Contribution from the Whittier Research Laboratory,
American Potash & Chemical Corporation, Whittier, California

P-Hexaalkyl-B-hexahalocyclotriborophanes[1,2]

By MARVIN H. GOODROW,[3] ROSS I. WAGNER, and ROBERT D. STEWART

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Syntheses have been developed for the B-halogenated cyclotriborophanes, $(RR'PBX_2)_3$, wherein the hydridic hydrogens of the cyclotriborophanes were replaced by halogen using either alkyl halides, aluminum halide catalyzed alkyl halides, N-halosuccinimides, or anhydrous hydrogen fluoride. Rapid replacement of bromine by chlorine on the cyclotriborophane ring was observed in the presence of aluminum halides. Relative effects of boron substituents on chemical properties of borophanes have been established by a simple screening test for oxidative and hydrolytic stability.

Two basic approaches leading to useful borophane polymers have involved altering the substituents on the boron and/or phosphorus atoms and changing the degree of polymerization. In particular, attention has centered on varying the substituents on the phosphorus moiety of the monomer unit, $RR'PBH_2$, due to the availability of the parent phosphines and diborane, with the type and extent of such substitution having considerable bearing on the degree of polymerization. Thus, cyclic trimers and tetramers, fused polycyclic, linear, and cross-linked borophane polymers, have been prepared by pyrolytic dehydrogenation of organophosphine borines as intermediates by a variety of synthetic routes and reaction conditions.[4]

To prepare B-dimethyl-substituted borophane polymers, Burg and Wagner[4a] allowed dimethylphosphine (I) to react with a dimethylhaloborine (II) in the presence of triethylamine to obtain well-defined dodecamethylcyclotriborophane (III). Application of this

$$\underset{\text{I}}{3(CH_3)_2PH} + \underset{\text{II}}{3(CH_3)_2BX} \rightarrow \underset{\text{III}}{[(CH_3)_2PB(CH_3)_2]_3} + 3HX \qquad (1)$$

technique to prepare a B-dihalo-substituted cyclotriborophane using dimethylphosphine and trichloroborine, however, provided only poorly characterized materials which appeared to be low molecular weight linear polymers.[5] Recently, Nöth and Schrägle[6] have synthesized cyclodiborophanes, $[R_2PBX_2]_2$, from BCl_3 and $LiP(C_2H_5)_2$ and from pyrolysis of the adduct $(CH_3)_3SiP(n\text{-}C_4H_9)_2{:}BX_3$, derived from $(CH_3)_3SiP(n\text{-}C_4H_9)_2$ and BX_3; a similar pyrolysis of $(CH_3)_3SiP(CH_3)_2$ and dipropylchloroborine at 140° formed P-hexamethyl-B-hexa-*n*-propylcyclotriborophane.

Cyclic dimers, P-tetraphenyl-B-tetrabromocyclodiborophane and P-tetraphenyl-B-tetraiodocyclodiborophane, have also been obtained by dehydrohalogenation of the appropriate diphenylphosphine trihaloborine with triethylamine.[7]

Early in the research on borophane polymers a convenient method for halogenation of the preformed cyclotriborophane nucleus was inadvertently discovered.[4c] An attempt was made using the Friedel–Crafts reaction to B-alkylate P-hexamethylcyclotriborophane since successful alkylations of pentaborane-9 and decaborane had been achieved but have only recently been reported.[8] A mixture of P-hexamethylcyclotriborophane, methyl bromide, and aluminum chloride was observed to evolve methane rather than hydrogen halide, suggesting that halogenation of the boron had occurred in preference to methylation. The stoichiometry of the reaction indicated by eq. 2 was definitively established by isolation and characterization

$$\underset{\text{IV}}{(RR'PBH_2)_3} + \underset{\text{V}}{6R''X} \rightarrow \underset{\text{VI}}{(RR'PBX_2)_3} + \underset{\text{VII}}{6R''H} \qquad (2)$$

of the methane and B-halogenated cyclotriborophanes (Table I). *n*-Butyl chloride with aluminum chloride catalyst proved an equally effective halogenating

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[2] The nomenclature used in this paper is suggested as a system capable of unambiguously describing all compounds derived either from the as yet unknown monomer units, (H_2PBH_2) and $(HPBH)$, or from any combination of these units. Although the currently used system of nomenclature (wherein the title compounds would be called dialkylphosphinoborine trimers) is adequate for simple compounds which are multiples of a single monomer unit, it is not amenable to closely related derivatives of two or more monomer units nor is it capable of describing polycyclic compounds. The authors express their appreciation to Dr. Kurt L. Loening, Chemical Abstracts Service, for the suggestion that the nomenclature of the Ring Index be used thus eliminating new trivial names (Ring Index name for $(H_2PBH_2)_3$, borphosphane, First Supplement No. 7740). With due regard for the general applicability of the "a" system and the convenience it offers in indexing, we feel that the euphonious trivial name cyclotriborophane would be preferable to 1,3,5-triphosphonia-2,4,6-triboratocyclohexane for the hexaatomic ring system. Furthermore, we feel (Dr. Loening and one referee concur) that the "siloxane type" nomenclature [see *Chem. and Eng. News*, **30**, 4517 (1952)] for inorganic systems of alternating elements is gaining wider acceptance and is in fact currently under consideration by the IUPAC Organic and Inorganic Nomenclature Commissions. For symmetrically substituted compounds, numerical locants have been replaced by the more abbreviated atomic symbols.

[3] Agriculture Research Division, Shell Development Company, Modesto, Calif.

[4] (a) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953); (b) A. B. Burg and G. Brendel, *ibid.*, **80**, 3198 (1958); (c) A. B. Burg, *J. Inorg. Nucl. Chem.*, **11**, 258 (1959); (d) R. I. Wagner and F. F. Caserio, Jr., *ibid.*, **11**, 259 (1959); (e) R. I. Wagner, F. F. Caserio, Jr., L. D. Freeman, and R. D. Stewart, Abstracts of Papers, 135th National Meeting, American Chemical Society, April, 1959, p. 49-O; (f) A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **82**, 2145, 2148 (1960); (g) R. H. Biddulph, M. P. Brown, R. C. Cass, R. Long, and H. B. Silver, *J. Chem. Soc.*, 1822 (1961); (h) R. I. Wagner, L. D. Freeman, H. N. Hammer, E. M. Evleth, Jr., R. D. Stewart, H. J. Rockoff, F. F. Caserio, Jr., and S. E. Gordon, "Preparation of Some P-Hexaorganocyclotriborophanes and P-Octaorganocyclotetraborophanes," manuscript in preparation.

[5] R. I. Wagner, unpublished observation.

[6] H. Nöth and W. Schrägle, *Z. Naturforsch.*, **16b**, 473 (1961); *Angew. Chem. Intern. Ed. Engl.*, **1**, 457 (1962).

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[8] N. J. Blay, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 424 (1960); N. J. Blay, I. Dunstan, and R. L. Williams, *ibid.*, 430 (1960); G. E. Ryschkewitsch, S. W. Harris, E. J. Mezey, H. H. Sisler, E. A. Weilmuenster, and A. B. Garrett, *Inorg. Chem.*, **2**, 890 (1963); E. R. Altwicker, G. E. Ryschkewitsch, A. B. Garrett, and H. H. Sisler, *ibid.*, **3**, 454 (1964); T. P. Onak and F. J. Gerhart, *ibid.*, **1**, 742 (1962).

TABLE I

PREPARATION OF P-HEXAALKYL-B-HEXAHALOCYCLOTRIBOROPHANES

Reactants					Products, %	
$(CH_3RPBH_2)_3$ (IV)		CH_3X[a] (V)	AlX_3[a] catalyst,	Time, hr., at ambient	$(CH_3RPBX_2)_3$	CH_4
R	mmoles	X	mmoles	temp.	(VI)	(VII)
CH_3	1.148	Cl	1.37	1.0	99.1	97.1
C_2H_5	0.7330	Cl	2.344	17.0	91.2	98.5
CH_3	1.080	Br	1.485	0.5[b]	98.2	97.2[b]
CH_3	1.261	Br	1.409[c]	67.0	[d]	...
CH_3	1.466	I	1.777	16.0[e]	94.7	98.6[e]

[a] Excess (*ca.* 3 ml.) methyl halide used as reaction solvent with corresponding aluminum halide catalyst. [b] An additional 100 min. at 60° increased the quantity of methane from the initial 96.6% observed. [c] Aluminum chloride catalyst. [d] Elemental analyses (C, 11.94; H, 3.20; Br, 53.8; Cl, 10.6) of the 0.6830 g. of product, m.p. 405° dec., indicated the empirical formula $C_{2.03}H_{6.49}BPR_{1.38}Cl_{0.61}$ assuming a B:P ratio of 1:1. [e] An additional 55 hr. at 50° increased the quantity of methane from the initial 86.6% observed.

agent by producing a 91% yield of P-hexamethyl-B-hexachlorocyclotriborophane although the isolation was considerably more difficult. The by-products in this case were hydrogen, hydrogen chloride, butane, isobutane, *sec*-butyl chloride, and difficultly volatile polymerization products derived from the alkyl halide. Aluminum chloride catalyzed chlorobenzene degraded rather than halogenated P-hexamethylcyclotriborophane.

Other halogenated hydrocarbons were found to serve as halogenating agents for P-hexamethylcyclotriborophane. Carbon tetrachloride reacted slowly (113 hr.) at elevated temperatures (130°) to produce P-hexa-

$$(RR'PBH_2)_3 + 6CCl_4 \rightarrow (RR'PBCl_2)_3 + 6HCCl_3 \quad (3)$$

methyl-B-hexachlorocyclotriborophane in 97.7% yield, while the presence of the Lewis acid catalyst, aluminum chloride, markedly accelerated the reaction which was complete after 1.25 hr. at 77°. Evidence for formation of the coproduct chloroform was obtained by repeated observation of the spectrum of the uncatalyzed reaction mixture (eq. 3, $R = R' = CH_3$) in an infrared cell. During the 52.4-hr. period that the cell remained in the beam steady decreases in the BH_2 stretching (2380 and 2340 cm.$^{-1}$) and deformation (1108 cm.$^{-1}$) bands[9] were observed while there was a corresponding increase in the intensity of the 1218 cm.$^{-1}$ chloroform band.[10]

The reaction of P-hexamethylcyclotriborophane with chloroform proceeded extremely slowly to form methylene chloride, which was characterized by infrared analysis. Reaction according to eq. 4 was only 26% complete after 13 hr. at 130°.

$$(RR'PBH_2)_3 + 6HCCl_3 \rightarrow (RR'PBCl_2)_3 + 6H_2CCl_2 \quad (4)$$

The catalytic nature of the aluminum halides was further demonstrated by the failure of aluminum chloride to chlorinate P-hexamethylcyclotriborophane in hydrocarbon media and by the nearly instantaneous and quantitative conversion of P-hexamethyl-B-hexabromocyclotriborophane (VIII) to P-hexamethyl-B-hexachlorocyclotriborophane (IX) in chloroform solution containing dissolved aluminum bromide (eq. 5). In the absence of the catalyst, P-hexamethyl-B-hexabromocyclotriborophane was recovered unchanged from chloroform solution after 2 hr. at ambient temperature.

$$\underset{\text{VIII}}{[(CH_3)_2PBBr_2]_3} + 6HCCl_3 \rightarrow \underset{\text{IX}}{[(CH_3)_2PBCl_2]_3} + 6HCCl_2Br \quad (5)$$

Although no detailed study has been undertaken to elucidate the halogenation mechanism, the following sequence appears plausible as justification for the products and supports the role of the Lewis acid (AlX_3) as a catalyst. A B-hexahalocyclotriborophane mixture, with an empirical formula $C_{2.03}H_{6.49}PBBr_{1.38}Cl_{0.61}$ (based on a P:B ratio of 1:1), derived from the reaction of P-hexamethylcyclotriborophane and methyl bromide–aluminum chloride (eq. 6) lends credence to the proposal that the AlX_4^- ion is the halogenating species (eq. 8).

$$RX + AlX_3 \rightarrow \overset{+}{R}\,\overset{-}{A}lX_4 \quad (6)$$

$$\equiv B{-}H + \overset{+}{R}\,\overset{-}{A}lX_4 \rightarrow \equiv\overset{+}{B}\,\overset{-}{A}lX_4 + RH \quad (7)$$

$$\equiv\overset{+}{B}\,\overset{-}{A}lX_4 \rightarrow \equiv B{-}X + AlX_3 \quad (8)$$

P-Hexamethyl-B-hexabromocyclotriborophane, $[(CH_3)_2PBBr_2]_3$, was conveniently prepared by high vacuum techniques from P-hexamethylcyclotriborophane, methyl bromide, and aluminum bromide catalyst in high yield (Table I); however, the product was found to contain a small quantity of chlorine derived from impurities present in commercial methyl bromide. To obtain chlorine-free material it was first necessary to treat the methyl bromide and aluminum bromide with a small amount of P-hexamethylcyclotriborophane with which the chlorine-containing impurities reacted preferentially. The reagents were then volatilized and condensed onto more cyclotriborophane for reaction and subsequent work-up to yield a chlorine-free product. Refluxing methylene bromide and aluminum bromide catalyst provide a more convenient method of halogenation. However, when applied to the bromination of *sym*-P-hexamethyl-B-tribromocyclotriborophane,[11] the yield was unusually low.

A mixture of isomeric *sym*-P-trimethyltriethylcyclotriborophanes (IV, $R = CH_3$, $R' = C_2H_5$) and methyl chloride–aluminum chloride reacted smoothly to replace all six hydridic hydrogens by chlorine according to eq. 2. One of the *sym*-P-trimethyltriethyl-B-hexa-

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[9] A. C. Chapman, *Trans. Faraday Soc.*, **59**, 806 (1963).

[10] T. G. Gibian and D. S. McKinney, *J. Am. Chem. Soc.*, **73**, 1431 (1951).

[11] Manuscripts are in preparation describing the isolation and characterization of these triborophanes.

chlorocyclotriborophane isomers was isolated by fractional crystallization and appeared from the sharpness of the melting point (210–211°) to be pure. With uncatalyzed carbon tetrachloride steric repulsion by the large ethyl groups appeared to be an important factor so that only partial chlorination occurred. The tetrachlorocyclotriborophane was the major product (57.7%); hexachloro-, pentachloro-, and trichlorocyclotriborophanes were also present, but in lesser amounts.[11]

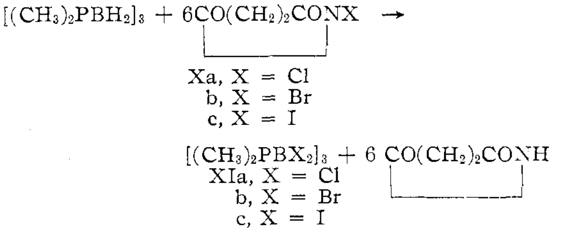
P-Hexamethyl-B-hexaiodocyclotriborophane, $[(CH_3)_2PBI_2]_3$, was prepared from P-hexamethylcyclotriborophane in 94.7% yield using methyl iodide–aluminum iodide (eq. 2) and in 87.5% yield using methylene iodide–aluminum iodide. The 58% yield of methane in the latter experiment based on the equations

$$[(CH_3)_2PBH_2]_3 + 3CH_2I_2 \rightarrow [(CH_3)_2PBHI]_3 + 3CH_3I \quad (9)$$

$$[(CH_3)_2PBHI]_3 + 3CH_3I \rightarrow [(CH_3)_2PBI_2]_3 + 3CH_4 \quad (10)$$

suggests that the B–H function has a considerably greater tendency to react with the intermediate, methyl iodide, than with the large excess of methylene iodide. On the other hand, a single attempt at preparing $[(CH_3)_2PBI_2]_3$ employing the procedure of Biddulph, *et al.*,[4g] iodine in refluxing ethyl iodide, gave only partially B-iodinated cyclotriborophanes.[11]

The N-halosuccinimides provided a convenient, though far from quantitative, means of halogenating the polyborophanes. Thus, N-chlorosuccinimide (Xa) and P-hexamethylcyclotriborophane in a ratio in excess of 6:1 under reflux in carbon tetrachloride gave a 80.5% yield of P-hexamethyl-B-hexachlorocyclotriborophane (XIa) according to the equation


(11)

$$[(CH_3)_2PBH_2]_3 + 6\underline{CO(CH_2)_2CON}X \rightarrow$$

Xa, X = Cl
b, X = Br
c, X = I

$$[(CH_3)_2PBX_2]_3 + 6\ \underline{CO(CH_2)_2CON}H \quad (11)$$

XIa, X = Cl
b, X = Br
c, X = I

With N-bromosuccinimide (Xb) in heptane solution the hexabromocyclotriborophane (XIb) was formed in 63% yield and in methylene bromide solution in only 23% yield. N-Iodosuccinimide (Xc) and P-hexamethylcyclotriborophane failed to give the desired hexaiodinated cyclotriborophane (XIc). It was found that as the substitution on the ring progressed, the partially iodinated species became less soluble and precipitated, thus inhibiting further iodination. Some of these partially iodinated P-hexamethylcyclotriborophanes were isolated by tedious fractional crystallization and characterized.[11] The failure of this reaction to produce P-hexamethyl-B-hexaiodocyclotriborophane was in keeping with the observed trend of decreasing yield with increasing atomic number of the halogen and was attributed to decreasing solubility of the halogenated products and to increasing steric requirements of the halogen.

P-Hexamethyl-B-hexafluoro- (XIIIa) and P-hexaethyl-B-hexafluorocyclotriborophanes (XIIIb) were obtained in yields of 98 and 41.5%, respectively, according to the equation

$$(RR'PBH_2)_3 + 6HF \rightarrow (RR'PBF_2)_3 + 6H_2 \quad (12)$$

XIIa, R = R′ = CH_3	XIIIa, R = R′ = CH_3
b, R = R′ = C_2H_5	b, R = R′ = C_2H_5
c, R = CH_3, R′ = C_6H_5	c, R = CH_3, R′ = C_6H_5
d, R = R′ = C_6H_5	d, R = R′ = C_6H_5

Hydrogen evolution commenced at approximately −60° after warming from −78° and was complete in less than 1 hr. The stoichiometry was confirmed by conducting the reaction with XIIa in a stainless steel bomb and collecting the hydrogen; 6.18 moles (103% of theoretical) of hydrogen were produced per mole of cyclotriborophane.

Reaction of the *sym*-P-trimethyltriphenylcyclotriborophane (XIIc) isomer,[4h] m.p. 125–126°, and anhydrous hydrogen fluoride proceeded slowly at ambient temperature. At 50° the evolution of hydrogen was accelerated, eventually liberating 99.7% of theoretical. The cyclotriborophane ring, however, apparently underwent extensive decomposition since the hexafluorinated cyclotriborophane was not found. A strong phosphine odor was evident and the only isolable solid product decomposed rapidly and dissolved in water with rapid color changes. In contrast with the P-alkyl-substituted compounds, P-hexaphenylcyclotriborophane (XIId) failed to react with anhydrous hydrogen fluoride, probably because the bulky phenyl groups shielded the boron atoms from attack by the reagent.

The hydrolyses of P-hexamethylcyclotriborophane and dodecamethylcyclotriborophane have been studied earlier[4a] but under such drastic experimental conditions that a comparison of the relative hydrolytic stabilities of these derivatives and the B-hexahalo derivatives was difficult. Therefore, a procedure for screening polyborophanes for hydrolytic stability was adopted in which a weighed sample was sealed in a Pyrex tube with 1.0 ml. of water and heated for 24 hr. at 202°.

The results of the hydrolysis studies shown in Table II were based on the generalized equation

$$(R_2PBX_2)_3 + 15H_2O \rightarrow 3R_2POOH + 3H_3BO_3 + 6HX + 6H_2 \quad (13)$$

The oxidation of R_2PH to give R_2POOH was not quantitative under the experimental conditions used and did not serve as a good measure of the degree of hydrolysis. The extent of hydrolysis was not precise when based on boron analysis due to the large blank. Determination of the B-substituent appeared to be the most reliable measure of the degree of hydrolysis. The relative hydrolytic stabilities of the B-substituted P-hexamethylcyclotriborophanes studied were F, I < Br < Cl < CH_3 < H.

The spontaneous ignition temperature (s.i.t.) of the polyborophanes in air was selected as a qualitative measure of their oxidative stability because of the ease and rapidity of the screening test and the small quantity of material required. The data are summarized in Table II.

TABLE II

HYDROLYTIC[a] AND OXIDATIVE STABILITY STUDIES

$[(CH_3)_2PBX_2]_3$		Hydrolysis products			
X	mmoles	H_3BO_3,[b] %	HX, %	H_2,[c] %	S.i.t., °C.
H[d]	0.5487	0.00–0.41	...	0.08	240
CH_3[d]	0.143	1.66–3.07	1.2[e]	...	302
F	0.0631	95.6–98.8	105	33.3	165
Cl	0.3589	5.00–5.55	6.6	0.8	395
Br	0.1839	15.0–16.1	16.0	1.5	>420[f]
I	0.1459	98.5–99.8	99.4	24.0	>430[f]

[a] In 1.0 ml. of water, 24 hr. at 202°. [b] The quantity of boric acid leached from the Pyrex glass was found to average 0.010 ± 0.003 mmole for five blank runs. [c] The expected hydrolysis product, $(CH_3)_2PH$, is oxidized by neutral water to the extent of 5% as shown in a blank run wherein 0.0222 mmole of H_2 was obtained from 0.223 mmole of $(CH_3)_2PH$. [d] See ref. 4a for hydrolysis at 300°. [e] Trace of H_2 in CH_4. [f] Sample did not ignite up to this temperature; however, decomposition was evident from the evolution of fumes and discoloration of the sample.

Experimental

All melting points were determined in sealed capillary tubes under dry nitrogen and were uncorrected. Unless otherwise noted, all molecular weights were determined in *ca.* 0.05 *M* benzene solution by the vapor pressure osmometric method.[12] The isopiestic method[13] was used to obtain molecular weights of compounds having limited solubility in benzene.

Infrared spectra were determined using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Vapor phase chromatographic analyses were done employing a Perkin-Elmer 154B vapor fractometer with a 2-m. silicone oil–Celite column.

P-Hexamethyl-B-hexachlorocyclotriborophane Synthesis Using (a) Carbon Tetrachloride.—P-Hexamethylcyclotriborophane, 13.7 g. (61.8 mmoles), and 137.3 g. (893 mmoles) of degassed carbon tetrachloride were heated in a 123-ml. capacity heavy-walled tube at 130° for 113 hr. The solvent was recovered by vacuum distillation; the weight loss, 12.5 g., indicated that 5.86 g.-atoms (97.7% of the theoretical 6.00 g.-atoms) of chlorine had exchaged per mole of triborophane.[14] The product was purified by repeated crystallizations from chloroform to give transparent orthorhombic crystals,[15] m.p. 384–385°,[16] d^{25} 1.44 g./cc.

Anal. Calcd. for $C_6H_{18}B_3P_3Cl_6$: C, 16.82; H, 4.24; B, 7.58; P, 21.69; Cl, 49.67; mol. wt., 428.3. Found: C, 16.79; H, 4.31; B, 7.66; P, 21.42; Cl, 49.8; mol. wt., 431 (isopiestic in chloroform).

(b) **Carbon Tetrachloride–Aluminum Chloride.**—A mixture of 10.04 g. (45.3 mmoles) of P-hexamethylcyclotriborophane, 2.85 g. (21.4 mmoles) of aluminum chloride, and 110 ml. of carbon tetrachloride was heated under reflux for 1 hr. The cooled mixture was washed with 12 *N* hydrochloric acid followed by water. The carbon tetrachloride solution was evaporated to dryness and the 19.4-g. (45.3 mmoles, 100%) residue was recrystallized from chloroform, m.p. 378–382°.[17]

(c) **Chloroform.**—After removal of excess methyl bromide, the residual solid, derived from 0.1977 g. (0.892 mmole) of P-hexamethylcyclotriborophane, 0.7579 g. (2.84 mmoles) of aluminum bromide, and 2–3 ml. of methyl bromide and containing P-hexamethyl-B-hexabromocyclotriborophane in an apparent 97.9% yield (117.3 cc., 5.24 mmoles of coproduct methane), was first dissolved in chloroform and then water-washed immediately to remove aluminum bromide. On evaporation of the solution to dryness 0.3835 g. (0.895 mmole, 100.3%) of P-hexamethyl-B-hexachlorocyclotriborophane, m.p. 373–379°, was observed.

In a separate experiment 0.0634 g. of pure P-hexamethyl-B-hexabromocyclotriborophane was partially dissolved in 1.8 ml. of pure chloroform, allowed to stand for 2 hr. at ambient temperature, and recovered unchanged on evaporation of the solvent.

A 0.0325-g. (0.147 mmole) sample of P-hexamethylcyclotriborophane was sealed in a tube with 2.6390 g. (22.1 mmoles) of chloroform and heated at 130° for 13 hr. The weight loss (0.0080 g.) of the recovered volatile portion of the reaction mixture, found by infrared analysis to contain methylene chloride, corresponded to partial chlorination (26.4% of the theoretical) of the triborophane ring.

(d) **Alkyl and Aryl Chlorides.**—Typical of the preparations summarized in Table I is the reaction of 0.2544 g. (1.148 mmoles) of P-hexamethylcyclotriborophane, 0.1830 g. (1.37 mmoles) of aluminum chloride, and 2–3 ml. of methyl chloride in an evacuated sealed bomb tube. During 1 hr. at ambient temperature evolution of a gas and formation of a crystalline precipitate was observed. The 149.8 cc. (6.69 mmoles, 97.1%) of methane obtained indicated that the reaction was essentially quantitative. The crude product was dissolved in chloroform and freed of aluminum chloride by washing with water to obtain 0.4875 g. (1.138 mmoles, 99.1%) of P-hexamethyl-B-hexachlorocyclotriborophane on evaporation of the solvent.

A 0.2437-g. (1.10 mmoles) quantity of P-hexamethylcyclotriborophane was sealed *in vacuo* in a tube with 0.4205 g. (3.15 mmoles) of aluminum chloride and 4 ml. (3.6 g., 39 mmoles) of *n*-butyl chloride. As the tube warmed to room temperature a vigorous gas evolution was apparent and in contrast to the preparation using methyl chloride (*cf.* Table I), the mixture changed to an orange-colored gum. After standing 4 days without further change, the tube was opened and the volatile components were removed and analyzed by high vacuum, infrared, and vapor chromatographic techniques, with the following results: 2.84 cc. of hydrogen, 323 cc. of hydrogen chloride, 215 cc. of butane, 34.4 cc. of isobutane, and the solvent fraction which assayed 58.5% *n*-butyl chloride, 35.9% *s*-butyl chloride, and lesser amounts of C_2 and C_3 chlorides. From the residue, which was dissolved in chloroform and washed with dilute hydrochloric acid, was isolated a 0.8138-g. mixture of an orange oil and a colorless solid. P-Hexamethyl-B-hexachlorocyclotriborophane, m.p. 378–385°, was isolated in 91% yield (0.4301 g., 1.00 mmole) by crystallization from chloroform.

A mixture of 0.1031 g. (0.465 mmole) of P-hexamethylcyclotriborophane, 0.2464 g. (1.847 mmoles) of aluminum chloride, and 2.2233 g. (19.738 mmoles) of chlorobenzene in an 8-ml. bomb tube was heated at 135° for 74.5 hr. to produce 10.5 cc. (0.469 mmole) of hydrogen and 2.8 cc. (0.13 mmole) of benzene. This quantity of benzene limits the amount of substitution to a maximum of 0.27 g.-atom of chlorine per mole of cyclotriborophane. After removal of chlorobenzene and aqueous extraction of aluminum chloride, the absence of P-hexamethylcyclotriborophane in the residue suggested that it had been degraded by the aluminum chloride.

(e) **N-Chlorosuccinimide.**—A magnetically-stirred mixture of 0.1310 g. (0.591 mmole) of P-hexamethylcyclotriborophane and 0.5207 g. (3.90 mmoles) of N-chlorosuccinimide (freshly purified by recrystallization from benzene) in 10 ml. of carbon tetrachloride was heated under reflux for 7 hr. The reaction mixture was cooled in an ice–salt bath and filtered to remove a white insoluble mixture of succinimide and product. The mixture was extracted with 15 ml. of boiling water, filtered, and dried to obtain 0.2041 g. (0.476 mmole, 80.5% yield) of crude P-hexa-

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(12) J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).

(13) C. E. Childs, *Anal. Chem.*, **26**, 1963 (1954).

(14) A solution of 0.0328 g. of P-hexamethylcyclotriborophane in 1.500 g. of carbon tetrachloride was used to establish the identity of coproduct chloroform by infrared analysis.

(15) The dimensions of the unit cell, $a = 11.59$, $b = 13.75$, $c = 11.86$ Å., space group P_{nam}-$D_{2h}16$ or P_{na}-$C_{2v}9$, were determined on a sample supplied in 1955 to Dr. Riley Schaeffer at Iowa State College and published by L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1751 (1957).

(16) Reference 4g gives m.p. 393–394° when the product was crystallized from benzene, possibly because of more complete removal of the pentachloro derivative which forms a solvate with benzene.[11] However, this property may be a poor criterion of purity since the melting point of our material was lowered to 361–365° on heating to 357° for 60 min. and after 150 min. the crystals had turned orange and exploded when placed in a 300° bath.

(17) In one separate experiment, the replacement of 6.01 g.-atoms of hydrogen by chlorine per mole of P-hexamethylcyclotriborophane was established by loss in weight of the volatile liquid portion of the reaction mixture; in another experiment the reaction of 0.0835 g. (0.377 mmole) of P-hexamethylcyclotriborophane and 0.8723 g. (6.542 mmoles) of aluminum chloride in 2 ml. of benzene at 120° for 15 hr. failed to produce any P-hexamethyl-B-hexachlorocyclotriborophane.

methyl-B-hexachlorocyclotriborophane, m.p. 361–374°. Recrystallization from chloroform gave pure material, m.p. 384–385°.

(f) **Hydrogen Chloride.**—To 0.0955 g. (0.431 mmole) of P-hexamethylcyclotriborophane in a 100-ml. stainless steel cylinder was added approximately 18 ml. of anhydrous hydrogen chloride *in vacuo*. During 89 hr. at ambient temperature 13.6 cc. (0.607 mmole) of hydrogen was evolved; an additional 121.5 hr. produced only an additional 2.5 cc. (0.11 mmole) of hydrogen. After removal of excess hydrogen chloride, the product was extracted with methanol and sublimed. The 0.1001 g. of inhomogeneous colorless crystalline sublimate contained 18.3% chlorine, indicating 1.2 g.-atoms of chlorine per mole of cyclotriborophane had been introduced (*cf*. reaction with HCl gas[4a] and HF).

***sym*-P-Trimethyltriethyl-B-hexachlorocyclotriborophane.**—On crystallization of the crude product (Table I) from chloroform, an analytical sample assaying by vapor chromatography 100% pure *sym*-P-trimethyltriethyl-B-hexachlorocyclotriborophane, m.p. 210–211°, was obtained.

Anal. Calcd. for $C_9H_{24}B_3P_3Cl_6$: C, 22.98; H, 5.14; mol. wt., 470.4. Found: C, 22.83; H, 5.05; mol. wt., 457.2.

P-Hexamethyl-B-hexabromocyclotriborophane Synthesis Using (a) Methyl and Methylene Bromides—Aluminum Bromide.—Methyl bromide was removed from the crude product (Table I) and the residue was taken up in methylene bromide and washed thoroughly with water. The solvent was removed to give 0.7369 g. (1.060 mmoles, 98.2%) of P-hexamethyl-B-hexabromocyclotriborophane, m.p. above 411° (decomposition was rapid at this temperature, commencing at approximately 350°). Material obtained by crystallization from methylene bromide had d^{25} 2.16 g./cc. and contained a significant amount of chlorine.

Anal. Calcd. for $C_6H_{18}B_3P_3Br_6$: Br, 68.98. Found: Br, 68.25; Cl, 1.41.

To prepare chlorine-free P-hexamethyl-B-hexabromocyclotriborophane, 20.0 g. (211 mmoles) of methyl bromide, 0.3492 g. (1.575 mmoles) of P-hexamethylcyclotriborophane, and 8.39 g. (31.4 mmoles) of aluminum bromide were allowed to react at room temperature overnight in a sealed 40-ml. bomb tube connected by a magnetic break-off seal to a 200-ml. bomb tube containing 3.2019 g. (14.44 mmoles) of P-hexamethylcyclotriborophane. After removal of the methane, the chlorine-free methyl bromide and aluminum bromide were volatilized and condensed into the 200-ml. tube, leaving the chlorine-containing hexahalocyclotriborophanes which were discarded. The sealed reaction tube was then allowed to stand at room temperature for 70 hr. before 1899 cc. (84.78 mmoles, 97.8%) of methane was removed from the opened tube. After removal of excess methyl bromide, the solid product was washed thoroughly with distilled water and methanol and crystallized repeatedly from toluene to provide 5.384 g. (7.74 mmoles, 53.5%) of P-hexamethyl-B-hexabromocyclotriborophane free of detectable chlorine.

To 15.157 g. (56.82 mmoles) of aluminum bromide in 50 ml. of hot methylene bromide in a nitrogen atmosphere was added dropwise 8.408 g. (18.34 mmoles) of *sym*-P-hexamethyltribromocyclotriborophane[11] in 50 ml. of methylene bromide. After heating under reflux for 2 hr., the mixture was cooled and washed with water, and the solvent was removed at reduced pressure at 100°. Recrystallization of the residue from methylene bromide gave 3.95 g. (5.68 mmoles, 31.0%) of crude P-hexamethyl-B-hexabromocyclotriborophane.

Anal. Calcd. for $C_6H_{18}B_3P_3Br_6$: B, 4.67; P, 13.37; Br, 68.98. Found: B, 4.67; P, 13.25; Br, 68.78; Cl, 0.48.

(b) **N-Bromosuccinimide.**—A mixture of 0.2056 g. (0.928 mmole) of P-hexamethylcyclotriborophane and 1.0900 g. (6.12 mmoles) of N-bromosuccinimide in 10 ml. of heptane was heated under reflux for 2.5 hr. The insoluble precipitate was washed with hot methanol to give 0.4091 g. (0.589 mmole, 63%) of crude P-hexamethyl-B-hexabromocyclotriborophane. Crystallization from methylene bromide provided 0.2720 g. (0.391 mmole, 42%) of pure material, d^{25} 2.21 g./cc., as shown by its infrared spectrum.

Anal. Calcd. for $C_6H_{18}B_3P_3Br_6$: Br, 68.98; mol. wt., 695.1. Found: Br, 68.9; Cl, nil; mol. wt., 701 (isopiestic in methyl bromide).

Employing a similar technique, 0.2151 g. (0.971 mmole) of P-hexamethylcyclotriborophane and 1.2960 g. (9.19 mmoles) of N-bromosuccinimide under reflux for 6 hr. in 20 ml. of methylene bromide yielded 0.1575 g. (0.227 mmole, 23%) of P-hexamethyl-B-hexabromocyclotriborophane after crystallization from methylene bromide–cyclohexane.

P-Hexamethyl-B-hexaiodocyclotriborophane Synthesis Using (a) Methyl and Methylene Iodides–Aluminum Iodide.—To 1.1323 g. (5.10 mmoles) of P-hexamethylcyclotriborophane in a 150-ml. heavy-wall tube was added 5.5 g. (13.5 mmoles) of aluminum iodide by distillation of the latter from aluminum chips *in vacuo*. Methylene iodide, 68.8978 g. (257.2 mmoles), was added by syringe, and the tube was sealed and heated at 50° for 18 hr. On opening the tube *in vacuo*, 198.5 cc. (8.86 mmoles) of methane was measured. The dark red reaction mixture was thoroughly washed with water containing several crystals of sodium thiosulfate. On addition of 20 ml. of acetone to the methylene iodide solution, 4.3584 g. (4.46 mmoles, 87.5%) of colorless product precipitated and was crystallized from methyl iodide as prisms, d^{23} 2.75 g./cc., m.p. above 411° (decomposition was rapid at this temperature, commencing at approximately 300°). Crystalline material was obtained from methylene iodide solution only with considerable difficulty.

Anal. Calcd. for $C_6H_{18}B_3P_3I_6$: C, 7.38; H, 1.86; I, 77.9; mol. wt., 977.0. Found: C, 7.69; H, 1.94; I, 78.1; mol. wt., 936 (isopiestic in methyl iodide).

(b) **N-Iodosuccinimide.**—A 1.8700-g. (8.311 mmoles) quantity of N-iodosuccinimide was added to a well-stirred solution of 0.3056 g. (1.379 mmoles) of P-hexamethylcyclotriborophane in 12 ml. of methylene iodide. On warming to 60–65° the yellow color of the solution slowly darkened to a deep red-brown and deposited a brown residue during 16 hr. at this temperature. The residue was thoroughly washed with hot water. Repeated attempts to obtain a pure crystalline material by fractional crystallization from methylene iodide, hydrocarbons, or alcohols were unsuccessful.

P-Hexamethyl-B-hexafluorocyclotriborophane.—To 4.000 g. (18.04 mmoles) of P-hexamethylcyclotriborophane in a polyethylene bottle at −78° was added 10 ml. of anhydrous hydrogen fluoride. On warming to approximately −60° the solid dissolved rapidly with an accompanying evolution of hydrogen. The excess hydrogen fluoride was allowed to evaporate slowly at room temperature giving rise to a viscous oil which eventually crystallized when vacuum dried. Sublimation *in vacuo* at 90–105° provided a crude product, 5.8554 g. (17.76 mmoles, 98%), m.p. 127–128°, which was repeatedly crystallized from methylcyclohexane as needles and finally sublimed under high vacuum at 80–85° to give an analytical sample, m.p. 129–130°, d^{25} 1.24 g./cc.

Anal. Calcd. for $C_6H_{18}B_3P_3F_6$: C, 21.86; H, 5.51; mol. wt., 329.6. Found: C, 21.92; H, 5.65; mol. wt., 327 (isopiestic in chloroform).

To confirm the stoichiometry of the fluorination reaction, 0.1054 g. (0.4755 mmole) of P-hexamethylcyclotriborophane was placed in a 10-ml. stainless steel cylinder and approximately 2 ml. of anhydrous hydrogen fluoride was condensed into the cylinder *in vacuo*. The cylinder was warmed slowly to room temperature and allowed to stand for 5 days with occasional shaking. The 65.98 cc. (2.94 mmoles, 103%) of hydrogen which had formed corresponded to 6.18 moles per mole of P-hexamethylcyclotriborophane (theoretical, 6.00).

P-Hexaethyl-B-hexafluorocyclotriborophane.—In a manner similar to that used to obtain $[(CH_3)_2PBF_2]_3$, 1.0242 g. (3.35 mmoles) of P-hexaethylcyclotriborophane and 15 ml. of anhydrous hydrogen fluoride provided a yellow crystalline product, which on heating under high vacuum distilled at a bath temperature of 100–170°. The 0.5757 g. (1.39 mmoles, 41.5%) of solid condensate was recrystallized three times from methylcyclohexane to give colorless needles, m.p. 69.0–70.0°.

Anal. Calcd. for $C_{12}H_{30}B_3P_3F_6$: C, 34.83; H, 7.31; mol. wt., 413.7. Found: C, 34.54; H, 7.50; mol. wt., 420.

***sym*-P-Trimethyltriphenylcyclotriborophane and Hydrogen Fluoride.**—A 10-ml. quantity of anhydrous hydrogen fluoride was added to a 30-ml. stainless steel cylinder cooled to −78° and containing 0.6250 g. (1.532 mmoles) of *sym*-P-trimethyltriphenylcyclotriborophane (isomer m.p. 125–126°). The cylinder was cooled to −196° and the contents degassed by warming to −78°. After standing at ambient temperature for 48 hr. the cylinder was opened *in vacuo* at −196° and 145.6 cc. (6.54 mmoles 71.2%) of hydrogen recovered. An additional 21 hr. at ambient temperature raised the total volume of gas to 153.6 cc. (6.86 mmoles; 74.7%). Finally, it was necessary to heat the tube to 50° for 28.5 hr. to complete the reaction; 208.3 cc. (9.30 mmoles; 101.3%) of noncondensable gas was found which assayed 99.6% hydrogen and 0.4% methane on combustion analysis and corresponded to the replacement of 5.95 moles of hydrogen per mole of triborophane. Work-up of the reaction product provided a brown residue which could not be crystallized. On washing with water the solid appeared to undergo decomposition accompanied by color changes and a strong phosphine odor.

P-Hexaphenylcyclotriborophane and Hydrogen Fluoride.—To 0.300 g. (0.505 mmole) of P-hexaphenylcyclotriborophane in a polyethylene tube at −78° was added 5 ml. of anhydrous hydrogen fluoride. The solid appeared insoluble even as the mixture was allowed to warm to the boiling point. Following evaporation of the hydrogen fluoride the residual white solid was crystallized from benzene–ethanol to recover 0.290 g. (97%) of starting material.

Repetition of the above experiment using 0.2160 g. (0.364 mmole) of P-hexaphenylcyclotriborophane, 3 ml. of anhydrous hydrogen fluoride, and 5 ml. of benzene as a common solvent likewise proved unsuccessful. A 90% recovery of starting material was obtained after one crystallization.

Hydrolysis Experiments.—For these experiments a weighed sample of cyclotriborophane (Table II) was sealed under vacuum in a new Pyrex tube of 5.5-ml. capacity with 1.0 ml. of degassed distilled water. The tube was then heated for 24 hr. at 202° (refluxing acetophenone bath), opened on the vacuum line, and noncondensable gas formed during hydrolysis was collected. The aqueous solution was then analyzed for boric acid and halide ion.

Oxidative Studies.—The apparatus consisted of a 0.5-in. diameter × 3 in. copper cylinder with a 0.375-in. diameter hemispherical sample well at one end wound with a Nichrome wire heating element and insulated with magnesia. A thermowell extended from the bottom of the block to within $^{1}/_{32}$ in. of the bottom of the sample well. The temperatures were determined with a copper–constantan thermocouple. The apparatus was allowed to warm at a rate of 5–10°/min. in the vicinity of the ignition temperature. As the block was heated small samples (*ca.* 5 mg.) were dropped into the carefully cleaned sample well (decomposition and combustion deposits showed a marked but variable lowering of the ignition temperature) until ignition of a fresh sample was observed (Table II).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS

Metal Atom Clusters in Oxide Systems[1]

BY F. A. COTTON[2]

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Compounds of the type $M^{II}_2Mo_3O_8$, described earlier by McCarroll, Katz, and Ward, contain metal atom clusters, Mo_3O_{13}. In this paper, these are treated by an LCAO–MO method similar to that used previously for other metal atom clusters. The pattern of molecular orbital energies which is obtained accounts satisfactorily for the strong metal-to-metal bonding and the absence of unpaired electrons. Moreover, using the orbital energy pattern, a number of predictions can be made of other mixed metal oxides which might be isostructural, and a suggestion is made regarding the nature of molybdenum blue.

Introduction

Several recent publications[3–5] from this laboratory have discussed some compounds belonging to a general class for which we have suggested the name "metal atom cluster" compounds. The term cluster seems an appropriate one for a finite group of metal atoms which are held together mainly, or at least to a significant extent, by bonds directly between the metal atoms, even though some nonmetal atoms may also be intimately associated with the cluster.[6] It has been shown that for several of the best known and most symmetrical of these clusters, fairly simple and straightforward molecular orbital treatments give patterns of orbital energies which well explain their stability and diamagnetism.[4] In all of the ones treated so far, the nonmetal atoms have been halogens.

In 1957, McCarroll, Katz, and Ward[7,8] reported the preparation and X-ray structure determination of compounds with the general formula $M^{II}_2Mo_3O_8$, in which there are triangular groups of Mo atoms with Mo–Mo

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[1] Supported by the United States Atomic Energy Commission.

[2] Fellow of the Alfred P. Sloan Foundation.

[3] J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, **2**, 1166 (1963).

[4] F. A. Cotton and T. E. Haas, *ibid.*, **3**, 10 (1964). In Fig. 3, the lower $T_{2g}(xz,yz)$ orbital should be designated $T_{1g}(xz,yz)$.

[5] F. A. Cotton and J. T. Mague, *ibid.*, **3**, 1094 (1964).

[6] The term "cage" was avoided, since these closely packed groups of metal atoms do not, in general, enclose any other atoms.

[7] W. H. McCarroll, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **79**, 5410 (1957).

[8] The author is grateful to Professor Ward for directing his attention to this paper, and to Professor Katz for further correspondence concerning it.