authors found that the alkoxy or phenoxy groups of the phosphite are successively exchanged by the chlorine atoms of the boron trichloride, the final products being trialkyl(aryl) borates and phosphorus trichloride. No coordination compounds involving a phosphorus–boron bond could be detected.[1,3] Boron tribromide was reported to behave similarly.[4] This is somewhat surprising since trialkyl phosphites have been shown to be about as nucleophilic as triethylamine[5] and should thus be expected to be good electron donators for boron trihalides. This communication describes the synthesis of stable trialkyl phosphite–boron tribromide coordination compounds by bromination of the corresponding trialkyl phosphite–borane[5] complexes in which the P–B bond is already present

$$\underset{\text{I}}{(RO)_3PBH_3} + 3Br_2 \longrightarrow \underset{\text{II}}{(RO)_3PBBr_3} + 3HBr$$

The syntheses, elemental analyses, and ^{31}P nmr spectra of compounds II are consistent with the proposed structure. It is interesting that the phosphite moiety in I survives the attack by bromine. This is evidenced by the titration[6] of the phosphorous acid which is formed on heating II overnight on a steam bath with concentrated hydrochloric acid and methanol. The presence of the phosphite moiety furthermore follows from the fact that II (R = i-C_3H_7) could be independently prepared by the direct reaction of triisopropyl phosphite with boron tribromide.

The ^{31}P nmr spectra of the compounds are in accord with the proposed structure. Compounds of the type $(RO)_3PBBr_3$ would be expected to exhibit a single ^{31}P resonance split into a 1:1:1:1 quartet by the boron nucleus. This quartet is indeed observed in all cases (centering in the range −33.5 to −40.9 ppm, relative to H_3PO_4). Similar quartets were found for trialkyl phosphite–boranes $(RO)_3PBH_3$.[7]

Table I lists the products and some of their properties.

TABLE I

TRIALKYL PHOSPHITE–BORON TRIBROMIDE COORDINATION COMPOUNDS

Formula	Yield, %	Mp, °C	^{31}P nmr, ppm, rel to H_3PO_4	J_{PB}, Hz	% decompn[a] in dioxane at room temp after 3 days
$(i\text{-}C_3H_7O)_3PBBr_3$	85	82	−33.5	285	1.9
$(n\text{-}C_4H_9O)_3PBBr_3$	82	42	. . .	. . .	7.0
$(C_2H_5O)_3PBBr_3$	92	33–34	−36.2	271	10.5
$(CH_3O)_3PBBr_3$	57	102–103	−40.9	271	33.0
$(i\text{-}C_3H_7O)_3PBH_3$	80	*b*	−111	80	No decompn

[a] The decomposition in dioxane was determined by precipitation with H_2O and recovery of the products. The extent of decomposition was checked by titration of the ionic bromine in the aqueous phase. [b] Bp 42° (1.1 mm).

It is interesting to compare the relative stabilities of the coordination compounds in dioxane solution. The rate of decomposition decreases with increasing alkyl substitution in the $P(OR)_3$ moiety. This may be due to steric hindrance in the assumed exchange of the bromine with the alkoxy group in II especially when the group R is the bulky isopropyl substituent. Preliminary attempts to chlorinate $(RO)_3PH_3$ led to crystalline products the identification of which is still to be performed.

Method of Preparation.—The bromine compounds were prepared by slowly adding a small excess of bromine to a mixture of trialkyl phosphite–borane[5] in an excess of finely divided ice (vigorous stirring!). The excess halogen was removed by treatment with sodium sulfite. The oily products crystallized and were filtered, washed with water, and dried in the air. The compounds were purified by dissolving in dioxane and treating with dilute sodium hydroxide. The precipitates were then washed with water, dried under vacuum, and recrystallized from methanol or hexane. Compound II, R = i-C_3H_7, was also prepared by adding a solution of boron tribromide in hexane to a solution of isopropyl phosphite in hexane at −40°.

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(5) T. Reetz, *J. Amer. Chem. Soc.*, **82**, 5039 (1960).

(6) Titrated with I_2 in $NaHCO_3$ solution. Back-titration with arsenite.

(7) We are indebted to Dr. M. M. Crutchfield for the spectra of $(i\text{-}C_3H_7O)_3PBBr_3$ and $(RO)_3PBH_3$ and their interpretation and to Mr. L. F. Johnson of the Varian Co. for the spectra of the other compounds listed in Table I.

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Structural Ambiguity of the $B_{10}H_{14}^{2-}$ Ion

BY WILLIAM N. LIPSCOMB, RICHARD J. WIERSEMA,
AND M. FREDERICK HAWTHORNE*

Received July 6, 1971

The structure of $B_{10}H_{14}^{2-}$, not previously established, has been assumed[2] to be similar to that of $B_{10}H_{12}(NCCH_3)_2$, with which it is isoelectronic in the sense that the ligand CH_3CN is replaced by H^-. In this structure of 2632 topology[2] there are BH_2 groups at B_6 and B_9 (Figure 1) and hydrogen bridges between B_5 and B_{10} and between B_7 and B_8. However, the hydrogen atom arrangement observed in $B_{10}H_{14}$ is also a possibility in a structure of 4450 topology having bridges B_5HB_6, B_6HB_7, B_8HB_9, and B_9HB_{10}. This ^{11}B nmr study resolves this structural ambiguity and suggests relative emphasis on three-center resonance as compared with uniform charge distribution as a preferred criterion for resolving structural ambiguity when steric and other factors are comparable.

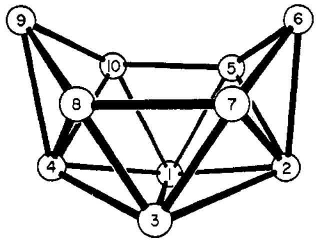

Figure 1.—Numbering system and the B_{10} fragment of the icosahedron seen in $B_{10}H_{14}$.

Experimental Section

Various salts of $B_{10}H_{14}^{2-}$ were prepared according to the pro-

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* To whom correspondence should be addressed at the University of California.

(1) Contribution No. 2875.

(2) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 183.

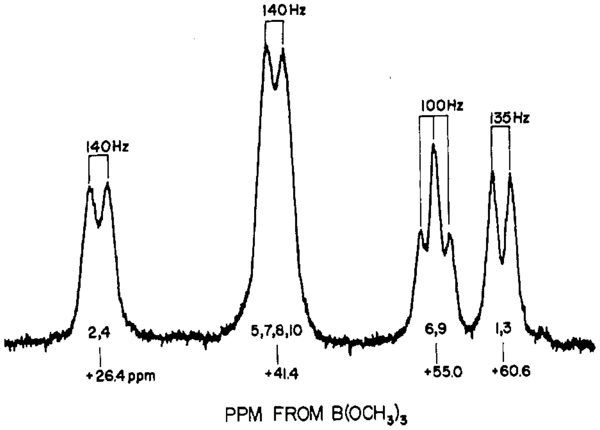

Figure 2.—The 80.5-MHz ^{11}B nmr spectrum of $Rb_2B_{10}H_{14}$ in H_2O.

cedure outlined in the literature.[3] The 80.5-MHz ^{11}B nmr spectra were obtained on an instrument designed by Professor F. A. L. Anet of the Department of Chemistry, University of California, Los Angeles, Calif. The ^{11}B nmr spectra of the rubidium, sodium, and tetra-*n*-butylphosphoniun salts of $B_{10}H_{14}^{2-}$ were obtained in water and methylene chloride, respectively. The spectra were identical indicating that any cation or solvent effects were negligible in determining the structure of $B_{10}H_{14}^{2-}$.

Discussion

The 80.5-MHz ^{11}B nmr spectrum of $Rb_2B_{10}H_{14}$ in H_2O clearly indicated (Figure 2) the presence of a BH_2 group at positions 6 and 9 in $B_{10}H_{14}^{2-}$ (Table I).

Table I

The 80.5-MHz ^{11}B Nmr Spectrum of $Rb_2B_{10}H_{14}$ in H_2O

Chemical shift[a] (J_{BH})	Signal (rel area)	Chemical shift[a] (J_{BH})	Signal (rel area)
+26.4 (140)	Doublet (2)	+55.0 (100)	Triplet (2)
+41.4 (140)	Doublet (4)	+60.6 (135)	Doublet (2)

[a] Chemical shift *vs.* an external capillary of methyl borate. The coupling constants are accurate to ±10 Hz.

We now compare the observed 2632 topology for $B_{10}H_{14}^{2-}$ based upon the $B_{10}H_{12}L_2$ structure with the 4450 topology based upon the hydrogen arrangement in $B_{10}H_{14}$. If for three-center bonds among boron atoms we retain only those of the central type,[4] there are 24 valence structures of the 2632 type: four each having single bonds 1-2, 3-8, 6-7; 1-2, 6-7, 8-9; 1-5, 3-7, 8-9; 1-5, 6-7, 8-9; 1-5, 6-7, 9-10; and two each having single bonds 1-3, 5-6, 8-9; 1-3, 5-6, 9-10. The 4450 topology has only one three-center valence structure, having single bonds 1-3, 2-6, 4-9, 5-10, 7-8. If we suppose that resonance confers stability, then the observed 2632 topology is favored.

On the other hand, the charge is much more evenly distributed in the 4450 topology, for which charges are 0.33− on B_1 and B_2, 0.17− on B_5, and 0.00 on B_6. By contrast, the equal weighting of charge distributions in the 2632 topology yields charges of 0.25− on B_1, 0.06− on B_2, 0.04− on B_5, and 0.61− on B_6. If the smoothing of the charge distribution is more important than resonance, we would therefore expect the 4450 topology to be favored contrary to these nmr results.

It has been noted that the formal replacement of a ligand, L, by H^- need not always yield the analogous structure. For example, this ambiguity was realized for $B_9H_{14}^-$ in the study[5] of the $B_9H_{13}(NCCH_3)$ structure. A recent X-ray diffraction study[6] has shown that $B_9H_{14}^-$ has a hydrogen arrangement not expected from analogy with $B_9H_{13}L$. The observed $B_9H_{14}^-$ structure is favored by both resonance and charge-smoothing arguments.[4] Thus $B_9H_{14}^-$ and $B_9H_{13}L$ make the structural ambiguity real; but only for the $B_{10}H_{14}^{2-}$ and $B_{10}H_{12}L_2$ pair do we have the first comparison of known structures which allows a choice of resonance stabilization, compared with an evened charge distribution, as a probable dominant factor in determining the hydrogen arrangement in the negative ion. Tests of the relative importance of these and other factors are to be expected in further studies of formally isoelectronic boron hydride ions and ligand derivatives.

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[3] E. L. Muetterties, *Inorg. Chem.*, **2**, 647 (1963).

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[5] F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1335 (1961), especially Figure 3.

[6] N. N. Greenwood, H. J. Gysling, and J. A. McGinnety, *Chem. Comm.*, 505 (1970).

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Synthesis and Characterization of Trichlorotetrahydrofuraniron(III)

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Considerable work by Kern[1] and Fowles, Rice, and Walton[2] has been done to investigate the complexes formed by transition metal chlorides and tetrahydrofuran, THF. Contrary to the results of Kern,[1] we have been able to synthesize a monomeric, neutral complex by the reaction of anhydrous iron(III) chloride with THF. Interest in such complexes stems from the use of transition metal ions as catalysts in polymerization reactions of cyclic ethers. Cyclic ethers smaller than THF open readily in the presence of transition metal chlorides[3,4] and, under certain conditions, ring opening occurs in the THF–$FeCl_3$ system.[1,2]

In this paper we report the synthesis and characterization of the complex $FeCl_3 \cdot C_4H_8O$. The molecular weight data, obtained cryoscopically in benzene solution, indicate concentration-dependent association of the complex. Infrared data support coordination of THF to the metal and magnetic susceptibility data support assignment of a sextet ground state for iron(III). Electronic spectral data in benzene and in 1,2-dichloroethane are also reported.

Experimental Section

Reagents.—Anhydrous ferric chloride was prepared by passing chlorine gas over heated iron card teeth[5] and subliming the prod-

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[3] A. E. Gurgiolo, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **4** (2), 252 (1963).

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