported previously, but not isolated, and no NMR spectral data were provided.[8]

The disproportionation of $[H_3BCl]^-$ in solution as a function of temperature was followed by $^{11}B$ NMR spectroscopy. Disproportionation was clearly evident above −50 °C and became more pronounced at higher temperatures. No intermediate species were detected in the $^{11}B$ NMR spectra: only the products $[BH_2Cl_2]^-$ and $[B_2H_7]^-$, in a 1:1 ratio, were observed. The overall disproportionation reaction is represented by eq 2. The $^{11}B$ NMR

$$3[H_3BCl]^- \rightarrow [BH_2Cl_2]^- + [B_2H_7]^- + Cl^- \tag{2}$$

spectra of samples allowed to stand at room temperature for over 24 h also showed the presence of $[B_3H_8]^-$, probably formed by the decomposition of $[B_2H_7]^-$.[12,13]

The reaction given by eq 2 is believed to proceed through a singly hydrogen-bridged intermediate, $[B_2H_6Cl]^-$. While no direct evidence for the presence of this anion was obtained here, analogous hydrogen-bridged species formed by $B_2H_6$ with various Lewis bases have been reported.[14]

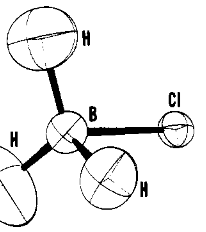

**Figure 1.** Molecular plot[23] of the $[BH_3Cl]^-$ anion. (In this and all subsequent diagrams, atoms are shown as 75% probability ellipsoids.)

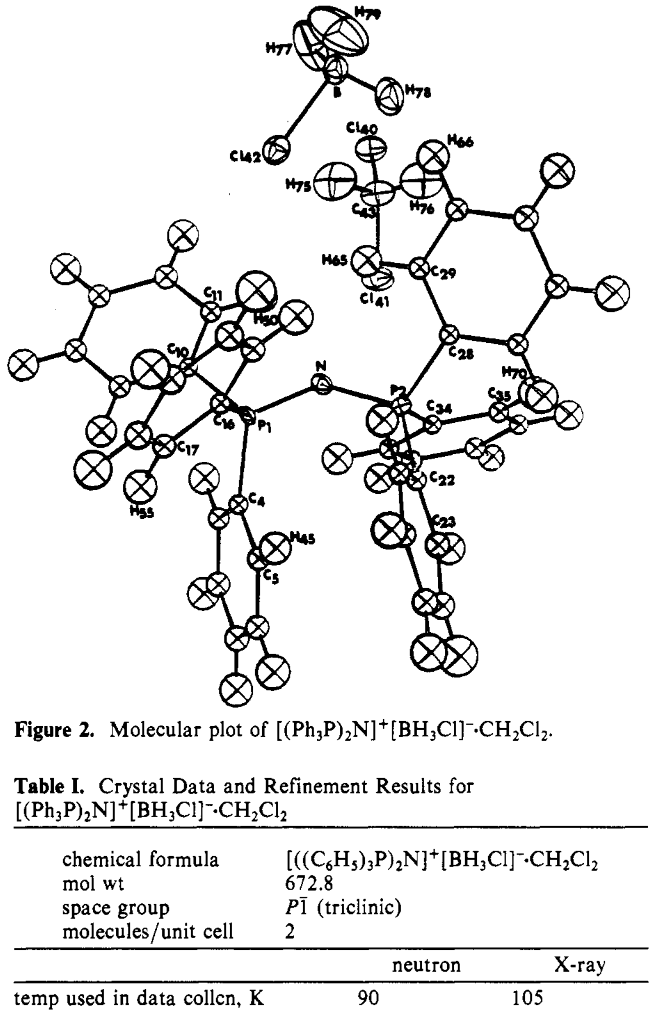

**Figure 2.** Molecular plot of $[(Ph_3P)_2N]^+[BH_3Cl]^-\cdot CH_2Cl_2$.

**Table I.** Crystal Data and Refinement Results for $[(Ph_3P)_2N]^+[BH_3Cl]^-\cdot CH_2Cl_2$

| | |
|---|---|
| chemical formula | $[((C_6H_5)_3P)_2N]^+[BH_3Cl]^-\cdot CH_2Cl_2$ |
| mol wt | 672.8 |
| space group | $P\bar{1}$ (triclinic) |
| molecules/unit cell | 2 |

| | neutron | X-ray |
|---|---|---|
| temp used in data collcn, K | 90 | 105 |
| $a$, Å | 9.514 (1) | 9.507 (3) |
| $b$, Å | 10.495 (3) | 10.491 (4) |
| $c$, Å | 16.982 (9) | 16.927 (7) |
| $\alpha$, deg | 90.74 (4) | 90.79 (4) |
| $\beta$, deg | 93.89 (5) | 93.84 (4) |
| $\gamma$, deg | 94.44 (2) | 94.48 (4) |
| unit cell vol, $Å^3$ | 1686 (2) | 1683 (2) |
| sample dimens, mm | 0.71 × 0.83 × 3.13 | 0.25 × 0.25 × 0.35 |
| $d_{calcd}$, d g $cm^{-3}$ | 1.33 | 1.33 |
| wavelength, Å | 1.1173 | 0.71069 |
| abs coeff, $cm^{-1}$ | 2.31 | 3.93 |
| data collcn limits | $5° < 2\theta < 75°$ | $4° < 2\theta < 50°$ |
| unique no. of reflcns measd | 4569 | 5968 |
| no. of reflcns used in structure refinement | 2917 | 5588 |
| $R_F = \sum \lvert F_o - \lvert F_c \rvert \rvert / \sum F_o$ | 0.071 | 0.075 |
| $R_{wF} = [\sum w(F_o - \lvert F_c \rvert)^2 / \sum w F_o^2]^{1/2}$ | 0.069 | 0.095 |
| $S = [\sum w(F_o - \lvert F_c \rvert)^2/(N_o - N_v)]^{1/2}$ | 2.0 | 1.66 |
| isotropic extinction param, $g \times 10^4$ | 0.43 (6) | |

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**Table II.** Selected Interatomic Distances (Å) and Angles (deg)

| | neutron | X-ray | | neutron | X-ray |
|---|---|---|---|---|---|
| | | $[BH_3Cl]^-$ Anion | | | |
| B(44)-Cl(42) | 2.003 (8) | 2.003 (5) | B(44)-H(78) | 1.193 (15) | 1.079 (71) |
| B(44)-H(77) | 1.221 (19) | 1.380 (22) | B(44)-H(79) | 1.196 (22) | 1.107 (53) |
| Cl(42)-B(44)-H(77) | 107.5 (8) | 122.5 (29) | H(77)-B(44)-H(78) | 111.2 (12) | 100.8 (35) |
| Cl(42)-B(44)-H(78) | 102.5 (7) | 108.6 (33) | H(77)-B(44)-H(79) | 116.6 (15) | 108.9 (28) |
| Cl(42)-B(44)-H(79) | 105.0 (10) | 102.6 (26) | H(77)-B(44)-H(79) | 112.6 (14) | 113.9 (44) |
| | | $CH_2Cl_2$ Molecule | | | |
| C(43)-Cl(40) | 1.773 (8) | 1.754 (5) | C(43)-H(75) | 1.095 (17) | 1.068 (42) |
| C(43)-Cl(41) | 1.764 (8) | 1.775 (5) | C(43)-H(76) | 1.029 (18) | 0.949 (51) |
| Cl(40)-C(43)-Cl(41) | 111.7 (4) | 111.9 (3) | Cl(41)-C(43)-H(75) | 108.8 (9) | 103.8 (23) |
| Cl(40)-C(43)-H(75) | 107.6 (10) | 108.4 (23) | Cl(41)-C(43)-H(76) | 109.4 (11) | 104.2 (3) |
| Cl(40)-C(43)-H(76) | 107.7 (11) | 104.8 (31) | H(75)-C(43)-H(76) | 111.6 (14) | 123.7 (38) |
| | | $[(Ph_3P)_2N]^+$ Cation | | | |
| P(1)-N(3)-P(2) | 137.5 (4) | 138.2 (2) | | | |
| N(3)-P(1) | 1.586 (7) | 1.578 (3) | | | |
| N(3)-P(2) | 1.591 (7) | 1.576 (3) | | | |
| P(1)-C(4) | 1.798 (9) | 1.805 (4) | P(2)-C(22) | 1.795 (7) | 1.800 (4) |
| P(1)-C(10) | 1.799 (7) | 1.787 (4) | P(2)-C(28) | 1.791 (7) | 1.802 (4) |
| P(1)-C(16) | 1.801 (7) | 1.800 (4) | P(2)-C(34) | 1.801 (7) | 1.805 (4) |
| C(4)-P(1)-C(10) | 107.5 (4) | 106.9 (2) | C(22)-P(2)-C(28) | 105.9 (3) | 105.8 (2) |
| C(4)-P(1)-C(16) | 109.0 (3) | 108.5 (2) | C(22)-P(2)-C(34) | 109.9 (3) | 109.9 (2) |
| C(10)-P(1)-C(16) | 106.0 (3) | 106.9 (2) | C(28)-P(2)-C(34) | 108.6 (3) | 108.4 (2) |
| N(3)-P(1)-C(4) | 115.1 (4) | 114.5 (2) | N(3)-P(2)-C(22) | 114.6 (4) | 113.9 (2) |
| N(3)-P(1)-C(10) | 106.9 (4) | 107.4 (2) | N(3)-P(2)-C(28) | 108.6 (4) | 109.1 (2) |
| N(3)-P(1)-C(16) | 111.8 (4) | 112.2 (2) | N(3)-P(2)-C(34) | 109.1 (4) | 109.5 (2) |

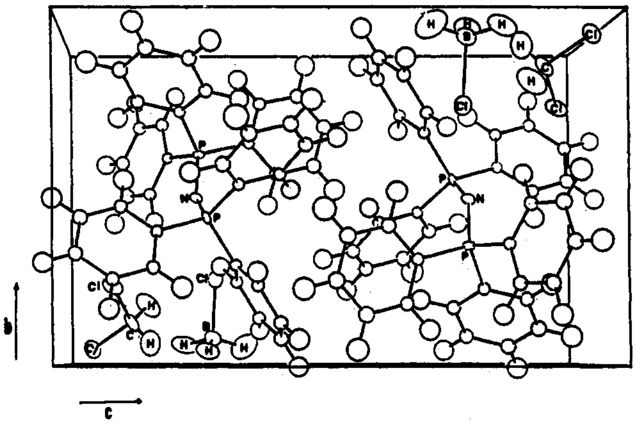

**Figure 3.** Unit cell plot of $[(Ph_3P)_2N]^+[BH_3Cl]^-\cdot CH_2Cl_2$.

**Structure Analyses.** The molecular structure of $[PPN]^+[BH_3Cl]^-\cdot CH_2Cl_2$ was analyzed concurrently by X-ray (J.C.H.) and neutron diffraction techniques (C.Y.W., R.B., T.F.K.). The $[BH_3Cl]^-$ anion is shown in Figure 1, a view of the molecular unit (cation, anion, solvent) is presented in Figure 2, and a unit cell diagram is shown in Figure 3. All three figures depict the results of the neutron analysis. Table I gives a summary of crystal data and refinement results for both the X-ray and neutron studies, while Table II lists selected interatomic distances and angles. Tables III and IV give the refined molecular parameters (atomic coordinates and temperature factors) from the neutron and X-ray analyses, respectively. Other results for the two structure determinations are available as supplementary material (see paragraph at end of paper for details).

The observed bonding parameters are quite normal, except that the B-Cl distance on the anion is anomalously long [2.003 (8) Å] (see Table V, which compares the distances and angles of compounds related to $[BH_3Cl]^-$). The $[(Ph_3P)_2N]^+$ cation and $CH_2Cl_2$ molecule of crystallization have expected geometries, with the former having the usual bent configuration [P-N-P = 137.5 (4)°]. The H-B-H angles [average 114 (2)°] of $[BH_3Cl]^-$ are all significantly larger than the H-B-Cl angles [average 105 (2)°], implying a greater degree of s character in the B-H bonds. The anomalously long B-Cl distance can be ascribed to incorporation of approximately 19% $[B_2H_7]^-$ into the $[BH_3Cl]^-$ site, with attendant superposition of the chlorine and the second boron atom from the $[B_2H_7]^-$ impurity. (The B···B distance in $[B_2H_7]^-$ is 2.27 (1) Å.[15] Subsequently, we have carried out both the X-ray[10] and neutron[15] structural analyses of crystals of pure $[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$. As mentioned above, $[PPN]^+[BH_3Cl]^-\cdot CH_2Cl_2$ (this work) and $[PPN]^+[B_2H_7]^-\cdot CH_2Cl_2$[10,15] are isostructural.[16]

## Experimental Section

**Method.** Materials were handled by using standard vacuum-line and inert-atmosphere techniques.[17]

**Materials.** Prior to use, dichloromethane ($CH_2Cl_2$, $CD_2Cl_2$) was stored over $P_4O_{10}$ in the absence of air and distilled into storage bulbs fitted with Kontes stopcocks. Bis(triphenylphosphine)nitrogen(1+) chloride, $[PPN]^+Cl^-$ (Alfa Products), was recrystallized twice from $CH_2Cl_2/Et_2O$ and dried under vacuum. Tetra-*n*-butylammonium chloride, $[Bu_4N]^+Cl^-$, and tetraethylammonium chloride, $[Et_4N]^+Cl^-$, were prepared from $[Bu_4N]^+Br^-$ (Alfa Products) and $[Et_4N]^+Br^-$ (Aldrich Chemical Co.), respectively, by anion exchange in ethanolic solution and were dried under vacuum. Bis(triphenylphosphine)nitrogen(1+) bromide and iodide, $[PPN]^+Br^-$ and $[PPN]^+I^-$, respectively, were prepared according to a literature method.[18] All solid reactants were stored in a glovebox under an atmosphere of dry, pure nitrogen. Diborane(6) (Callery), was fractionated once through a −135 °C trap and stored at −196 °C.

**Equipment.** Boron-11 FT-NMR spectra were obtained at 96.3 MHz with a Bruker WM-300 spectrometer and at 28.9 MHz with a Bruker HX-90 spectometer. Proton FT-NMR spectra were obtained at 300 MHz with the Bruker WM-300 spectrometer. Infrared spectra of solids were obtained from Nujol mulls between KBr plates by using a Perkin-Elmer 457 spectrophotometer. X-ray data were collected on a Picker four-circle goniostat equipped with a Furnas monochromator, and neu-

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**Table III.** Final Atomic Parameters for $[(Ph_3P)_2N]^+[BH_3Cl]^-\cdot CH_2Cl_2$ (Neutron Results)

| atom | $10^4x$ | $10^4y$ | $10^4z$ | $10^2B$, Å$^2$ | atom | $10^4x$ | $10^4y$ | $10^4z$ | $10^2B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| A. Nongroup Atoms | | | | | | | | | |
| P(1) | -3015 (6) | 6517 (6) | 2547 (4) | | B(44) | 265 (8) | 857 (7) | 2818 (5) | |
| P(2) | -5236 (6) | 4412 (6) | 2685 (4) | | H(75) | -8643 (16) | 8116 (1) | 8456 (9) | |
| N(3) | -3753 (4) | 5109 (3) | 2500 (2) | | H(76) | -7267 (18) | 9324 (17) | 8407 (9) | |
| Cl(40) | -8390 (5) | 9511 (4) | 9559 (3) | | H(77) | 944 (19) | 646 (12) | 2252 (10) | |
| Cl(41) | -6500 (5) | 7596 (4) | 9107 (3) | | H(78) | -936 (14) | 442 (11) | 2705 (8) | |
| Cl(42) | 96 (4) | 2746 (4) | 2880 (2) | | H(79) | 773 (26) | 558 (18) | 3452 (12) | |
| C(43) | -7741 (7) | 8664 (7) | 8768 (4) | | | | | | |
| B. Group Atoms | | | | | | | | | |
| Group I | | | | | | | | | |
| C(4) | -4113 (7) | 7739 (6) | 2196 (2) | 99 (8) | H(45) | -4999 (6) | 8039 (4) | 3314 (1) | 258 (20) |
| C(5) | -5027 (4) | 8280 (3) | 2692 (1) | 125 (9) | H(46) | -6692 (7) | 9552 (8) | 2775 (2) | 313 (22) |
| C(6) | -5979 (4) | 9130 (5) | 2388 (5) | 147 (9) | H(47) | -6757 (11) | 10102 (11) | 1353 (2) | 326 (23) |
| C(7) | -6014 (7) | 9438 (6) | 1590 (2) | 169 (10) | H(48) | -5128 (6) | 9139 (5) | 471 (1) | 333 (23) |
| C(8) | -5100 (5) | 8898 (3) | 1094 (1) | 167 (10) | H(49) | -3435 (7) | 7626 (8) | 1011 (2) | 302 (22) |
| C(9) | -4148 (4) | 8048 (5) | 1397 (1) | 124 (9) | | | | | |
| Group II | | | | | | | | | |
| C(10) | -1535 (3) | 6533 (3) | 1941 (2) | 88 (8) | H(50) | -1795 (4) | 4508 (2) | 1677 (3) | 241 (19) |
| C(11) | -1173 (3) | 5404 (2) | 1590 (2) | 118 (9) | H(51) | 272 (4) | 4545 (3) | 853 (2) | 319 (22) |
| C(12) | -11 (3) | 5425 (2) | 1127 (2) | 164 (9) | H(52) | 1693 (4) | 6591 (4) | 655 (3) | 306 (22) |
| C(13) | 787 (3) | 6575 (3) | 1016 (2) | 152 (9) | H(53) | 1047 (4) | 8600 (2) | 1280 (3) | 284 (21) |
| C(14) | 425 (3) | 7704 (2) | 1367 (2) | 137 (9) | H(54) | -1020 (4) | 8563 (3) | 2104 (2) | 268 (20) |
| C(15) | -737 (3) | 7683 (2) | 1830 (2) | 128 (9) | | | | | |
| Group III | | | | | | | | | |
| C(16) | -2290 (3) | 6945 (2) | 3531 (1) | 93 (8) | H(55) | -2191 (4) | 8976 (3) | 3332 (2) | 282 (21) |
| C(17) | -1968 (3) | 8227 (2) | 3750 (1) | 120 (9) | H(56) | -1109 (5) | 9549 (2) | 4677 (2) | 331 (23) |
| C(18) | -1360 (3) | 8549 (2) | 4506 (2) | 158 (9) | H(57) | -600 (5) | 7839 (4) | 5632 (2) | 320 (22) |
| C(19) | -1075 (3) | 7588 (2) | 5042 (1) | 173 (10) | H(58) | -1173 (5) | 5557 (3) | 5241 (2) | 364 (25) |
| C(20) | -1396 (3) | 6306 (2) | 4822 (1) | 173 (10) | H(59) | -2255 (5) | 4984 (2) | 3895 (2) | 298 (21) |
| C(21) | -2004 (3) | 5984 (2) | 4066 (2) | 136 (9) | | | | | |
| Group IV | | | | | | | | | |
| C(22) | -6284 (4) | 5337 (3) | 3280 (2) | 91 (8) | H(60) | -7965 (4) | 5558 (3) | 2385 (1) | 274 (21) |
| C(23) | -7531 (3) | 5826 (2) | 2979 (1) | 153 (9) | H(61) | -9195 (4) | 7042 (5) | 3207 (2) | 422 (27) |
| C(24) | -8222 (3) | 6660 (3) | 3442 (2) | 168 (10) | H(62) | -8205 (6) | 7653 (5) | 4565 (2) | 312 (22) |
| C(25) | -7665 (4) | 7002 (3) | 4204 (2) | 156 (9) | H(63) | -5985 (4) | 6781 (3) | 5099 (1) | 282 (21) |
| C(26) | -6418 (3) | 6513 (2) | 4505 (1) | 135 (9) | H(64) | -4755 (4) | 5298 (5) | 4277 (2) | 249 (20) |
| C(27) | -5727 (3) | 5680 (3) | 4043 (2) | 101 (8) | | | | | |
| Group V | | | | | | | | | |
| C(28) | -4924 (3) | 3001 (2) | 3232 (2) | 92 (8) | H(65) | -2738 (3) | 3041 (3) | 2958 (2) | 261 (20) |
| C(29) | -3581 (2) | 2543 (2) | 3265 (2) | 105 (9) | H(66) | -2275 (2) | 1087 (4) | 3717 (3) | 276 (21) |
| C(30) | -3321 (2) | 1445 (3) | 3691 (2) | 120 (9) | H(67) | -4200 (4) | -50 (3) | 4416 (3) | 284 (21) |
| C(31) | -4403 (3) | 807 (2) | 4084 (2) | 146 (9) | H(68) | -6588 (3) | 767 (3) | 4357 (2) | 306 (22) |
| C(32) | -5745 (2) | 1265 (2) | 4051 (2) | 132 (9) | H(69) | -7052 (2) | 2721 (4) | 3599 (3) | 277 (21) |
| C(33) | -6006 (2) | 2363 (3) | 3625 (2) | 103 (8) | | | | | |
| Group VI | | | | | | | | | |
| C(34) | -6216 (3) | 3945 (3) | 1769 (1) | 89 (8) | H(70) | -7296 (4) | 2262 (3) | 2232 (2) | 307 (22) |
| C(35) | -7139 (3) | 2841 (2) | 1713 (1) | 110 (9) | H(71) | -8581 (4) | 1619 (3) | 946 (2) | 277 (21) |
| C(36) | -7861 (3) | 2479 (2) | 990 (1) | 114 (9) | H(72) | -8223 (5) | 2940 (4) | -239 (1) | 254 (20) |
| C(37) | -7659 (3) | 3222 (3) | 325 (1) | 134 (9) | H(73) | -6579 (4) | 4905 (3) | -139 (2) | 288 (21) |
| C(38) | -6736 (3) | 4327 (2) | 381 (1) | 145 (9) | H(74) | -5294 (4) | 5549 (3) | 1147 (2) | 300 (21) |
| C(39) | -6014 (3) | 4688 (2) | 1103 (2) | 112 (9) | | | | | |

tron data were collected at the Brookhaven High Flux Beam Reactor.

**Analyses.** Product purity was established by $^{11}B$ NMR spectroscopy in conjunction with analysis for hydridic hydrogen, which was carried out by reacting an accurately weighed sample with an excess of degassed methanol, followed by measurement of the hydrogen gas generated.

**Tensimetric Titration of $[E]^+Cl^-$ with Diborane ($[E]^+ = [PPN]^+$, $[Bu_4N]^+$, $[Et_4N]^+$). Synthesis of $[E]^+[H_3BCl]^-$.** The general procedure employed for the tensimetric titration of halide salts with $B_2H_6$ was as follows: A 1-2-mmol sample of halide salt, weighed to the nearest 0.1 mg, was dissolved in a minimum of dichloromethane (2-4 mL) at -78 °C. Reaction and vapor pressure measurements were carried out at -78 °C. Prior to each addition of $B_2H_6$ the reaction bulb was cooled to -196 °C, and the $B_2H_6$ was condensed directly into the reaction bulb. The reaction bulb was opened to the tensimeter only for vapor pressure measurements.

After reaction was complete, most of the volatile materials were removed at -63 °C, after which the temperature was raised slowly to facilitate removal of any remaining solvent. The recovered volatile materials were fractionated through a -135 °C trap to recover the $B_2H_6$ removed from the reaction mixture. The colorless solid that remained was collected and stored in a glovebox under an atmosphere of pure dry nitrogen.

**Preparation of NMR Samples of $[E]^+[H_3BCl]^-$.** NMR samples intended for low-temperature studies were prepared by reacting $[E]^+Cl^-$ with $B_2H_6$ in $CD_2Cl_2$ at -78 °C, filtering the product mixture at -78 °C, and collecting the filtrate into an NMR sample tube. For studies at ambient temperature, solid $[E]^+[H_3BCl]^-$ was placed directly into an NMR sample tube and $CD_2Cl_2$ was then condensed into the tube. All NMR samples were sealed off under vacuum and stored at -196 °C until use.

**X-ray Data Collection and Structure Analysis.** Due to the reactive nature of the title compound, the crystal used in the X-ray data collection was transferred to the goniostat by using inert-atmosphere handling techniques. All data were collected at -168 °C. The sample was initially postulated to be $[PPN]^+[B_2H_7]^-$. Direct methods located several phenyl rings as well as three peaks of approximate density 17 e/Å$^3$. When the latter were assigned as chlorine atoms, subsequent Fourier techniques located all atoms in the $[PPN]^+$ cation, a $CH_2Cl_2$ solvent molecule, and a peak ca. 2.0 Å from the third Cl atom, which could reasonably be assigned as a boron atom.

**Table IV.** Fractional Coordinates for $[(Ph_3P)_2N]^+[BH_3Cl]^- \cdot CH_2Cl_2$

| atom | $10^4x$ | $10^4y$ | $10^4z$ | $10B_{iso}$(Å$^2$) | atom | $10^4x$ | $10^4y$ | $10^4z$ | $10B_{iso}$(Å$^2$) |
|---|---|---|---|---|---|---|---|---|---|
| P(1) | −3009 (1) | 6510 (1) | 2550 (1) | 9 | Cl(41) | −6503 (1) | 7598 (1) | 9102 (1) | 28 |
| P(2) | −5230 (1) | 4415 (1) | 2682 (1) | 8 | Cl(42) | −9900 (1) | 2739 (1) | 2874 (1) | 15 |
| N(3) | −3760 (3) | 5112 (3) | 2502 (2) | 11 | C(43) | −7761 (6) | 8672 (5) | 8772 (3) | 24 |
| C(4) | −4111 (4) | 7734 (4) | 2195 (2) | 12 | B(44) | 274 (6) | 849 (5) | 2824 (3) | 22 |
| C(5) | −5022 (4) | 8286 (4) | 2689 (2) | 13 | H(45) | −5055 (44) | 7935 (40) | 3210 (25) | 10 |
| C(6) | −5971 (5) | 9122 (4) | 2382 (3) | 19 | H(46) | −6523 (53) | 9509 (46) | 2678 (29) | 22 |
| C(7) | −5992 (4) | 9427 (4) | 1596 (3) | 17 | H(47) | −6606 (44) | 10099 (39) | 1377 (24) | 9 |
| C(8) | −5097 (5) | 8887 (4) | 1098 (3) | 17 | H(48) | −5093 (48) | 9129 (43) | 572 (27) | 14 |
| C(9) | −4154 (4) | 8043 (4) | 1397 (2) | 15 | H(49) | −3519 (47) | 7641 (42) | 1060 (26) | 14 |
| C(10) | −1547 (4) | 6531 (3) | 1939 (2) | 10 | H(50) | −1614 (52) | 4646 (48) | 1665 (29) | 21 |
| C(11) | −1176 (5) | 5412 (4) | 1582 (2) | 15 | H(51) | 294 (75) | 4555 (67) | 878 (42) | 57 |
| C(12) | −24 (4) | 5418 (4) | 1128 (2) | 15 | H(52) | 1517 (44) | 6659 (38) | 730 (24) | 6 |
| C(13) | 769 (4) | 6577 (4) | 1016 (2) | 16 | H(53) | 936 (43) | 8487 (39) | 1286 (24) | 7 |
| C(14) | 408 (4) | 7682 (4) | 1367 (2) | 15 | H(54) | −908 (39) | 8375 (36) | 2076 (22) | 0 |
| C(15) | −739 (4) | 7681 (4) | 1822 (2) | 12 | H(55) | −2292 (69) | 8927 (62) | 3439 (39) | 47 |
| C(16) | −2298 (4) | 6949 (3) | 3534 (2) | 10 | H(56) | −1274 (59) | 9275 (55) | 4744 (34) | 32 |
| C(17) | −1969 (4) | 8229 (4) | 3750 (2) | 13 | H(57) | −597 (42) | 7840 (36) | 5551 (24) | 5 |
| C(18) | −1364 (5) | 8548 (4) | 4494 (2) | 19 | H(58) | −1108 (48) | 5822 (43) | 5151 (28) | 15 |
| C(19) | −1074 (4) | 7595 (4) | 5031 (2) | 15 | H(59) | −2261 (52) | 5111 (47) | 3872 (28) | 21 |
| C(20) | −1398 (5) | 6327 (5) | 4818 (2) | 19 | H(60) | −7869 (74) | 5608 (65) | 2500 (42) | 52 |
| C(21) | −1996 (4) | 5995 (4) | 4067 (2) | 17 | H(61) | −9081 (49) | 7060 (42) | 3231 (27) | 15 |
| C(22) | −6278 (4) | 5354 (4) | 3277 (2) | 12 | H(62) | −8151 (46) | 7593 (41) | 4528 (25) | 11 |
| C(23) | −7535 (5) | 5826 (4) | 2979 (3) | 16 | H(63) | −6055 (64) | 6692 (5) | 5130 (36) | 41 |
| C(24) | −8201 (5) | 6657 (4) | 3444 (3) | 18 | H(64) | −4969 (42) | 5235 (37) | 4210 (23) | 5 |
| C(25) | −7660 (5) | 6999 (4) | 4201 (3) | 18 | H(65) | −2883 (43) | 2884 (38) | 3054 (24) | 5 |
| C(26) | −6419 (4) | 6513 (4) | 4507 (2) | 15 | H(66) | −2338 (47) | 1148 (41) | 3693 (25) | 12 |
| C(27) | −5743 (4) | 5686 (4) | 4045 (2) | 12 | H(67) | −4214 (49) | −6 (44) | 4371 (27) | 16 |
| C(28) | −4928 (4) | 3000 (4) | 3239 (2) | 12 | H(68) | −6439 (55) | 796 (48) | 4287 (30) | 23 |
| C(29) | −3580 (4) | 2535 (4) | 3261 (2) | 14 | H(69) | −6860 (47) | 2723 (44) | 3677 (25) | 12 |
| C(30) | −3335 (5) | 1452 (4) | 3696 (2) | 15 | H(70) | −7258 (38) | 2322 (34) | 2205 (21) | 0 |
| C(31) | −4405 (5) | 805 (4) | 4079 (2) | 16 | H(71) | −8421 (55) | 1713 (50) | 955 (30) | 25 |
| C(32) | −5740 (5) | 1276 (4) | 4045 (2) | 17 | H(72) | −8158 (50) | 3018 (44) | −83 (29) | 17 |
| C(33) | −6000 (4) | 2374 (4) | 3633 (2) | 12 | H(73) | −6612 (56) | 4920 (50) | 9976 (32) | 28 |
| C(34) | −6215 (4) | 3939 (3) | 1765 (2) | 11 | H(74) | −5428 (50) | 5430 (45) | 1148 (27) | 16 |
| C(35) | −7138 (4) | 2846 (4) | 1713 (2) | 12 | H(75) | −7172 (46) | 9338 (40) | 8425 (25) | 11 |
| C(36) | −7853 (4) | 2497 (4) | 992 (2) | 15 | H(76) | −8554 (55) | 8125 (48) | 8564 (30) | 23 |
| C(37) | −7647 (5) | 3210 (4) | 333 (2) | 14 | H(77) | 921 (23) | 203 (20) | 3434 (13) | 22 |
| C(38) | −6738 (5) | 4326 (4) | 390 (2) | 16 | H(78) | −9071 (71) | 645 (60) | 2342 (40) | 45 |
| C(39) | −6018 (4) | 4682 (4) | 1096 (2) | 13 | H(79) | −840 (56) | 465 (48) | 2727 (30) | 23 |
| Cl(40) | −8389 (1) | 9510 (1) | 9560 (1) | 26 | | | | | |

**Table V.** Structural Parameters for $BH_3X$-Type Molecules

| | $BH_3$-$PH_3$ | $P(NH_2)_3$-$BH_3$ | $PF_3BH_3$ | $C_7H_9N \cdot BH_3Cl$ | $[BH_3Cl]^-$ |
|---|---|---|---|---|---|
| method | X-ray | X-ray | microwave | X-ray | neutron |
| av B–X, Å | 1.93 | 1.887 (13) | 1.836 (12) | 1.901 (3) | 2.003 (8) |
| av B–H, Å | 1.20 | 1.11 | 1.207 (6) | 1.11 | 1.20 (2) |
| av H–B–H, deg | 115 | 115 | 115 | 117.4 | 114 (2) |
| av H–B–X, deg | 103 | 103 | 103 | 106.7 | 105 (2) |
| ref | *a* | *b* | *c* | *d* | this work |

[a] McGandy, E. L. *Diss. Abstr.* **1961**, *22*, 754. [b] Nordman, C. E. *Acta Crystallogr.* **1960**, *13*, 535–539. [c] Kuczkowski, R. L.; Lide, D. R., Jr. *J. Chem. Phys.* **1967**, *46*, 357–365. [d] Clayton, W. R.; Fratini, A. V.; Remmel, R.; Shore, S. G. *Cryst. Struct. Commun.* **1974**, *3*, 151–153.

Full-matrix refinement followed by difference Fourier techniques located all hydrogen atoms of the $[PPN]^+$ cation and solvent molecule, and three peaks, which could be assigned as hydrogens, in the vicinity of the boron atom. Refinement was then continued by using anisotropic thermal parameters for all nonhydrogen atoms. Due to the large number of parameters it was necessary to block the matrix.

The concurrent neutron experiment (vide infra) indicated disorder for the $[BH_3Cl]^-$ anion. For this reason further refinement was initiated in which the occupancy of the chlorine atoms was allowed to vary. The occupancies observed were 0.979 and 0.985 for the two chlorines of $CH_2Cl$ and 0.812 for the Cl in $[BH_3Cl]^-$. It thus appears that the crystal contain ca. 81% $[BH_3Cl]^-$ and a second ionic species (ca. 19%), strongly suspected to be $[B_2H_7]^-$.

**Neutron Data Collection and Structure Analysis.** A crystal with approximate dimensions 0.71 × 0.83 × 3.13 mm was mounted in a thin-walled quartz capillary on an aluminum pin oriented approximately along [001] and placed in a closed-cycle helium refrigerator.[19] Neutron diffraction data were collected at 90 K on an automated four-cycle diffractometer[20] using a beryllium-monochromated neutron beam of wavelength 1.1173 Å. The cell constants, determined from a least-squares fit of the centered setting angles of 32 reflections with general indices, are given in Table I. Intensities were measured in the $\theta/2\theta$ step-scan mode $[0.039 < (\sin\theta)/\lambda < 0.545\ \text{Å}^{-1}]$ with a scan width $[\Delta(2\theta)]$ of 3.0° and 75 steps in each scan. Throughout data collection, two intense reflections $[(207), (\bar{3}40)]$ were monitored at 80-reflection intervals. Intensities of these reference reflections showed only minor fluctuations throughout the course of the experiment. Background corrections were determined from seven steps on either end of each scan. Squared observed structure factors (a total of 4569) were obtained as $F_o^2 = I[\sin(2\theta)]$ and corrected for absorption by a modification of the analytical method of de Meulenaer and Tompa.[21] The crystal was bounded by eight planes belonging to forms {100}, {010}, {001}, and {043}.

The initial atomic positions for the P, N, Cl, and C atoms of bis(triphenylphosphine)nitrogen(1+) and methylene chloride were taken from the X-ray analysis at 107 K, and the H atoms on the phenyl rings were placed in calculated positions, assuming $d$(C–H) = 1.089 Å. A difference Fourier synthesis gave two strong positive peaks and three moderate and four weak negative peaks, in addition to the two strong negative peaks corresponding to the two hydrogen atomic positions in the methylene dichloride molecule. The four weak negative peaks surrounding the Cl position correspond to the one bridging and three terminal H atoms of

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(19) Air Products and Chemicals, Inc.; Displex Model CS-202.

(20) (a) McMullan, R. K.; Andrews, L. C.; Koetzle, T.F.; Reidinger, F.; Thomas, R.; Williams, G. J. B. "NEXDAS, Neutron and X-ray Data Acquisition System"; Brookhaven National Laboratory, unpublished work. (b) Dimmler, D. G.; Greenlaw, N.; Kelly, M. A.; Potter, D. W.; Randowitz, S.; Stubblefield, F. W. *IEEE Trans. Nucl. Sci.* **1976**, *NS-23*, 398.

(21) (a) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018. (b) Templeton, D. H.; Templeton, L. K. "Abstracts of Papers", American Crystallograpic Association Meeting, Storrs, CT, 1973; American Crystallograpic Association: Storrs, CT, p 143.

*Inorg. Chem.* **1985**, *24*, 3176–3181

the $[B_2H_7]^-$ impurity. Refinement of the populations corresponding to these four weak negative peaks resulted in an average H occupancy of 12 (3)%, a result (88% $[BH_3Cl]^-$/12% $[B_2H_7]^-$) consistent with the (81% $[BH_3Cl]^-$/19% $[B_2H_7]^-$) ratio obtained from the X-ray work (vide supra). Since the structure of the $[B_2H_7]^-$ anion subsequently has been solved on a pure sample of $[PPN]^+[B_2H_7]^-\cdot CH_2Cl_2$,[10,15] any discussion of the geometry of this minor $[B_2H_7]^-$ impurity would be superfluous here.

The structure of $[PPN]^+[BH_3Cl]^-\cdot CH_2Cl_2$ (ignoring the $[B_2H_7]^-$ impurity) initially was refined with a block-diagonal least-squares technique. The quantity minimized in the refinement was $\sum w^2(F_o - |F_c|)^2$, weights being chosen as $w = 1/\sigma^2(F_o)$, where $\sigma^2(F_o) = 4[\sigma_{count}{}^2(F_o{}^2) + (0.03F_o{}^2)^2]F_o{}^2$. In the later stages of full-matrix least-squares refinement, all reflections with $F_o{}^2 > 3\sigma_{count}(F_o{}^2)$ (2917 reflections) were included in the analysis. The six phenyl rings were treated as rigid groups with atoms placed in idealized positions (C–C = 1.397 Å; C–H = 1.089 Å) and individual isotropic thermal parameters; the rest of the atoms were refined with anisotropic thermal parameters. A final cycle (varying all positional and thermal parameters and scale and extinction[22] factors) resulted in $R_F = 0.071$ and $R_{wF} = 0.069$, with all shifts being less than 5% of their estimated standard deviations. The largest (negative) peak in the final difference Fourier synthesis was $-0.16 \times 10^{-12}$ cm/Å$^3$, corresponding to the bridging hydrogen of the $[B_2H_7]^-$ impurity. Neutron scattering factors used were (all $\times 10^{-12}$ cm) $b_B = 0.540$, $b_C = 0.665$, $b_N = 0.936$, $b_P = 0.513$, $b_{Cl} = 0.958$, and $b_H = -0.372$. An anomalous dispersion correction, $\Delta b'' = 0.021 \times 10^{-12}$ cm, was applied to boron.

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**Registry No.** $[PPN]^+[H_3BCl]^-$, 97391-09-8; $[Bu_4N]^+[H_3BCl]^-$, 69969-99-9; $[Et_4N]^+[H_3BCl]^-$, 97391-10-1; $B_2H_6$, 19287-45-7; $[PPN]^+Cl^-$, 21050-13-5; $[Bu_4N]^+Cl^-$, 1112-67-0; $[Et_4N]^+Cl^-$, 56-34-8; $[H_3BCl]^-$, 68011-52-9; $[BH_2Cl_2]^-$, 68011-51-8; $[B_2H_7]^-$, 27380-11-6.

**Supplementary Material Available:** Complete listings of anisotropic thermal parameters, bond distances, and bond angles from the X-ray analysis and anisotropic temperature factors from the neutron diffraction analysis of $[PPN]^+[BH_3Cl]^-\cdot CH_2Cl_2$ (9 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Texas Tech University, Lubbock, Texas 79409

# Electrochemistry and Reductant-Catalyzed Acid Hydrolysis of the ($\mu$-Oxo)bis(pentaaquochromium(III)) Ion

RANDY F. JOHNSTON and ROBERT A. HOLWERDA*

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Reductant-catalyzed acid hydrolysis of the ($\mu$-oxo)bis(pentaaquochromium(III)) ion (aquo dimer), giving $Cr(H_2O)_6{}^{3+}$ as the sole product, has been examined through cyclic voltammetric and stopped-flow kinetic approaches. The aquo dimer exhibits an irreversible one-electron cathodic wave with [acid]-independent (0.025–1.00 M $HClO_4$) $E_{pc} = +0.40$ V and $E_{1/2} = +0.52$ V vs. SHE (25 °C). This cathodic process, shifted by +0.93 V relative to that of the parent $Cr(H_2O)_6{}^{3+/2+}$ couple, may be understood as electron acceptance into the essentially nonbonding $e_g$ ($\pi$) molecular orbital of the linear, oxo-bridged reactant, followed by a rapid $C_{2v}$ Jahn–Teller distortion, which lifts the orbital degeneracy of the resultant $^2E_g$ ($D_{4h}$) ground state, disrupts $2p\pi(O)$–$3d\pi(Cr)$ overlap, and leads ultimately to bridge cleavage. Consistent with the electrochemical observations, $((H_2O)_5Cr)_2O^{4+}$ is susceptible to rapid reductant-catalyzed acid hydrolysis with $Cr^{2+}$(aq), $Ru(NH_3)_6{}^{2+}$, and even ascorbic acid ($H_2A$) as the electron donor. Rate-limiting outer-sphere one-electron transfer to $((H_2O)_5Cr)_2O^{4+}$ from $Cr^{2+}$(aq) ($k$(25 °C) = $2.50 \times 10^4$ M$^{-1}$ s$^{-1}$, $\Delta H^* = 6.0$ kcal/mol, $\Delta S^* = -17$ eu), $Ru(NH_3)_6{}^{2+}$ ($k$(25 °C) = $4 \times 10^5$ M$^{-1}$ s$^{-1}$), $H_2A$ ($k$(25 °C) = 6 M$^{-1}$ s$^{-1}$) and $HA^-$ ($k$(25 °C) = $7.2 \times 10^5$ M$^{-1}$ s$^{-1}$, $\Delta H^* = 7.7$ kcal/mol, $\Delta S^* = -6$ eu) is implied by the kinetic results at $I = 1.0$ M ($HClO_4/LiClO_4$). The apparent $((H_2O)_5Cr)_2O^{4+/3+}$ self-exchange electron-transfer rate constant calculated from these data on the basis of Marcus theory (ca. 10 M$^{-1}$ s$^{-1}$, 25 °C) is 6 orders of magnitude larger than that of the analogous $Cr(H_2O)_6{}^{3+/2+}$ couple, confirming the $\pi^n$ character (comparatively small Franck–Condon inner-sphere reorganizational barrier) of the aquo dimer redox orbital.

## Introduction

Since the discovery of $Cl_5RuORuCl_5{}^{4-}$, many other binuclear complexes with nearly linear M–O–M units have been structurally characterized.[1-7] The distinctive spectroscopic and magnetic properties of these linear $\mu$-oxo-bridged species have been interpreted from both spin–spin-coupling and molecular orbital standpoints.[6,7] While linear M–O–M structures generally are attributed to $p\pi(O)$–$d\pi(M)$ overlap,[8] the strength of such $\pi$ bonding is not easily assessed. Mechanistic studies of oxo-bridge cleavage should be revealing in this regard. This class of polynuclear complexes is susceptible to a variety of substitution reactions,[9] including exchange of nonbridging ligands and rearrangement to bis($\mu$-oxo) or hydroxo species, as well as rupture of the binuclear unit to give monomer fragments. The mechanistic characterization of these reactions has not advanced appreciably since Schwarzenbach and Magyar's pioneering study[10] of rearrangement coupled with substitution in the basic rhodo ($(NH_3)_5CrOCr(NH_3)_5{}^{4+}$) and related erythro chromium(III) ions (eq 1).

$$H_2O + (NH_3)_5CrOCr(NH_3)_4X^{(4-n)+} \rightarrow (NH_3)_5Cr(OH)Cr(NH_3)_4OH^{4+} + X^{n-} \quad (1)$$

$$X = NH_3,\ NCS^-,\ Cl^-,\ F^-$$

Although $(H_2O)_5CrOCr(H_2O)_5{}^{4+}$ (aquo dimer) has not been isolated in the solid state, this binuclear complex is readily obtained from the reaction of chromous ion with 1,4-benzoquinone in acidic

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