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Chemistry of Decaborane–Phosphorus Compounds.
V. Bromocarboranes and Their Phosphination[1]

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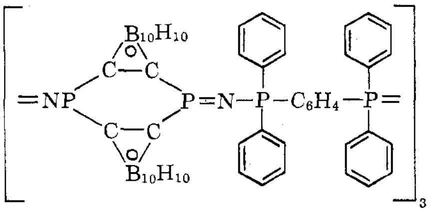
Aluminum halide catalyzed bromination of *o*-carborane and *m*-carborane resulted in a stepwise substitution with tribromo-*o*-carborane and dibromo-*m*-carborane, respectively, as the ultimate products. Further halogenation was achieved with chlorine to give *o*-$B_{10}H_2Br_3Cl_5C_2H_2$, *o*-$B_{10}Br_2Cl_8C_2H_2$, and *m*-$B_{10}Br_2Cl_8C_2H_2$. Some reactions of the bromocarboranes, including the preparation of phosphorus derivatives, are described.

The observation that *o*-carborane (*o*-$B_{10}H_{10}C_2H_2$)[3] participates in the formation of cyclic and oligomeric phosphino-*o*-carboranes[1] such as compound I prompted us to extend our studies to the use of B-substituted carboranes in such reactions. The preparation of higher melting and more stable products, which we hoped to obtain by these means, was especially desirable since compound I has found application as a binder in the preparation of high temperature stable composites with asbestos.[4]

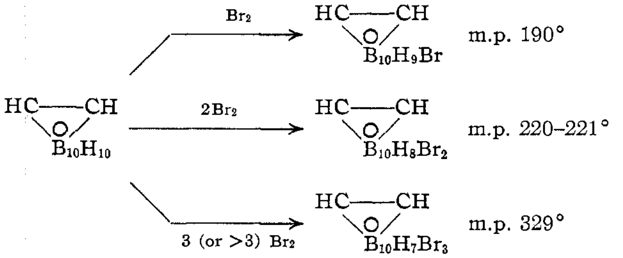


I

The facile chlorination[5] of *o*-carborane stimulated consideration of chloro- and polyhalocarboranes in general as a primary choice for a study of the effect of substituents attached to the carborane nucleus. An attempt to cause decachloro-*o*-carborane to react with chlorophosphines produced a rather insoluble reaction product, therefore the employment of less substituted halocarboranes, *e.g.*, with one to three halogens, appeared to be more preferable.

In a recent paper[5] we reported the preparation of di-, tri-, and tetrachloro-*o*-carborane as well as higher chlorinated products of *o*-carborane. Since the chlorination proceeds rapidly, the reaction leads, after initiation, immediately to the formation of mono-, di-, tri-, and tetrachloro-*o*-carborane, but only the most insoluble product, *o*-$B_{10}H_6Cl_4C_2H_2$, was obtained in satisfactory yield and purity.[6]

Because of the lower reaction rate of bromination (relative to chlorination) and the greater convenience of adding stoichiometric amounts of liquid bromine reactant, preparation of mono-, di-, and tribromo-*o*-carborane in high yields was successful. The results are given in Table I. Carbon disulfide or dichloromethane were used as solvents. In contrast to chlorination, bromination requires a catalyst, and aluminum chloride was slightly superior to aluminum bromide.



Increasing bromine substitution results in a corresponding raising of the melting point. At the same time, the relative intensity of the B–H infrared stretching frequency (2550 cm.$^{-1}$) declines while the C–H stretching frequency (3076 cm.$^{-1}$) remains unchanged, thus indicating that substitution occurs at the boron atoms only.

To furnish further evidence that the bromine atoms are attached to the cage borons and not to the carbon atoms, all three bromination products were converted with butyllithium to their dilithio salts which in turn were allowed to react with methyl iodide to give the corresponding dimethylpolybromocarboranes. Conclusive structure proof was established by showing that the dimethyl compounds obtained by this method are also available by the bromination of *o*-$B_{10}H_{10}C_2(CH_3)_2$[7] with the required amount of bromine. Unexpectedly it was found that in this reaction an additional bromine atom can be introduced to form $B_{10}H_6Br_4C_2(CH_3)_2$. The phenomenon of the presence of

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[1] Preceding communication: R. P. Alexander and H. Schroeder, *Inorg. Chem.*, **2**, 1107 (1963).

[2] To whom inquiries concerning this paper should be addressed.

[3] The synthesis of *p*-carborane [S. Papetti and T. L. Heying, *J. Am. Chem. Soc.*, **86**, 2295 (1964)] combined with the X-ray diffraction study of an *o*-carborane [J. A. Potenza and W. N. Lipscomb, *ibid.*, **86**, 1874 (1964)] and the ^{11}B n.m.r. spectral determination of the (neo) *m*-carborane skeleton [H. Schroeder and G. D. Vickers, *Inorg. Chem.*, **2**, 1317 (1963)] leaves no doubt of the structures of the three possible carboranes ($B_{10}C_2H_{12}$). This allows us to formally employ the terms *o*-, *m*-, and *p*-carborane for the 1,2-, 1,7-, and 1,12- isomers of dicarbaclovododecaborane(12).

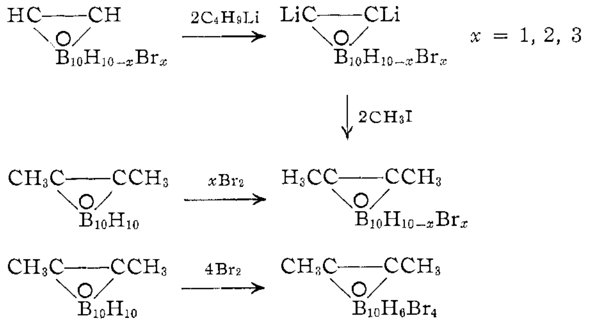
[4] R. P. Alexander and H. Schroeder, U. S. Patent, Ser. No. 323, 394 (1963).

[5] H. Schroeder, T. L. Heying, and J. R. Reiner, *Inorg. Chem.*, **2**, 1092 (1963).

[6] *o*-$B_{10}H_9ClC_2H_2$ has not yet been separated from this mixture. Purification of the similarly melting *o*-$B_{10}H_8Cl_2C_2H_2$ and *o*-$B_{10}H_7Cl_3C_2H_2$ is difficult because chlorocarboranes in general form mixed crystals with relatively sharp melting points. The proportion of the respective compounds is best determined by mass spectral analysis.

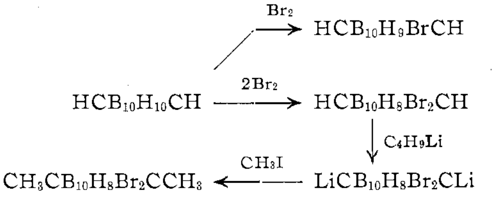
[7] This compound was previously prepared in these laboratories by reduction of *o*-$B_{10}H_{10}C_2(CH_2Br)_2$ and by hydrolysis of the di-Grignard of *o*-$B_{10}H_{10}C_2(CH_2Cl)_2$. These reactions were conducted by Dr. M. Hillmann and Mr. J. W. Szymanski. For this study it was obtained by the reaction of *o*-$B_{10}H_{10}C_2Li_2$ with methyl iodide (see Experimental section).

two methyl groups promoting further bromination is analogous to the facilitation of electrophilic substitution by replacement of hydrogen with methyl in aromatic chemistry.

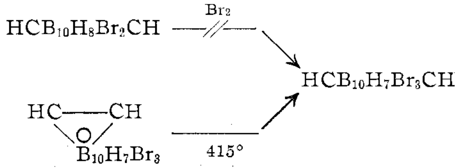


To obtain additional knowledge concerning the formation of such bromo compounds, *m*-carborane was treated with bromine under similar conditions. Again the monobromo derivative, *m*-$B_{10}H_9BrC_2H_2$, and the dibromo derivative, *m*-$B_{10}H_8Br_2C_2H_2$, were easily obtained by applying the proper stoichiometry. Unlike with *o*-carborane, the dibromo derivative was the final product of direct bromination. The observation that *o*-carboranes with four boron atoms nonadjacent to carbon can be tetrabrominated and *m*-carboranes with two boron atoms nonadjacent to carbon can be only dibrominated leads us to suggest that substitution occurs at those particular boron atoms. This is further corroborated by the fact that in the stepwise chlorination of *o*-carborane the two boron atoms adjacent to both carbons are the last sites at which substitution occurs.[8] Obviously electrophilic substitution on the carborane icosahedrons is determined by the positions of the carbon atoms which have a higher electronegativity than boron.

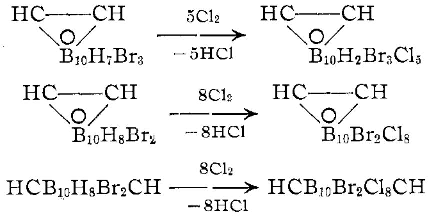
Methylation of the bromo-*m*-carboranes can be accomplished easily as shown by the conversion of *m*-$B_{10}H_8Br_2C_2H_2$ into *m*-$B_{10}H_8Br_2C_2(CH_3)_2$ when the dilithio salt of the former was treated with methyl iodide.[9]



A small amount of *m*-$B_{10}H_7Br_3C_2H_2$ could be obtained by heating *o*-$B_{10}H_7Br_3C_2H_2$ in a sealed tube at 415° for 10 hr. Isomerization leads to a 40% yield of a mixture (85:15) of *m*-$B_{10}H_7Br_3C_2H_2$ and *m*-$B_{10}H_6$-$Br_4C_2H_2$, which on recrystallization from hexane gave relatively pure product.

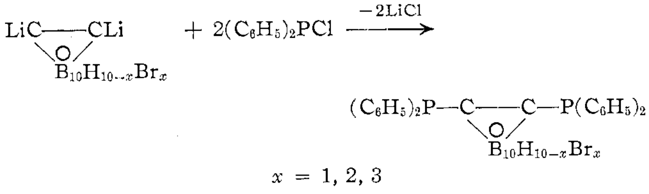


In the interest of securing further information regarding the attack of halogen on this specific type of organoborane and in determining what effect the boron-attached bromine atoms might have, three bromo compounds were subjected to chlorination in either refluxing carbon tetrachloride or chloroform. Indeed, chlorine proved to be reactive enough for further substitution and the following polybromochloro compounds were isolated after hydrogen chloride had ceased to evolve.

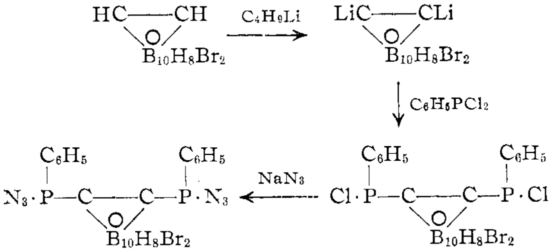


The results in the *o*-carborane series are remarkable in two ways: (1) apparently steric interference toward replacing all boron-bonded hydrogens with chlorine occurs as soon as a minimum of three bromine atoms is present, and (2) the final product of the chlorination of *o*-$B_{10}H_8Br_2C_2H_2$ is the decahalo compound while *o*-$B_{10}H_{10}C_2H_2$ itself is converted into undecachloro-*o*-carborane.[5] *o*-$B_{10}Br_2Cl_8C_2H_2$ therefore deserves interest as an easily available difunctional polymer intermediate, since the preparation of pure *o*-$B_{10}Cl_{10}C_2H_2$ requires repeated fractional recrystallization.[5]

In pursuit of our actual objective, the incorporation of partially B-substituted carboranes into phosphorus-containing polymer intermediates, several reactions between dilithio polybromo-*o*-carboranes and chlorophosphines were studied. The possibility of attaching phosphorus at the bromocarborane carbon atoms was established with the following examples.



Next a series of reactions was conducted in analogy to previous experiments[1] with the unsubstituted *o*-carborane nucleus.



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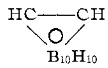
[8] J. A. Potenza and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 2295 (1964).

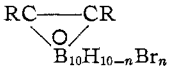
[9] In accord with current practice, $HCB_{10}H_{10}CH$ is used to represent *m*-carborane in formulas, tables, etc., while



represents *o*-carborane only.

TABLE I

BROMINATED DERIVATIVES OF *o*-CARBORANE AND *m*-CARBORANE



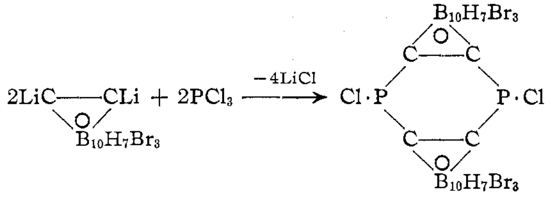
$RC—CR$ / $B_{10}H_{10-n}Br_n$

R	*n*	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Boron, % Calcd.	Boron, % Found	Bromine, % Calcd.	Bromine, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
H[a]	1	190	89.5	10.76	10.95	4.97	5.12	48.47	48.34	35.80	35.62		
H	2	220–221	79.0	7.95	8.15	3.34	3.50	35.81	35.92	52.90	52.60		
H[b]	3	329	70.0	6.30	6.42	2.38	2.07	28.40	28.13	62.92	62.90		
CH_3	1	133	88.8	19.12	19.22	6.02	5.72	43.06	43.05	31.80	32.12		
CH_3	2	256–257	90.0	14.55	14.68	4.27	4.27	32.77	32.75	48.41	48.50		
CH_3[c]	3	265–267	92.4	11.74	12.11	3.20	3.40	26.45	26.11	58.61	57.80		
CH_3	4	330–332	76.4	9.84	9.70	2.48	2.51	22.17	22.44	65.50	65.30		
$P(C_6H_5)_2$	1	217–219	82.0	52.79	52.40	4.94	5.24	18.29	17.60	13.51	14.00	10.47	9.95
$P(C_6H_5)_2$	2	235–237	73.5	47.28	48.10	2.76	3.15	16.38	15.43	24.20	23.80	9.38	8.82
$P(C_6H_5)_2$	3	236–238	64.5	41.66	41.95	3.63	3.67	14.44	14.16	32.00	33.00	8.26	8.33
$P(C_6H_5)Cl$[d]	2	199–200	69.2	28.64	28.63	3.09	3.22	18.42	18.50	27.22	27.20	10.55	10.16
$P(C_6H_5)N_3$[g]	2	125 dec.	85.0	...	...	...	...	18.02	18.08	26.62	26.50	10.32	10.06
					$RCB_{10}H_{10-n}Br_nCR$								
H	1	172	77.5	10.76	10.99	4.97	5.11	48.47	48.45	35.80	35.90		
H[e]	2	189	82.2	7.95	8.09	3.34	3.46	35.81	36.13	52.90	53.20		
H[f]	3	274–276	23.2	...	...	...	...	28.40	27.90	62.92	63.90		
CH_3	2	113–114	78.0	14.55	14.34	4.27	3.96	32.77	32.55	48.41	49.40		

[a] Mol. wt. (all obtained in acetone by the differential vapor pressure method) calcd. 223.2, found 215. [b] Mol. wt. calcd. 381.0, found 376. [c] Mol. wt. calcd. 409.1, found 396. [d] Mol. wt. calcd. 587.2, found 574. *Anal.* Calcd.: Cl, 12.08. Found: Cl, 12.10. [e] Mol. wt. calcd. 302.1, found 293. [f] Mol. wt. calcd. 381.0, found 388. [g] *Anal.* Calcd.: N, 14.00. Found: N, 14.09.

The diazide obtained in this three-step sequence explodes on impact, friction, or heating to 125°.

Simultaneous studies were aimed at the synthesis of compounds containing the diphosphacyclohexane ring in which the *o*-carborane moieties bear bromine or chlorine atoms.



In addition the cyclic compounds derived from *o*-$B_{10}H_8Br_2C_2H_2$ and *o*-$B_{10}H_6Cl_4C_2H_2$ were prepared. All three compounds obtained melt slightly above 400° whereas the unsubstituted $(B_{10}H_{10}C_2P \cdot Cl)_2$ melts at 240°. Thus we have gained our first objective of synthesizing higher melting polymer intermediates.

Further work on the application of these substituted phosphinocarboranes to the preparation of oligomeric and polymeric products will be reported in a subsequent publication. Also in progress is a study to determine the exact positions of the bromine atoms by interpretation of the respective and related ^{11}B n.m.r. spectra.

Experimental[10]

Starting Materials.—*o*-Carborane[11,12] of utmost purity was obtained by resublimation *in vacuo* followed by recrystallization from petroleum ether (b.p. 65–110°); *m*-carborane[13] prepared from pure *o*-carborane was refined by vacuum sublimation. Aluminum powder (J. T. Baker Chemical Co., U.S.P.), anhydrous aluminum chloride (B. & A., A.C.S. reagent), bromine (Mallinckrodt Chemical Works, A.R.), carbon disulfide (B. & A., A.C.S. reagent), phenyldichlorophosphine, and diphenylchlorophosphine (Victor Chemical Works, technical grade) were used as received.

Monobromo-*o*-carborane. (a).—Into a 500-ml. flask, equipped with a vapor-by-pass dropping funnel and a Teflon stirring bar, was charged aluminum powder (0.27 g., 0.01 g.-atom). Under a nitrogen atmosphere, bromine (15.2 g., 0.095 mole) was added dropwise with stirring and ice-cooling, until the amount (0.015 mole) required for the formation of aluminum bromide was consumed; the remainder was added rapidly followed by 100 ml. of carbon disulfide. *o*-Carborane (11.5 g., 0.08 mole) in cold carbon disulfide (125 ml.) was added in one portion, the dropping funnel was then exchanged for a reflux condenser, and the reaction mixture was slowly warmed to 25°. An exothermic reaction with evolution of hydrogen bromide began and, after subsiding, the reaction mixture was refluxed for 1 hr. After that time gas evolution had ceased and the reflux condensate had become colorless. The hot mixture was filtered and the filtrate evaporated to dryness to give 17 g. (95%) of crude product. Purification was achieved by recrystallization from petroleum ether (b.p. 65–110°) or hexane.

(b).—Repetition of the above using 0.01 mole of aluminum chloride in place of aluminum powder resulted in a clear solution which was evaporated to dryness. The residue was treated with water and, after drying, was recrystallized as above.

Dibromo-*o*-carborane.—The bromination was conducted as before except that a second equivalent of bromine was added. The reaction mixture was refluxed for 6 hr. and the crude reaction product was recrystallized from a mixture of heptane and benzene (10:1) to give colorless crystals.

Tribromo-*o*-carborane.—The absorption of a third equivalent of bromine required a 24-hr. reflux period. The reaction mixture was cooled to 25° and filtered. The insoluble reaction product was washed with water to remove all aluminum bromide, then recrystallized from a benzene–heptane mixture (7:3). For final purification the product then obtained was sublimed *in vacuo* and recrystallized as above.

Monobromo-*m*-carborane and dibromo-*m*-carborane were obtained by essentially the same procedures as described for the

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[10] Melting points are uncorrected (Mel-Temp capillary tube apparatus); elemental analyses were by R. Rittner, R. Culmo, J. D. Giunta, and A. C. Mayer of the Olin Mathieson Microchemical Section.

[11] T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2** 1089 (1963).

[12] We thank Mr. R. W. Blundon for preparing a continuing supply of carborane for this research.

[13] D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).

preparation of the respective *o*-carborane isomers. The former compound was recrystallized from hexane, the disubstituted derivative from heptane, carbon tetrachloride, or cyclohexane.

Tribromo-*m*-carborane.—Tribromo-*o*-carborane (7 g.) was heated in a sealed Pyrex tube at 415° for 10 hr. Partial decomposition had occurred as evidenced by the formation of an insoluble dark film on the walls of the tube. The main product was recovered as a waxy material which was triturated with hexane. The solid thus obtained was recrystallized several times from hexane.

1,2-Dimethylpolybromo-*o*-carboranes and *m*-Carboranes.—The following procedures are representative of the two different methods of synthesis.

1,2-Dimethyldibromo-*o*-carborane. (a) **From Dibromo-*o*-carborane.**—A dilithiodibromo-*o*-carborane slurry was prepared in a manner similar to that described for the preparation of dilithiocarborane[1,11] from 6.04 g. (0.02 mole) of dibromo-*o*-carborane in 50 ml. of ether and 0.45 mole of butyllithium in 150 ml. of ether. To this slurry was added dropwise a solution of methyl iodide (6 g., 0.42 mole) in 50 ml. of ether. The reaction mixture was stirred for 1 hr. and then washed with 50 ml. of water. Evaporation of the dried ether layer produced crude reaction product in quantitative yield which was recrystallized from ethyl acetate to give pure *o*-$B_{10}H_8Br_2C_2(CH_3)_2$ (90% yield).

(b) **From 1,2-Dimethyl-*o*-carborane.**—A procedure identical with that for the bromination of *o*-carborane was used except for the employment of 0.08 mole of dimethyl-*o*-carborane instead of the parent *o*-carborane. *o*-$B_{10}H_8Br_2C_2(CH_3)_2$ was obtained in slightly lower yield (76%) than in the preceding example and recrystallized from benzene and chloroform.

1,2-Dimethylmonobromo-*o*-carborane was recrystallized from petroleum ether (b.p. 65–110°), **1,2-dimethyltribromo-*o*-carborane** from a mixture of heptane and benzene, **1,2-dimethyltetrabromo-*o*-carborane** from a mixture of dichloroethane and carbon tetrachloride, and **1,7-dimethyldibromo-*m*-carborane** from pentane.

1,2-Dimethyl-*o*-carborane.—An ethereal solution of methyl iodide (142 g., 1 mole) was added in such speed as to maintain reflux to a dilithio-*o*-carborane (0.208 mole) slurry[14] in ether (500 ml.) prepared from 30 g. of carborane. A clear, pale yellow solution resulted and was refluxed for 0.5 hr. After cooling to 0°, it was washed with water (100 ml.). The ether layer was dried over magnesium sulfate and evaporated to dryness to give 32 g. (89.5%) of colorless *o*-$B_{10}H_{10}C_2(CH_3)_2$. A sample was recrystallized from pentane, m.p. 265° (sealed tube).

Anal. Calcd. for $C_4H_{16}B_{10}$ (172.3): C, 27.87; H, 9.36; B, 62.77. Found: C, 28.51; H, 9.45; B, 62.12.

Dibromooctachloro-*o*-carborane.—A fast stream of gaseous chlorine was passed through a refluxing solution of dibromo-*o*-carborane (7.55 g., 0.025 mole) in carbon tetrachloride (750 ml.) irradiated with ultraviolet. Evolution of hydrogen chloride began immediately and ceased after approximately 75 min. The reaction mixture was then filtered from traces of solids and the solvent removed. The crude product thus obtained in quantitative yield was recrystallized from carbon tetrachloride to give 13.2 g. (91.5%) of pure *o*-$B_{10}Br_2Cl_8C_2H_2$, m.p. 301–302°.

Anal. Calcd. for $C_2H_2B_{10}Br_2Cl_8$ (577.7): C, 4.16; H, 0.35; B, 18.73; Br, 27.67; Cl, 49.10. Found: C, 3.90; H, 0.5; B, 18.50; Br, 27.80; Cl, 48.80.

Dibromooctachloro-*m*-carborane.—The procedure as described above was repeated using a solution of dibromo-*m*-carborane in carbon tetrachloride. The product obtained by chlorination was recrystallized from petroleum ether (b.p. 65–110°) to give pure *m*-$B_{10}Br_2Cl_8C_2H_2$ in 94% yield, m.p. 232–234°.

Anal. Calcd. for $C_2H_2B_{10}Br_2Cl_8$ (577.7): C, 4.16; H, 0.35; B, 18.73; Br, 27.67; Cl, 49.10. Found: C, 4.18; H, 0.5; B, 18.65; Br, 28.7; Cl, 48.90; mol. wt., 573.

Tribromopentachloro-*o*-carborane.—The procedure as described for the preparation of *o*-$B_{10}Br_2Cl_8C_2H_2$ was employed using a solution of tribromo-*o*-carborane (7.7 g., 0.02 mole) in refluxing chloroform (800 ml.). The chlorinated product was recrystallized from a mixture of chloroform and carbon tetrachloride (5:1) to give 10 g. (90.5%) of pure *o*-$B_{10}Br_3Cl_5H_2C_2H_2$, m.p. 346–348°.

Anal. Calcd. for $C_2H_4B_{10}Br_3Cl_5$ (553.3): C, 4.34; H, 0.73; B, 19.56; Br, 43.33; Cl, 32.04. Found: C, 4.00; H, 0.78; B, 19.50; Br, 44.00; Cl, 31.74.

1,2-Bis(diphenylphosphino)dibromo-*o*-carborane.—A solution of diphenylchlorophosphine (7.3 g., 0.033 mole) in ether (30 ml.) was added, with stirring and ice-cooling, to a dilithiodibromo-*o*-carborane slurry in ether (50 ml.) prepared from 4.54 g. (0.015 mole) of dibromo-*o*-carborane as described in the example for the synthesis of 1,2-dimethyldibromo-*o*-carborane. As stirring was continued for 30 min. more, the white translucent slurry turned opaque. The insoluble reaction product was recovered by filtration and recrystallized from heptane.

1,2-Bis(diphenylphosphino)monobromo-*o*-carborane and **1,2-bis(diphenylphosphino)tribromo-*o*-carborane** were obtained by the same general procedure and recrystallized either from heptane or benzene.

Dimeric Chlorophospha(III)tetrachloro-*o*-carborane.—An ethereal dilithiotetrachloro-*o*-carborane slurry was prepared by adding a solution of tetrachloro-*o*-carborane[5] (5.64 g., 0.02 mole) to a commercially available solution of butyllithium (0.044 mole) in hexane (50 ml.) which had been diluted with 100 ml. of ether. The resulting white slurry was stirred for 4 hr. with ice-cooling. After filtration, the insoluble dilithio salt was washed with ether and then slurried with 200 ml. of ether. This slurry was added in small portions, with ice-cooling, to a stirred solution of phosphorus trichloride (8.2 g., 0.06 mole) in ether (500 ml.). After stirring for 12 hr. at 25° the reaction mixture was filtered and the insoluble reaction product washed with ether and then with water to give 6.2 g. (89.5%) of colorless $(B_{10}H_6Cl_4C_2P\cdot Cl)_2$, m.p. 426–427°.

Anal. Calcd. for $C_4H_{12}B_{20}Cl_{10}P_2$ (693.1): C, 6.93; H, 1.75; B, 31.22; Cl, 51.16; P, 8.94. Found: C, 7.44; H, 1.88; B, 30.06; Cl, 50.70; P, 8.35.

Dimeric Chlorophospha(III)tribromo-*o*-carborane was prepared by the procedure described above converting first an ethereal solution of 24.0 g. (0.06 mole) of tribromo-*o*-carborane into an ethereal *o*-$B_{10}H_7Br_3C_2Li_2$ slurry, and then allowing it to react with 24.6 g. (0.18 mole) of phosphorus trichloride. $(B_{10}H_7Br_3C_2P\cdot Cl)_2$ was obtained in 90% yield; it can be recrystallized from xylene, m.p. 412–414°.

Anal. Calcd. for $C_4H_{14}B_{20}Br_6Cl_2P_2$ (890.9): C, 5.39; H, 1.59; B, 24.29; Br, 53.82; Cl, 7.96; P, 6.95. Found: C, 5.77; H, 1.87; B, 24.00; Br, 53.00; Cl, 8.00; P, 6.39.

Dimeric Chlorophospha(III)dibromo-*o*-carborane was obtained accordingly from *o*-$B_{10}H_8Br_2C_2Li_2$ and PCl_3 and recrystallized from either xylene or a large amount of benzene, m.p. 415° (72% yield).

Anal. Calcd. for $C_4H_{16}B_{20}Br_4Cl_2P_2$ (733.1): Br, 43.60; Cl, 9.67. Found: Br, 43.16; Cl, 9.14.

1,2-Bis(chlorophenylphosphino)dibromo-*o*-carborane.—A dilithiodibromo-*o*-carborane (0.03 mole) slurry in 100 ml. of ether was slowly added to a cooled solution of phenyldichlorophosphine (10.74 g., 0.06 mole) in 100 ml. of ether. The resulting orange reaction mixture turned white after stirring for 12 hr. and was then filtered. Evaporation of the ether solution produced a semisolid yellow residue which was triturated with 300 ml. of petroleum ether. The colorless solid thus obtained (m.p. 178–185°) was recrystallized from heptane to give pure *o*-$B_{10}H_8Br_2C_2(C_6H_5\text{-}P\cdot Cl)_2$, m.p. 199–200°.

1,2-Bis(azidophenylphosphino)dibromo-*o*-carborane.—A mixture of *o*-$B_{10}H_8Br_2C_2(C_6H_5P\cdot Cl)_2$ (5.87 g., 0.01 mole), sodium azide (2.6 g., 0.04 mole), and ethanol (90 ml.) was stirred in a nitrogen atmosphere with ice-cooling for 1 hr. After filtration the insoluble reaction products were washed with 100 ml. of water. The remaining bis-azide was thoroughly dried; m.p. 125° (explosive decomposition).

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(14) For the preparation of an ethereal *o*-$B_{10}H_{10}C_2Li_2$ slurry, see ref. 1; for the preparation of an ethereal *m*-$B_{10}H_{10}C_2Li_2$ solution, see S. Papetti and T. L. Heying, *Inorg. Chem.*, **3**, 1448 (1964).

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Notes

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The Chemistry of Dichloro[phthalocyaninato(2−)]titanium(IV)

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In the course of our study of coordination polymers we investigated the titanium analog of the [phthalocyaninato(2−)]germanium and -silicon polymers reported by Joyner and Kenney.[1] At the time we undertook this study there were no details on titanium derivatives of phthalocyanine in the literature, but recently Taube has reported the synthesis of TiPcCl and its conversion to TiPcO[2] and Shklover, *et al.*, have reported the synthesis of $Ti(C_{32}H_{15}ClN_8)(OH)_2$.[3] We also have isolated TiPcO, but from another intermediate, $TiPcCl_2$, and wish to report at this time on the synthesis of $TiPcCl_2$ and some of its reactions.

Dichloro[phthalocyaninato(2−)]titanium(IV) was made by the reaction shown in eq. 1. This reaction is very convenient in that the titanium(III) furnishes the

$$2TiCl_3 + 4C_6H_4(CN)_2 \longrightarrow TiPcCl_2 + TiCl_4 \tag{1}$$

electrons necessary to convert phthalonitrile to the phthalocyanine anion and in that the titanium(IV) not incorporated into $TiPcCl_2$ is readily removed by volatilization. Consequently the preparation of $TiPcCl_2$ proceeds smoothly in a homogeneous medium, and a clean product is obtained in good yield. This is a more convenient route to titanium(IV) derivatives of phthalocyanine than either of the previously published procedures, the reaction of $TiCl_3$ with Li_2Pc and subsequent oxidation[2] or the reaction of $TiCl_4$ with o-$C_6H_4(CN)_2$.[3]

Although $TiPcCl_2$ does not appear to react readily with water because it is not wet by water, an infrared study showed that it hydrolyzes in air. The band at 808 $cm.^{-1}$ in $TiPcCl_2$ gradually disappears, and the band at 972 $cm.^{-1}$ in $(TiPcO)_x$ grows, as samples of $TiPcCl_2$ sit in the atmosphere. Thus it is necessary to protect $TiPcCl_2$ from moisture. The chloride ions are relatively easy to replace in general, as shown by ready conversion to other derivatives of $TiPc^{2+}$.

All our attempts to convert $TiPcCl_2$ to $TiPc(OH)_2$ failed; in every case the product corresponded to $(TiPcO)_x$. This is in marked contrast to the germanium and silicon systems in which the dihydroxy compounds were first isolated and subsequently polymerized by thermal dehydration.[1] It is probable that the oxide is a high-molecular-weight polymer analogous to $(GePcO)_x$ and $(SiPcO)_x$ since there is no evidence for hydroxyl absorption in its infrared spectrum.

The intractability of $(TiPcO)_x$ could well be due to a rigid backbone, *i.e.*, the bulky $TiPc^{2+}$ units when held together by O^{2-} anions should interfere considerably with each other's movement, so we sought to introduce some flexibility into the system by using a chain of atoms between the titanium atoms instead of just a single oxygen atom. One approach was to make a phosphonate derivative by the reaction of $TiPcCl_2$ with phenylphosphonic acid. Although the products isolated did not prove to be high polymers, their analyses suggest an impure oligomer containing five or six units with a phosphonic acid end group, *i.e.*, $H[OP(C_6H_5)O_2TiPc]_{5-6}OP(C_6H_5)O_2$. These products, too, are insoluble in a wide range of solvents and do not melt, so that purification and definitive characterization as a polymer is not possible. Higher reaction temperatures and longer reaction times did not lead to a substantially greater degree of polymerization.

Several attempts to make polymers of the type $(TiPcOSiR_2O)_x$ with $R_2 = (C_6H_5)_2$, $(CH_3)_2$, or $(C_6H_5)(CH_3)$ by the reaction of $TiPcCl_2$ with $R_2Si(OH)_2$, $R_2Si(ONa)_2$, $R_2Si(C_2H_3O_2)_2$, or $R_2Si(OC_2H_5)_2$ under various conditions were unsuccessful. It is interesting that the prototype reaction between $TiPcCl_2$ and $NaOSi(C_6H_5)_3$ goes quite smoothly in refluxing benzene to yield $TiPc[OSi(C_6H_5)_3]_2$, one of the few phthalocyanines that melts rather than sublimes and that is soluble in an organic solvent.

None of the infrared absorption bands common to the titanium(IV) derivatives of phthalocyanine reported here appears diagnostic. They all occur in the spectra for various of the other metallic derivatives of phthalocyanine reported in the literature.[4]

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[1] R. D. Joyner and M. E. Kenney, *J. Am. Chem. Soc.*, **82**, 5790 (1960); *Inorg. Chem.*, **1**, 717 (1962).

[2] R. Taube, *Z. Chem.*, **3**, 194 (1963). Pc is used here, as has become customary, to represent the phthalocyanine anion, $C_{32}H_{16}N_8^{2-}$.

[3] L. P. Shklover, V. E. Plyuschev, I. A. Rozdin, and N. A. Novikova, *Zh. Neorgan. Khim.*, **9**, 478 (1964).

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