TABLE II

X-RAY DATA FOR $CsFeF_3$

hkl	d_{calcd}	d_{obsd}	I/I_0	*hkl*	d_{calcd}	d_{obsd}	I/I_0
103	3.628	3.62	5.3	214	1.772	1.772	4.9
110	3.079	3.07	10.0	215	1.668	1.668	0.4
104	3.044	3.05	6.3	207	1.661	1.660	0.8
021	2.625	2.624	0.6	118	1.590	1.590	0.6
105	2.595	2.592	0.4	109	1.577	1.577	0.6
202	2.509	2.506	1.6	220	1.540	1.539	1.8
006	2.475	2.473	1.4	208	1.524	1.524	0.6
203	2.347	2.347	4.9	217	1.463	1.462	0.6
204	2.166	2.164	6.5	313	1.417	1.418	0.6
205	1.984	1.984	1.0	209	1.403	1.403	0.6
107	1.972	1.971	1.0	314	1.374	1.374	1.8
116	1.930	1.929	0.6	226	1.307	1.307	0.6
213	1.867	1.867	0.8	403	1.287	1.287	0.3
300	1.778	1.777	3.1	404	1.255	1.256	0.7

The melting point of $CsFeF_3$ was found to be 708 ± 5°. The transparent crystals are uniaxial positive with $n_\omega = 1.544$ and $n_\epsilon = 1.560$.

Summary

Single crystals of FeF_2, $RbFeF_3$, and $CsFeF_3$ were successfully prepared. X-Ray diffraction data obtained at room temperature indicate $RbFeF_3$ to possess the cubic perovskite structure with $a = 4.174$ A and $CsFeF_3$ to exhibit a hexagonal distortion of the ideal perovskite structure with $a = 6.158$ A and $c = 14.855$ A. The distortion from cubic symmetry involves a shortening of one (111) direction which becomes one-half the c axis of the hexagonal unit cell.

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The Reaction of Cyclopolyphosphines with Boron Halides[1]

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The behavior of cyclopolyphosphines toward transition metal compounds has received some attention recently.[2] However, very little has been published concerning the reactivity of cyclopolyphosphines toward Lewis acids such as the boron halides. Mahler and Burg[3] report that $(CF_3P)_4$ is not attacked by BF_3, B_2H_6, or protic acids within reasonable temperature limits, whereas Kuchen and Buchwald[4] were able to isolate a material of empirical composition $(C_6H_5P)_3\cdot BF_3$ from the reaction of form A of $(C_6H_5P)_n$ (n has been shown to be 5 for this form[5]) with BF_3 in benzene solution. The objects of the present work were (a) to see if Kuchen and Buchwald's interesting observations could be repeated and (b) to extend the scope of the reaction to include other boron halides and other cyclopolyphosphines.

Experimental Section

Reagents.—The boron halides were obtained from commercial sources and were used without further purification. Form A of $(C_6H_5P)_n$ was prepared by the magnesium coupling of $C_6H_5PCl_2$ following the directions of Henderson, *et al.*[6] Tetra-*n*-butylcyclotetraphosphine was prepared by Rauhut and Semsel's method.[7] We found that the ethyl and *n*-propyl homologs could also be prepared in comparable yields by the same method.

General Procedure.—The BF_3 and BCl_3 compounds were prepared by bubbling BF_3 or BCl_3 through a benzene or *n*-hexane solution of the cyclopolyphosphine [at 0° in the case of $(C_6H_5P)_n$]. The BBr_3 compounds were prepared by adding a slight excess of BBr_3 (diluted with solvent) to a benzene or *n*-hexane solution of the cyclopolyphosphine. In each case the product was isolated by vacuum evaporation of the solvent plus excess boron halide. Generally, this left oily materials which slowly solidified upon standing under a nitrogen atmosphere. Several days was required for the solidification of compounds IV through XII. With the exception of I and II the compounds gradually softened over a wide range of temperatures. Compound I melted at 130–140° and compound II at 185–195°. No suitable recrystallization solvents were discovered. The analytical data are presented in Table I.

All operations were carried out under a dry nitrogen atmosphere owing to the ease of hydrolysis and/or oxidation of both products and starting materials.

Spectra.—The infrared spectra of Nujol mulls or liquid films were run on a Beckman IR 7 spectrophotometer equipped with NaCl and CsI optics. Oxidation of the mulls or films was prevented by the insertion of thin Teflon gaskets between the NaCl or CsI plates.

Discussion

Like Kuchen and Buchwald[4] we have been able to isolate a compound of empirical composition $(C_6H_5P)_3\cdot BF_3$ from the reaction of form A of $(C_6H_5P)_n$ with BF_3. The observed stoichiometry would imply an equation such as[8]

$$3(C_6H_5P)_4 + 4BF_3 \longrightarrow 4(C_6H_5P)_3\cdot BF_3$$

It is also evident that other boron halides will react with the same cyclopolyphosphine to give the analogous products II and III. The fact that two BBr_3 molecules react per three C_6H_5P units (compound III) probably relates to the higher acid strength of BBr_3. Products of empirical composition $(RP)_2\cdot BX_3$ are obtained from the reaction of alkyl-substituted cyclopolyphosphines with

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(1) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(2) A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, **80**, 2334 (1958); K. Issleib and W. Seidel, *Z. Anorg. Allgem. Chem.*, **303**, 155 (1960); H. G. Ang and J. S. Shannon, *Chem. Commun.*, 10 (1965); G. W. A. Fowles and D. K. Jenkins, *ibid.*, 61 (1965); D. G. Hicks and J. A. Dean, *ibid.*, 172 (1965).

(3) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

(4) W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2296 (1958).

(5) J. J. Daly, *J. Chem. Soc.*, 6147 (1964).

(6) W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963).

(7) M. M. Rauhut and A. M. Semsel, *J. Org. Chem.*, **28**, 473 (1963).

(8) Although form A of $(C_6H_5P)_n$ has recently been shown to be $(C_6H_5P)_5$ in the solid phase (ref 5), we have written the equation in terms of $(C_6H_5P)_4$ because this appears to be the molecular form in solution. See W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963); W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2296 (1958); and F. Pass and H. Schindlbaur, *Monatsh.*, **90**, 148 (1959).

Table I

Boron Halide Adducts of Cyclopolyphosphines

Compd no.	Compd	Analysis[a] Calcd, % C	H	P	X[b]	Found, % C	H	P	X[b]
I	$(C_6H_5P)_3 \cdot BF_3$	55.14	3.86	23.70	17.30	54.16	4.58	24.59	...
II	$(C_6H_5P)_3 \cdot BCl_3$	48.98	3.43	21.05	24.10	49.25	3.50	20.97	24.04
III	$(C_6H_5P)_3 \cdot 2BBr_3$	26.19	1.83	11.26	58.10	26.63	4.65	11.50	58.96
IV	$(C_2H_5P)_2 \cdot BF_3$	25.47	5.73	32.85	35.95	25.85	5.92	33.25	...
V	$(C_2H_5P)_2 \cdot BCl_3$	20.25	4.25	25.30	44.86	20.15	4.52	...	...
VI	$(C_2H_5P)_2 \cdot BBr_3$	12.96	2.72	16.71	67.61	13.22	3.03	16.46	...
VII	$(n\text{-}C_3H_7P)_2 \cdot BF_3$	33.34	6.53	28.67	31.46	33.71	6.68	29.00	...
VIII	$(n\text{-}C_3H_7P)_2 \cdot BCl_3$	23.34	5.31	23.34	48.01	22.91	5.65	...	...
IX	$(n\text{-}C_3H_7P)_2 \cdot BBr_3$	18.08	3.54	15.54	60.13	17.70	3.83	...	...
X	$(n\text{-}C_4H_9P)_2 \cdot BF_3$	39.35	7.43	25.38	27.84	31.98	8.04	23.86	...
XI	$(n\text{-}C_4H_9P)_2 \cdot BCl_3$	32.73	6.18	21.11	39.98	32.42	6.29	...	35.87
XII	$(n\text{-}C_4H_9P)_2 \cdot BBr_3$	22.51	4.25	14.52	58.72	22.45	4.36	14.25	...

[a] All analyses performed by Alfred Bernhardt, Mülheim, Ruhr, Germany. [b] X = F, Cl, or Br.

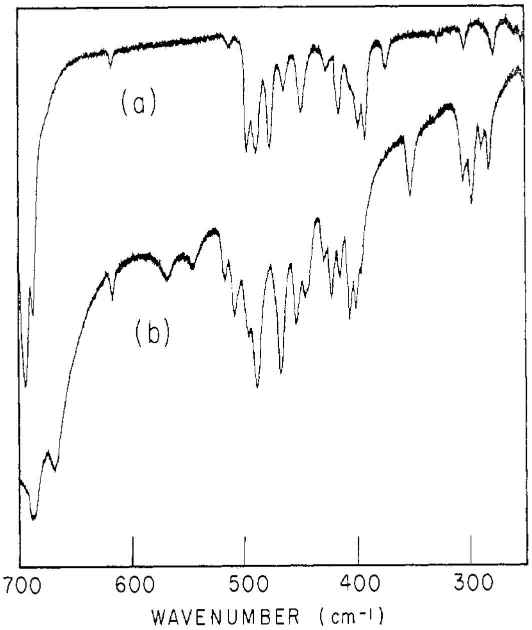

Figure 1.—Infrared spectra of (a) $(C_6H_5P)_5$ and (b) $(C_6H_5P)_3 \cdot BCl_3$ in the 250–700-cm^{-1} range.

boron halides. As noted in the Experimental Section these adducts do not precipitate from solution yet, once isolated by evaporation of the solvent, are reactive with or insoluble in common solvents. It is therefore possible that the adducts as formed in solution are different from those which we isolated.

The intractable nature of the adducts limited us to indirect structural evidence. The general similarity of the infrared spectra of the cyclopolyphosphines and their boron halide reaction products (see Figure 1 for a comparison of $(C_6H_5P)_5$ and $(C_6H_5P)_3 \cdot BCl_3$) would suggest that the phosphorus rings are intact.[9] The infrared spectra of I, II, and III show the characteristic monosubstituted benzene frequencies v and f in the 680–747 cm^{-1} range,[10] indicating that the BX_3 molecules are most likely associated with the phosphorus atoms in these compounds. Frequencies which could be assigned to tetrahedrally bonded BX_3 groups[11] were also found in some of the spectra. In the others, these were probably obscured by the phenyl or alkyl group modes.

One structural interpretation is that the compounds involve phenyl- or alkyl-substituted polyphosphine rings coordinated to the appropriate number of BX_3 groups. If the alkyl-substituted compounds IV–XII do involve phosphorus rings, then the molecular formulas might be twice the empirical formulas shown in Table I. Likewise, the molecular formulas of the phenyl-substituted adducts I, II, and III might also be twice their empirical formulas since there appears to be no evidence for the existence of a three-membered phosphorus ring. However, higher degrees of polymerization or mixtures of polymers cannot be excluded on the basis of the present evidence.

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[9] R. L. Amster, W. A. Henderson, and N. B. Colthup, *Can. J. Chem.*, **42**, 2577 (1964), have identified the asymmetric ring stretch near 500 cm^{-1} in the phenyl-P rings. R. L. Amster, N. B. Colthup, and W. A. Henderson, *Spectrochim. Acta*, **19**, 1841 (1963), found that this frequency lies in the range 465–490 cm^{-1} in the alkyl-P rings. The symmetric ring stretch occurred at 390–410 cm^{-1} in the alkyl-P rings.

[10] For assignments and notation, see D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).

[11] R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, **20**, 1487 (1964) and references therein.

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Fluorophosphine Ligands. II. The Preparation and Characterization of Difluoroiodophosphine

By R. W. Rudolph, J. G. Morse, and R. W. Parry

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Although difluoroiodophosphine was previously described as unstable and difficult to characterize,[1] it has now been obtained in pure form and characterized unequivocally.

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[1] R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).