TABLE I

MASS SPECTRA OF CYCLOPOLYPHOSPHINES[a]

m/e	Rel intensity	Assignment	m/e	Rel intensity	Assignment
	$(CH_3P)_5$			$(C_2H_5P)_n$	
230	53.6	$(CH_3P)_5^+$	393	2.3	$(C_2H_5P)_5P_3^+$
215	39.0	$(CH_3P)_4P^+$	300	61.2	$(C_2H_5P)_5^+$
184	4.5	$(CH_3P)_4^+$	271	100.0	$(C_2H_5P)_4P^+$
122	100.0	$(CH_3)_4P_2^+$	240	3.9	$(C_2H_5P)_4^+$
61	60.1	$(CH_3)_2P^+$	161	93.8	$C_2H_5PH^+$
	$(n\text{-}C_3H_7P)_n$			$(n\text{-}C_4H_9P)_n$	
389	3.7	$(C_3H_7P)_4P_3^+$	440	0.1	$(C_4H_9P)_5^+$
370	2.5	$(C_3H_7P)_5^+$	352	0.2	$(C_4H_9P)_4^+$
327	21.7	$(C_3H_7P)_4P^+$	264	9.5	$(C_4H_9P)_3^+$
296	1.4	$(C_3H_7P)_4^+$	48	87.8	$CH_3PH_2^+$ (?)
43	100.0	$(C_3H_7)^+$	41	100.0	$C_3H_5^+$ (?)
	$(CF_3P)_4$			$(CF_3P)_5$	
400	90.6	$(CF_3P)_4^+$	500	0.1	$(CF_3P)_5^+$
331	38.8	$(CF_3)_3P^+$	400	26.1	$(CF_3P)_4^+$
169	2.2	$(CF_3)_2P^+$	231	14.1	$(CF_3)_2P^+$
143	100.0	CF_3PPC^+	143	44.9	CF_3PPC^+
69	70.3	CF_3^+	69	100	CF_3^+

[a] Only includes peaks of high intensity and those germane to the discussion.

others[5] when distilling these compounds. Additional small peaks were also found in the P^{31} nmr spectra of the ethyl, *n*-propyl, and *n*-butyl compounds.[8] These may be due to impurities, of course, but the original compounds were found to yield satisfactory elemental analyses,[9] and, furthermore, the *n*-butyl compound gave the same P^{31} nmr spectrum regardless of whether it was prepared by Rauhut and Semsel's method[5] or by the magnesium coupling of $n\text{-}C_4H_9PCl_2$.

The Raman spectra of several alkyl-substituted cyclopolyphosphines have been interpreted on the assumption that they are pure cyclotetraphosphines.[10] In this study the appearance of more than one Raman-active P–C stretching mode was attributed to either coupling effects or the presence of rotational isomers. In view of the foregoing it is also possible that the additional P–C stretches could arise from admixture of the cyclotetraphosphines with higher polymers. The interpretation of the Raman spectra[11] of forms A and B of $(C_6H_5P)_n$ in terms of different conformers of tetraphenylcyclotetraphosphine is at variance with the X-ray crystallographic data.[1,2]

Studies of the reaction of form A of $(C_6H_5P)_n$ with metal carbonyls indicate that the nature of the product is highly dependent upon reaction conditions. For instance, Ang and Shannon[12] isolated a compound of formula $(C_6H_5P)_4 \cdot Ni(CO)_3$ from the reaction of form A of $(C_6H_5P)_n$ with $Ni(CO)_4$ in diethyl ether at 15°, whereas we isolated $(C_6H_5P)_5 \cdot Ni(CO)_3$ under comparable conditions but in the absence of ether.

Until the conditions for the isolation of a particular cyclopolyphosphine have been determined it may be expedient to use $(CF_3P)_4$ and $(CF_3P)_5$ for spectroscopic studies, etc. These compounds do not appear to be complicated by the presence of higher polymers and the conditions for ring interconversion have been precisely determined.[13]

Acknowledgment.—The authors are grateful to the Robert A. Welch Foundation and the United States Public Health Service (Grant 12437-02) for financial support.

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[8] W. A. Henderson, *et al.*,[3] report P^{31} chemical shifts of −17, −13, and −14 ppm relative to 85% H_3PO_4 for $(C_2H_5P)_4$, $(n\text{-}C_3H_7P)_4$, and $(n\text{-}C_4H_9P)_4$, respectively. We found a broad singlet at −16 ppm in the ethyl compound, peaks at −53, −16, and −12 ppm in the *n*-propyl compound, and peaks at −13 and −17 ppm in the *n*-butyl compound.

[9] For instance, Calcd for $(C_2H_5P)_n$: C, 40.01; H, 8.39; P, 51.60. Found: C, 39.88, H, 8.42; P, 51.39.

[10] R. L. Amster, N. B. Colthup, and W. A. Henderson, *Spectrochim. Acta*, **19**, 1841 (1963).

[11] R. L. Amster, W. A. Henderson, and N. B. Colthup, *Can. J. Chem.*, **42**, 2577 (1964).

[12] H. G. Ang and J. S. Shannon, *Chem. Commun.*, 10 (1965).

[13] A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, **83**, 2388 (1961).

CONTRIBUTION FROM THE OLIN RESEARCH CENTER,
CHEMICALS DIVISION, NEW HAVEN, CONNECTICUT

A New Series of Organoboranes. VIII. The Reaction of Phosgene with the Dilithium Salts of *o*- and *m*-Carborane[1,2]

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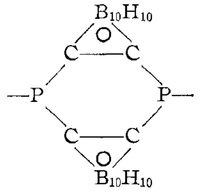
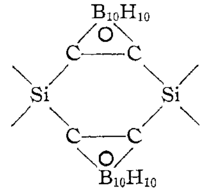
The ability of the carbon atoms of the *o*-carborane moiety to participate in the formation of a six-membered heterocyclic ring skeleton has recently been displayed with the examples of a diphospha-[3] and a disilacyclohexane[4] system





The simplest such ring system yet to be described is the cyclohexane-like skeleton composed of carbon atoms only, four of which are contributed from two carborane nuclei.

When phosgene was allowed to react with $o\text{-}B_{10}H_{10}C_2Li_2$ to generate the desired type of compound, $(o\text{-}B_{10}H_{10}C_2 \cdot CO)_2$ was obtained as a high-melting solid (mp 315°) in 50% yield. All chemical and instrumental analyses including molecular weight de-

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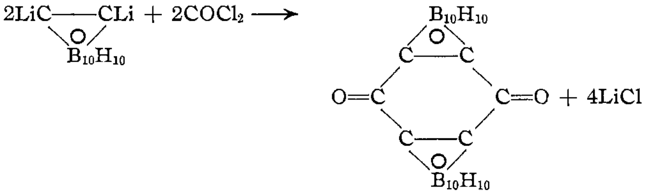
[1] Preceding communication: S. Papetti, B. B. Schaeffer, A. P. Gray, and T. L. Heying, Paper 33 in Symposium on Inorganic Polymers and Plastics, Division of Organic Coatings and Plastics Chemistry, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[2] The nomenclature of the clovo boron–carbon hydrides is discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963); the terms *o*- and *m*-carborane are used to designate 1,2- and 1,7-dicarbaclovododecaborane.

[3] R. P. Alexander and H. Schroeder, *Inorg. Chem.*, **2**, 1107 (1963).

[4] S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963).

termination were in agreement with the assigned structure.



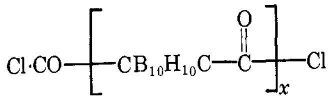
It is of interest to note that the carbonyl-stretching frequency appears as a single sharp band at 1720 cm^{-1} (Figure 1) which indicates a planar ring configuration as represented in Figure 2. A chair configuration would require nonequivalent carbon (carborane) bonding orbitals, and a boat configuration appears improbable because it would involve an unlikely distortion of the over-all symmetry of the molecule.

Further characterization of the diketo compound, *e.g.*, as a hydrazine, failed either because of its insolubility or lack of ketonic character since the carbonyl groups are adjacent to extremely electron-withdrawing units. An attempt to react (o-$B_{10}H_{10}C_2 \cdot CO)_2$ with H_2N-$N(CH_3)_2$ in refluxing chloroform did not produce the desired hydrazine but led (1) to ring cleavage and (2) to partial degradation of the *o*-carborane moieties. The structure of the compounds thus obtained has not yet been unequivocally elucidated.

In the analogous reaction between m-$B_{10}H_{10}C_2Li_2$ and phosgene, employment of a large excess of $COCl_2$ produced the diacid dichloride, m-$B_{10}H_{10}C_2(CO \cdot Cl)_2$, which could be expected from this reaction but was obtained in only 20% yield. Its boiling point corresponded closely to that of the dichloride obtained by chlorination of the corresponding diacid.[5] Conclusive proof of structure was achieved by conversion into the known diamide.[5]

$$LiCB_{10}H_{10}CLi \xrightarrow{COCl_2} Cl \cdot OC\text{-}CB_{10}H_{10}C\text{-}CO \cdot Cl \xrightarrow{NH_3} H_2N \cdot OC\text{-}CB_{10}H_{10}C\text{-}CO \cdot NH_2$$

The other products isolated consisted of a pentane-soluble, highly viscous material and a pentane-insoluble solid which could be recrystallized from ethylene dichloride. By elemental analysis and molecular weight determination both products were found to be polymeric; however, of different chain length as shown in formula a for the former and in b for the latter.



$$Cl{\cdot}CO\left[CB_{10}H_{10}C-\overset{\overset{O}{\|}}{C}\right]_x Cl$$

a: $x = 3$
b: $x = 5$

When equimolar amounts of the two reactants were allowed to interact, only traces of the diacid dichloride were isolated. However, again the polymer having five repeating units proved to be the product with the highest molecular weight. In this type of polymer, the icosahedral nuclei are linked through single carbon atoms only and are similar in structure to those reported recently[6] joined *via* single phosphorus atoms.

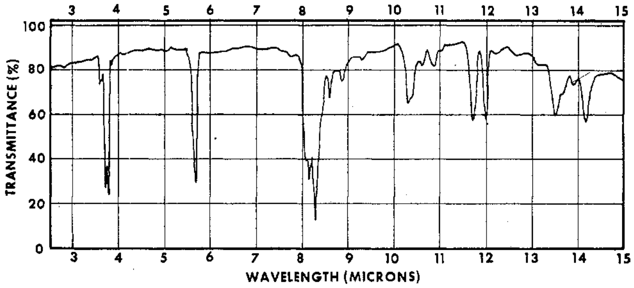


Figure 1.—Infrared spectrum of dimeric carbonyl-*o*-carborane (Kel-F and Nujol mulls).

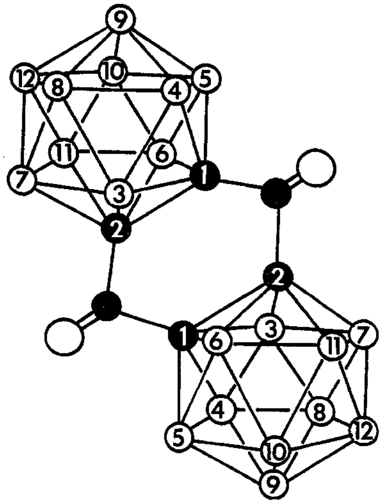


Figure 2.—Assumed structure of dimeric carbonyl-*o*-carborane.

Experimental Section[7]

(o-$B_{10}H_{10} \cdot CO)_2$.—Dilithio-*o*-carborane was prepared[8] from *o*-carborane (60 g, 0.416 mole) and butyllithium (1.0 mole) and, after removal of the ether, slurried with 900 ml of toluene. To it was added, with stirring and ice-cooling, a solution of phosgene (120 g, 1.21 moles) in 600 ml of toluene over a 1-hr period. After the addition was complete, the reaction mixture was kept at 40° for 15 min, then filtered, and the filtrate was evaporated to dryness. The solid residue was triturated with 200 ml of petroleum ether (bp 30–60°) to give 41 g (58%) of crude product. Purification was achieved either by recrystallization from carbon tetrachloride or by vacuum sublimation; yield of pure (o-$B_{10}H_{10} \cdot CO)_2$: 35 g (49%); mp 315°. *Anal.* Calcd for $C_6H_{20}B_{20}O_2$: C, 21.16; H, 5.92; B, 63.53; mol wt, 340.6. Found: C, 21.41; H, 5.90; B, 63.27; mol wt (in *o*-dichlorobenzene at 100°), 334. The mass spectrum contains a sharp cutoff at m/e 344, while the most intense peak observed in the molecular ion region is 339.

Reaction of Dilithio-*m*-carborane with Phosgene.—A dilithio-*m*-carborane (0.18 mole) slurry in toluene (400 ml) was added, with stirring and ice-cooling, to a solution of phosgene (54 g, 0.55 mole) in toluene (400 ml). The resulting mixture was stirred for 6 hr at ambient temperature and then filtered. After removal of the toluene from the filtrate by vacuum distillation,

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

[6] R. P. Alexander and H. Schroeder, *ibid.*, **5**, 493 (1966).

[7] Melting points are uncorrected (Mel-Temp apparatus); elemental analyses were by the Olin Microchemical Section under the supervision of Dr. R. C. Rittner; the mass spectra were obtained and interpreted by H. Hoberecht; the molecular weights were determined by N. Poginy using a Mechrolab vapor pressure osmometer, Model 301. Measurements in each case were conducted at four different concentrations ranging between 5 and 25 g/l.

[8] For a detailed procedure see ref 3.

the remaining viscous liquid was triturated with 400 ml of petroleum ether (bp 30–60°) to give 7.2 g of solid product which was recrystallized from ethylene dichloride; mp 138–143°. *Anal.* Calcd for $C_{16}H_{50}B_{50}Cl_2O_6$: C, 20.22; H, 5.30; B, 56.92; Cl, 7.46; mol wt, 950.5. Found: C, 19.56; H, 5.34; B, 56.28; Cl, 7.19; mol wt (in chloroform), 971.

From the above filtrate the petroleum ether was evaporated and the remainder subjected to vacuum distillation. The highly viscous distillation residue (8 g) was free of volatile products and not further purified. *Anal.* Calcd for $C_{10}H_{30}B_{30}Cl_2O_4$: C, 19.69; H, 4.96; B, 53.22; Cl, 11.63; mol wt, 609.9. Found: C, 20.84; H, 5.33; B, 51.08; Cl, 11.60; mol wt (in benzene), 586. The yield of distillate [m-$B_{10}H_{10}C_2(CO \cdot Cl)_2$] was 9.7 g (20%); bp 67° (0.1 mm); $n^{26}D$ 1.5443.

m-$B_{10}H_{10}C_2(CO \cdot NH_2)_2$.—Ammonia was passed through a benzene solution of m-$B_{10}H_{10}C_2(CO \cdot Cl)_2$ to give the corresponding diamide in quantitative yield; mp (after recrystallization from xylene) 183° (lit.[5] 184–185.5°).

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CONTRIBUTION FROM THE SPERRY RAND RESEARCH CENTER,
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Preparation, Single Crystal Growth, and Crystallographic Properties of FeF_2, $RbFeF_3$, and $CsFeF_3$

BY M. KESTIGIAN, F. D. LEIPZIGER,
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Received March 11, 1966

This note is concerned with the preparation, single crystal growth, and crystallographic properties of $RbFeF_3$ and $CsFeF_3$ and with the single crystal growth of FeF_2. The crystal structure of FeF_2 was reported by Stout and Reed to be of the rutile type.[1] Recently, Baur[2] redetermined the atomic parameters of FeF_2 and found that two of the Fe–F distances were more than 6% shorter than the other four in the FeF_6 octahedra. The existence of $RbFeF_3$ and $CsFeF_3$ has not been reported previously. The magnetic properties of $RbFeF_3$ have been measured by Wang and Kestigian.[3]

Experimental Section

Single crystals of FeF_2 were prepared by sublimation. Either $FeF_2 \cdot xH_2O$ or C + Fe_2O_3 was heated to 950–1000° in an HF–Ar carrier gas transport system. The temperature was maintained for 2 to 3 days. Long, colorless, transparent needles, typically 2 cm in length × 2 mm in cross section, were deposited in the cooler regions of the furnace.

Single crystals of $RbFeF_3$ and $CsFeF_3$ were obtained by the horizontal Bridgman and/or temperature gradient techniques. Equimolar mixtures of the respective anhydrous fluorides were intimately mixed and heated in dense graphite containers. An HF–Ar atmosphere was used to protect the sample during the crystal growth procedure. Colorless, transparent single crystals of 2 in. × 0.5 in. dimensions were usually obtained.

Analysis.—Samples were weighed and dissolved in dilute HCl. The ferrous content was determined as follows. Sulfuric acid was added and the sample heated to fuming to expel all of the fluorine. After dilution, the solution was passed through a Jones reductor and titrated with standardized dichromate solution.

Anal. Calcd for FeF_2: Fe, 59.51. Found: Fe, 58.68.

Anal. Calcd for $RbFeF_3$: Fe, 28.16. Found: Fe, 28.08.

Anal. Calcd for $CsFeF_3$: Fe, 22.72. Found: Fe, 22.55.

The rubidium, cesium, and fluoride contents were calculated by difference. The iron present in the samples was determined to be divalent. The concentration of trivalent iron in the crystals was found to be 10 ppm (or less). Spectrographic analysis of ferrous fluoride single crystals revealed the presence of trace amounts (1–10 ppm range) of copper, silicon, nickel, cobalt, manganese, chromium, and aluminum as the total impurities.

Crystallography

The values of the crystallographic cell constants for FeF_2 reported by Baur[2] were essentially confirmed.

Anhydrous $RbFeF_3$ was found to possess the ideal (cubic) perovskite structure with a = 4.174 A. The data reported in Table I were taken with a high angle diffractometer using a curved crystal monochromator and a scintillation counter detector. Copper radiation was used.

TABLE I

X-RAY DATA FOR $RbFeF_3$

hkl	d_{calcd}	d_{obsd}	I/I_0	*hkl*	d_{calcd}	d_{obsd}	I/I_0
110	2.95	2.94	10.0	321	1.115	1.115	0.6
111	2.41	2.40	1.5	400	1.0435	1.0433	0.2
200	2.086	2.081	5.0	410	1.012	1.0125	<0.1
211	1.704	1.700	2.4	411–330	0.9837	0.9834	1.3
220	1.475	1.473	1.9	331	0.9573	0.9577	0.1
310	1.320	1.319	1.0	420	0.9331	0.9332	0.3
311	1.258	1.258	0.2	332	0.8899	0.8899	0.1
222	1.205	1.204	0.3				

Prolonged exposure did not reveal the presence of any extraneous weak lines or line splitting indicative of slight distortions of the cubic lattice. The density of $RbFeF_3$ was determined experimentally to be 4.53 at 21° as compared with the theoretical density of 4.54. The optically isotropic single crystals were found by the immersion method to have a refractive index of 1.508. The compound melts congruently at 880 ± 5° as indicated by its sharpness of melting on a hot stage microscope. Although precautions were taken to prevent oxidation of the sample by flushing the microscope heating chamber with helium that had passed through a trap cooled with liquid nitrogen, the transparent crystals discolored upon melting.

Cesium ferrous trifluoride ($CsFeF_3$) exhibits hexagonal symmetry caused by a slight distortion along a threefold axis of the ideal perovskite structure. The unit cell parameters were found to be a = 6.158 A and c = 14.855 A. The c dimension derived from the cubic unit cell had to be doubled to index weak X-ray reflections that are observed. X-Ray data for $CsFeF_3$ are presented in Table II. The density of $CsFeF_3$ was 4.94 as measured in toluene at 21°. The calculated density assuming six molecules of $CsFeF_3$ per unit cell is 5.02.

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[1] J. W. Stout and S. A. Reed, *J. Am. Chem. Soc.*, **76**, 5279 (1954).

[2] W. H. Baur, *Acta Cryst.*, **11**, 488 (1958).

[3] F. F. Y. Wang and M. Kestigian, presentation, American Physical Society, Nov 1965, San Francisco, Calif.