Figure 12. Computed distributions for the hydrogen-bonding angles, θ (O–H···O) and ϕ (H···O–H), between monomers with dimerization energies below -2.25 kcal/mol. The units for the ordinate are mole percent per degree.

however, the bulk of IR data rules out their dominance in the liquid.[19] The changes in thermodynamic properties of the lower alcohols are also most readily rationalized by increasing H bonding and average chain length as the temperature is lowered toward the freezing point. The prediction that there is branching of the chains corresponding to the 11% of monomers in three hydrogen bonds should be considered in future analyses of spectral results.

The distributions for the hydrogen bond angles, θ (O–H···O) and ϕ (H···O–H), from the Monte Carlo simulation are displayed in Figure 12. The results for methanol are nearly identical.[5] The average hydrogen bond is bent 15–20° and a wide variety of angular combinations is indicated. Thus, the picture that consistently emerges from liquid simulations is that hydrogen bonds are easily distorted and their geometries and energies are smoothly

distributed over substantial ranges.[4,5,11,16] The distributions also eliminate the possibility of a significant fraction of small cyclic oligomers since they would be represented by values of θ near 60–120°. Of course, their population could be affected by the neglect of three-body effects.

IV. Conclusion

Simulations of liquid water, methanol, and ethanol have now been described by using the TIP model for the intermolecular interactions.[4,5] The results compare favorably with experimental thermodynamic and structural data and with the outcomes of simulations using other potential functions. No severe discrepancies with experiment have been found, though the computed flatness of g_{OO} beyond the first peak for water was disappointing. The combined simplicity, transferability, and utility of the TIP functions is certainly impressive in view of the difficulties that have previously been encountered in generating useful intermolecular potential function. The approach and TIP parameters will be extended and may require some revisions.

As shown here, the results of liquid simulations can be most valuable in interpreting experimental diffraction and spectroscopic data. The potential for studying conformational problems in the liquid phase via Monte Carlo calculations has also been established. Thus, important strides have been made toward opening up organic chemistry in solution to theoretical investigation at the molecular level.

(22) **Note Added in Proof:** A recent microwave study of ethanol yielded a trans-gauche energy difference of 0.12 ± 0.01 kcal/mol which is significantly lower than the ab initio value of 0.64 kcal/mol.[23] Thus, the actual trans populations in the gas and liquid may be ca. 20% lower at 25 °C than computed here.

(23) Kakar, R. K.; Quade, C. R. *J. Chem. Phys.* **1980**, *72*, 4300.

Synthesis and Structure of Carborane-Substituted Cyclic and Polymeric Phosphazenes

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Abstract: The synthesis of the first carborane-substituted cyclophosphazenes together with the preparation, by two different approaches, of the first carborane-substituted phosphazene linear polymers is reported. The cyclic derivatives IV are both precursors and model compounds for the analogous polymeric derivatives VI. The crystal and molecular structure of IV (R = phenyl) has been investigated by single-crystal X-ray diffraction techniques. The molecule contains a planar phosphazene trimer ring bound directly to the phenyl carboranyl group through a P–C bond. The absence of steric and electronic influences by the phosphazene and carboranyl units on each other is discussed. The crystals of IV (R = phenyl) are monoclinic with the space group $P2_1/n$ and with $a = 9.476$ (3) Å, $b = 12.984$ (2) Å, $c = 18.726$ (3) Å, and $\beta = 100.11$ (3)° with $V = 2268.2$ (3) Å^3 and $Z = 4$. The P–N bond distances are all similar and average 1.574 Å. The P–C bond length is 1.820 Å, and the Cl–P–C angle was found to be 102.4°. The reaction between high molecular weight poly(dichlorophosphazene), $(NPCl_2)_n$, and methyl- or phenyl-1-lithio-o-carborane was also studied. Chlorine substitution is a slow process, and is accompanied by chain cleavage. The nucleophilic replacement of the halogen atoms yielded high polymers of structure IX that contain up to 15% of the side groups as carboranyl units. The remaining chlorine atoms were replaced by treatment with sodium trifluoroethoxide. The properties and structure of the macromolecules are discussed.

In recent years wide ranging synthetic advances have taken place in two separate areas of main group inorganic chemistry—in phosphazene chemistry on the one hand and in the chemistry of polyhedral boranes and carboranes[1,2] on the other. In this paper

we make a connection between these two fields and explore the influence of a linked carborane cage on a phosphazene ring and on a phosphazene high polymeric chain.

Modern phosphazene chemistry is dominated by nucleophilic substitution reactions that involve the use of halophosphazene cyclic trimers or high polymers (I or II) as substrates for reactions with alkoxides, aryloxides, or amines (Scheme I).[3-7] To a more

(1) Grimes, R. N. "Carboranes"; Academic Press: New York, 1970.
(2) Hawthorne, M. F. *J. Organomet. Chem.* **1975**, *110*, 97.

Substituted Cyclic and Polymeric Phosphazenes

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Scheme I

X = F or Cl; R = alkyl or aryl; $n \simeq 15\,000$
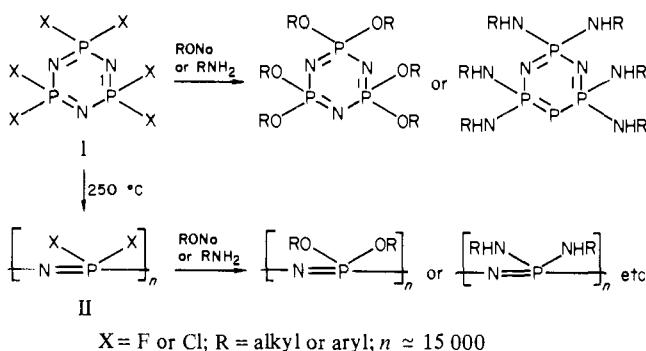
restricted degree, organophosphazenes may also be prepared by the interaction of I or II with Grignard reagents,[8] organolithium compounds,[8] or organocopper species.[9-11] Skeletal cleavage reactions often accompany the substitution processes when Grignard or organolithium reagents are employed. Recently, the organometallic nucleophile, NaFe(CO)$_2$Cp, has been used to prepare the first cyclophosphazenes with P–metal side group bonds.[12]

The lithiation reactions of carboranes have been reported elsewhere.[13,14] In this present work we have explored the possibility that lithio derivatives of *o*-carboranes can be used to connect a carborane cage to a phosphazene ring or chain via the formation of a C–P bond. The subsequent objectives were to determine (1) the influence of the carborane on the substitution chemistry of the remaining P–Cl bonds of the phosphazene ring or chain, (2) the structural influence on each other of the carborane cage and the phosphazene ring, and (3) the influence of the carborane cage on the ring-opening polymerization behavior of the phosphazene component. A longer range interest (to be discussed in a later paper) was the prospect that transition metals might be connected to a phosphazene ring or chain via an attached, open-cage carborane residue. Item 2 has been studied by means of a single-crystal X-ray structure determination.

Results and Discussion

Overall Synthetic Approach. The reaction sequences employed in this work are summarized in Scheme II. First, it was proposed to establish the feasibility of the linkage reaction by the interaction of hexachlorocyclotriphosphazene (III) with the C-lithio derivative of methyl- and phenyl-*o*-carboranes to yield IV. These reactions would serve two purposes. They would provide "model" derivatives (IV) for structural and reactivity studies that would facilitate the design of conditions for the reaction between poly(dichlorophosphazene) (VIII) and the lithiocarboranes to yield high polymers of structures IX and X. They would also provide "monomers" (IV) for ring-opening polymerization to carboranylphosphazene high polymers such as VI and VII. Thus, two independent routes to the high polymers would be available. These individual reactions are discussed in the following sections, together with the structural characterization of IV, V, VII, and X.

Reactions of (NPCl$_2$)$_3$ with the Lithio Derivatives of Methyl- and Phenyl-*o*-carboranes. The methyl- and phenyl-*o*-carboranes were synthesized respectively by the hydrolysis of (1-carboranylmethyl)magnesium bromide[14] and by the reaction between phenylacetylene and decarborane.[13] Lithiation of both
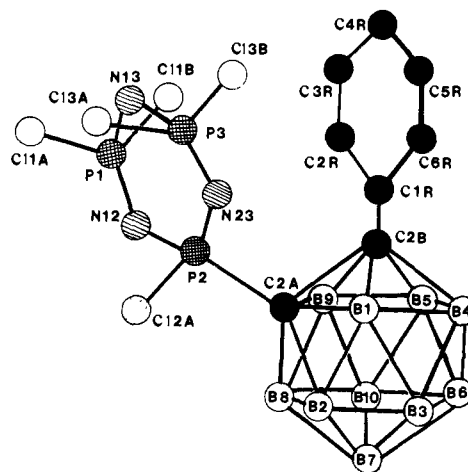
(3) Allcock, H. R.; Cook, W. J.; Mack, W. J. *Inorg. Chem.* **1972**, *11*, 2584.
(4) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.
(5) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(6) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(7) Allcock, H. R.; Chu, C.-T. W. *Macromolecules* **1979**, *12*, 551.
(8) Ritchie, R. J. Ph. D. Thesis, The Pennsylvania State University, 1979.
(9) Harris, P. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1978**, *100*, 6512.
(10) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.
(11) Harris, P. J.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1979**, 714.
(12) Greigger, P. P.; Allcock, H. R. *J. Am. Chem. Soc.* **1979**, *101*, 2492.
(13) Heying, T. L.; Ager, J. W.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. *Inorg. Chem.* **1963**, *2*, 1089.
(14) Heying, T. L.; Ager, J. W.; Clark, S. L.; Alexander, R. P.; Papetti, S.; Reid, J. A.; Trotz, S. I. *Inorg. Chem.* **1963**, *2*, 1097.

Figure 1. Perspective view of the molecular structure of C$_8$H$_{15}$B$_{10}$N$_3$-P$_3$Cl$_5$ (hydrogen atoms not shown).

carboranes was accomplished by treatment with *n*-butyllithium. Both lithiocarboranes reacted cleanly with III to yield the two species with the general structure IV (R = CH$_3$ and C$_6$H$_5$). The two derivatives of type IV were converted to V (R = CH$_3$ and C$_6$H$_5$) by treatment with sodium trifluoroethoxide. Confirmation of structures IV and V was obtained from infrared, ^{31}P NMR, mass spectral, and microanalytical data. For example, the infrared spectrum of IV showed peaks at 1200 cm^{-1} (br in KBr disk) (P=N), 2600 cm^{-1} (br) (B—H), 3100–2900 cm^{-1} (w) (C—H), and 1580 cm^{-1} (m) (C=C). In addition, the spectra of species V showed additional bands at 650–500 cm^{-1} (C-F). The ^{31}P NMR spectra of both species of type IV consisted of a limiting AB$_2$ pattern centered at 19 ppm. For V, the ^{31}P NMR spectra showed an AB$_2$ pattern, with A centered at 26 ppm and B at 13 ppm. The mass spectral and microanalytical data are summarized in the Experimental Section. As discussed in the following section, the structure of IV (R = C$_6$H$_5$) was confirmed by a single-crystal X-ray structure determination.

Crystal and Molecular Structure of IV (R = C$_6$H$_5$). The X-ray structural analysis confirmed that the carborane unit was linked to the phosphazene ring by a C–P covalent bond. The structure of this molecule is illustrated in Figure 1 and in the stereoscopic view shown in Figure 2. The structural parameters are summarized in Tables I–III. All features of the molecule were identified, including the hydrogen atoms attached to boron.

The phosphazene ring was planar, with a mean P–N distance of 1.574 (3) Å. The P–Cl bond distances were 1.982 (2) Å. Of special interest is the finding that the P–C bond distance is 1.820 (4) Å, C–C (within the carborane cage) = 1.709 (5) Å and C–B = 1.721 (5) Å. These values are normal for chlorocyclotriphosphazenes[15] and for *o*-carboranes.[16] The P–C distance is similar to the values reported elsewhere[15] for alkyl- and aryl-cyclophosphazenes. The bond angles are normal for the two components, with N–P–N = 118.5°, P–N–P = 119.2°, Cl–P–Cl = 108.5°, Cl–P–C = 102.4°, and P–C–C = 118.5°. Other structural values are listed in Table III. The phenyl group attached to the carboranyl unit lay roughly 30° from coplanarity with the phosphazene ring. No evidence was found for a structural or electronic perturbation of the phosphazene ring by the carborane or vice versa.

Thermal Polymerization of IV. Hexachlorocyclotriphosphazene (III) undergoes a well-known ring-opening polymerization to VIII when heated at 250 °C. This reaction forms the starting point for the synthesis of a wide range of organophosphazene high polymers.[4-6] Recently it has been shown that pentachloroalkyl-cyclotriphosphazenes, N$_3$P$_3$Cl$_5$R (where R is CH$_3$, C$_2$H$_5$, C$_3$H$_7$, etc.) also polymerize. However, cyclophosphazenes that contain

(15) Marsh, W. C.; Trotter, J. *J. Chem. Soc. A* **1971**, 569.
(16) Potenza, J. A.; Lipscomb, W. N. *Inorg. Chem.* **1964**, *3*, 1673.
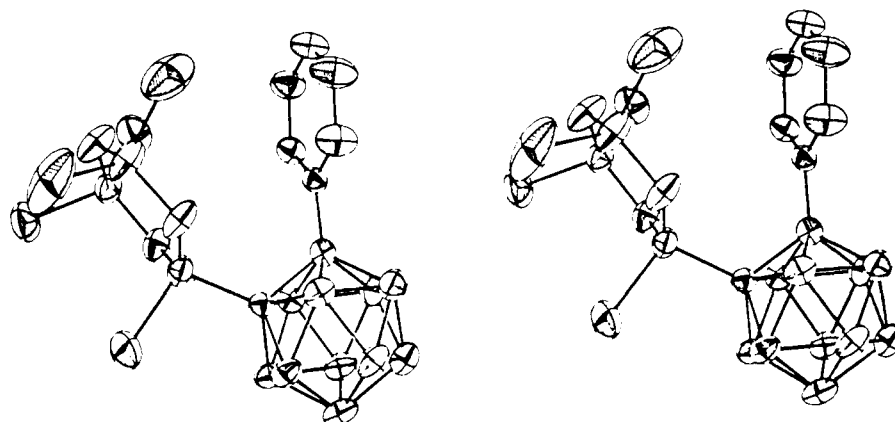(17) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1975**, *8*, 377.

Figure 2. Stereoscopic view of the molecular structure of $C_8H_{15}B_{10}N_3P_3Cl_5$ (hydrogen atoms not shown).

Table I.   Positional and Thermal Parameters[a] and Their Estimated Standard Deviations

atom	x	y	z	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Cl(1A)	0.5711 (1)	1.0795 (1)	0.08618 (7)	0.0122 (2)	0.00736 (9)	0.00407 (5)	0.0003 (2)	0.001 (2)	0.0045 (1)
Cl(1B)	0.8671 (1)	1.0084 (1)	0.16316 (7)	0.0082 (1)	0.01224 (12)	0.00432 (5)	−0.0029 (2)	0.0026 (1)	0.0044 (1)
Cl(2B)	0.7445 (1)	0.8166 (1)	0.32815 (8)	0.0098 (2)	0.01599 (15)	0.00403 (5)	0.0110 (3)	0.0024 (2)	0.0052 (2)
Cl(3A)	0.4511 (2)	0.6996 (1)	0.05051 (8)	0.0314 (3)	0.0156 (13)	0.00471 (5)	−0.0161 (3)	0.0111 (2)	−0.0068 (1)
Cl(3B)	0.7531 (2)	0.6581 (1)	0.13572 (10)	0.0353 (2)	0.01144 (13)	0.00805 (6)	0.0241 (3)	0.0221 (2)	0.0036 (2)
P(1)	0.6638 (1)	0.96417 (10)	0.14548 (7)	0.0082 (1)	0.00559 (8)	0.00251 (4)	−0.0007 (2)	0.0029 (1)	0.0014 (1)
P(2)	0.5745 (1)	0.85511 (9)	0.25359 (6)	0.0081 (1)	0.00485 (8)	0.00228 (3)	0.0029 (2)	0.0033 (1)	0.0013 (1)
P(3)	0.5959 (1)	0.75996 (10)	0.12732 (7)	0.0171 (2)	0.00495 (9)	0.00350 (4)	0.0018 (2)	0.0094 (1)	−0.0006 (1)
N(12)	0.6068 (3)	0.9620 (3)	0.2195 (2)	0.0091 (4)	0.0046 (2)	0.0028 (1)	−0.0019 (6)	0.0035 (4)	−0.0003 (3)
N(23)	0.5341 (4)	0.7691 (3)	0.2003 (2)	0.0158 (5)	0.0035 (2)	0.0029 (1)	0.0020 (6)	0.0085 (4)	0.0005 (3)
N(13)	0.6480 (4)	0.8637 (3)	0.0982 (2)	0.0185 (5)	0.0058 (3)	0.0029 (1)	−0.0037 (7)	0.0091 (4)	−0.0009 (3)
C(2A)	0.4351 (4)	0.8731 (3)	0.3081 (2)	0.0070 (5)	0.0037 (3)	0.0016 (1)	0.0005 (6)	0.0011 (4)	0.0003 (3)
C(2B)	0.2643 (4)	0.8976 (3)	0.2647 (2)	0.0069 (4)	0.0025 (2)	0.0020 (1)	0.0003 (6)	0.0010 (4)	0.0002 (3)
C(1R)	0.2257 (4)	0.8986 (3)	0.1836 (2)	0.0062 (5)	0.0037 (3)	0.0018 (1)	0.0012 (6)	0.0002 (4)	0.0002 (3)
C(2R)	0.1551 (5)	0.8150 (3)	0.1478 (3)	0.0169 (7)	0.0043 (3)	0.0026 (2)	−0.0049 (9)	−0.0003 (6)	0.0008 (4)
C(3R)	0.1097 (6)	0.8184 (4)	0.0739 (3)	0.0201 (8)	0.0052 (3)	0.0029 (2)	−0.0037 (9)	−0.0025 (7)	−0.0018 (4)
C(4R)	0.1324 (5)	0.9026 (4)	0.0350 (2)	0.0137 (7)	0.0068 (4)	0.0019 (2)	−0.0002 (9)	−0.0016 (6)	−0.0003 (4)
C(5R)	0.2034 (5)	0.9855 (4)	0.0693 (2)	0.0126 (6)	0.0060 (3)	0.0022 (1)	−0.0018 (8)	−0.0000 (5)	0.0016 (4)
C(6R)	0.2482 (4)	0.9846 (3)	0.1437 (2)	0.0085 (5)	0.0042 (3)	0.0021 (1)	−0.0010 (7)	0.0002 (5)	0.0000 (4)
B(1)	0.3672 (5)	0.9967 (4)	0.3102 (3)	0.0076 (5)	0.0033 (3)	0.0019 (1)	0.0003 (8)	0.0009 (5)	−0.0005 (4)
B(2)	0.4735 (5)	0.9387 (4)	0.3885 (3)	0.0103 (6)	0.0051 (4)	0.0015 (2)	−0.0009 (8)	0.0012 (5)	−0.0006 (4)
B(3)	0.3142 (6)	1.0044 (4)	0.3952 (3)	0.0123 (7)	0.0042 (4)	0.0020 (2)	0.0012 (9)	0.0025 (6)	−0.0017 (4)
B(4)	0.1850 (5)	0.9798 (4)	0.3176 (3)	0.0082 (6)	0.0046 (4)	0.0024 (2)	0.0028 (8)	0.0021 (5)	−0.0006 (4)
B(5)	0.1474 (5)	0.8467 (4)	0.3144 (3)	0.0095 (6)	0.0056 (4)	0.0024 (2)	−0.0015 (9)	0.0030 (5)	−0.0002 (5)
B(6)	0.1775 (5)	0.9128 (4)	0.3982 (3)	0.0103 (6)	0.0057 (4)	0.0026 (2)	0.0009 (9)	0.0042 (5)	−0.0002 (5)
B(7)	0.3530 (6)	0.8871 (4)	0.4422 (3)	0.0142 (7)	0.0052 (4)	0.0016 (2)	0.0017 (9)	0.0032 (5)	0.0001 (4)
B(8)	0.4341 (5)	0.8049 (4)	0.3857 (3)	0.0111 (6)	0.0041 (3)	0.0019 (2)	0.0022 (8)	0.0030 (5)	0.0013 (4)
B(9)	0.3068 (5)	0.7791 (4)	0.3064 (3)	0.0109 (6)	0.0030 (3)	0.0021 (2)	−0.0008 (8)	0.0024 (5)	0.0004 (4)
B(10)	0.2503 (6)	0.7890 (4)	0.3914 (3)	0.0132 (7)	0.0046 (4)	0.0026 (2)			

atom[b]	x	y	z	atom[b]	x	y	z
H–C(2)	0.133 (4)	0.761 (3)	0.171 (2)	H–B(4)	0.118 (4)	1.031 (3)	0.288 (2)
H–C(3)	0.071 (4)	0.767 (3)	0.056 (2)	H–B(5)	0.044 (4)	0.817 (3)	0.281 (2)
H–C(4)	0.109 (4)	0.903 (3)	−0.015 (2)	H–B(6)	0.092 (4)	0.926 (3)	0.426 (2)
H–C(5)	0.220 (4)	1.042 (3)	0.044 (2)	H–B(7)	0.388 (4)	0.883 (3)	0.503 (2)
H–C(6)	0.297 (4)	1.044 (3)	0.165 (2)	H–B(8)	0.516 (4)	0.748 (3)	0.401 (2)
H–B(1)	0.410 (4)	1.057 (3)	0.282 (2)	H–B(9)	0.310 (4)	0.713 (3)	0.274 (2)
H–B(2)	0.582 (4)	0.582 (4)	0.970 (3)	H–B(10)	0.214 (4)	0.724 (3)	0.413 (2)
H–B(3)	0.322 (4)	1.072 (3)	0.422 (2)				

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta(1,1)h^2 + \beta(2,2)k^2 + \beta(3,3)l^2 + \beta(1,2)hk + \beta(1,3)hl + \beta(2,3)kl)]$.   [b] $B = 4.0000$ (0) Å^2.

more than one organic group often resist polymerization, possibly for steric reasons.[18]   Thus, it was of considerable interest to ascertain the influence of the bulky carboranyl residue in IV on the ability of the cyclophosphazene ring to undergo ring-opening polymerization.

It was found that both compounds of formula IV polymerized to open chain macromolecules of type VI when heated in the molten state at 250 °C. Because the phosphorus–chlorine bonds in polymer VI were sensitive to reaction with atmospheric moisture, the halogen was replaced by reaction with sodium trifluoroeth-

oxide. The resultant polymers (VII) were stable to water, were soluble in organic media, and, thus, possessed an open-chain (i.e., uncross-linked) structure.

The basic structure of the polymers of type VI and VII was determined by a combination of microanalytical, ^{31}P NMR, and infrared techniques. The molecular weights were estimated by gel permeation chromatography. Because of the sensitivity of VI to moisture, most of the characterization was carried out with VII. First, the microanalytical data for VII (see Experimental Section) were compatible with a ratio of 1:5 carboranyl residue:trifluoroethoxy groups. Hence, the ratio of the two types of repeating units in the trimer was retained in the polymer. Second, the ^{31}P NMR spectra showed two peaks (at 7.4 and −9.4 ppm where R

(18) Allcock, H. R. *Chem. Rev.* **1972,** *72,* 315.
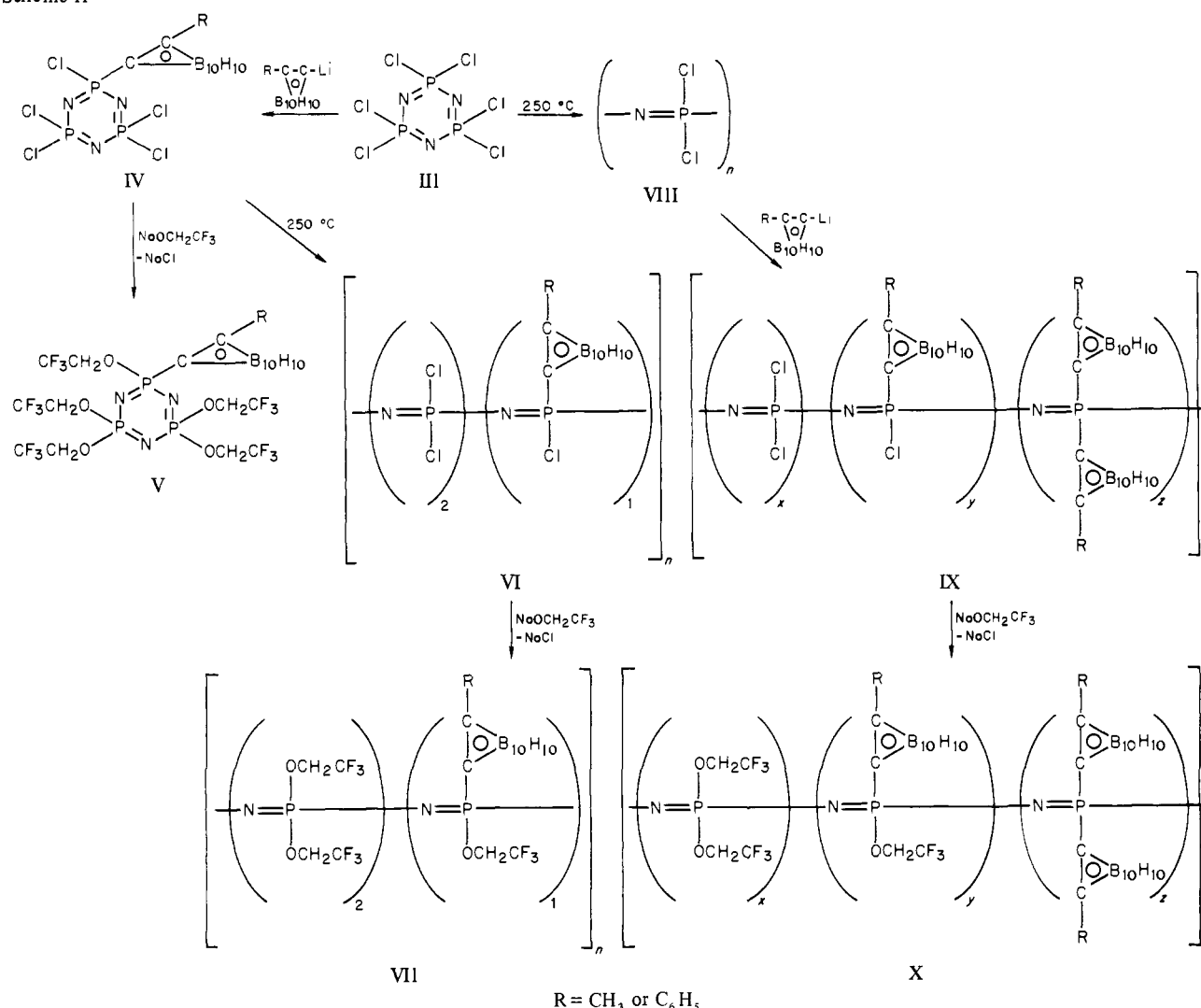
Scheme II

R = CH$_3$ or C$_6$H$_5$

Table II. Least-Squares Planes

A. Equations Defining Least-Square Planes

plane I, through P(1), P(2), P(3), N(12), N(23), N(13)
$-0.8974x + 0.2435y - 0.3679z - 3.1467 = 0$

plane II, through P(1), P(2), P(3), N(12), N(23), N(13),
C(1R), C(2R), C(3R), C(4R), C(5R), C(6R)
$-0.8930x + 0.2467y - 0.3764z - 3.0998 = 0$

plane III, through C(1R), C(2R), C(3R), C(4R), C(5R), C(6R)
$-0.9148x - 0.3803y - 0.1364z - 3.5030 = 0$

plane IV, through P(2), C(2A), C(2B)
$-0.1848x - 0.9815y - 0.0492z - 11.9805 = 0$

plane V, through Cl(2A), P(2), C(2A)
$-0.2310x - 0.9653y - 0.1218z - 12.3523 = 0$

B. Distances (Å) of Some Atoms from Plane I

P(1)	−0.005	C(1R)	3.339	Cl(2A)	−0.00
P(2)	−0.032	C(2R)	3.811	P(2)	−0.00
P(3)	−0.013	C(3R)	4.502	C(2A)	−0.00
N(12)	0.174	C(4R)	4.737		
N(23)	0.225	C(5R)	4.264		
N(13)	−0.013	C(6R)	3.584		

C. Distances (Å) of Some Atoms from Plane II

C(1R)	0.003	P(1)	−0.005	Cl(1A)	1.5884
C(2R)	0.001	P(2)	−0.032	Cl(2A)	6.0496
C(3R)	−0.000	P(3)	−0.013	Cl(3A)	2.5205
C(4R)	−0.006	N(12)	0.174	Cl(3B)	0.9294
C(5R)	0.010	N(23)	0.225	Cl(2B)	6.0496
C(6R)	−0.007	N(13)	−0.013	C(2A)	5.6801

D. Angles (Deg) between Normals to Planes

I and II	0.6	II and III	−30.8
I and V	89.0	II and IV	−86.6

= C$_6$H$_5$, and at 7.2 and −9.1 ppm where R = CH$_3$). The peak areas were in a ratio of 1:2. Those peaks at −9.4 and −9.1 ppm were assigned to P(OCH$_2$CF$_3$)$_2$ units by comparison with the similar value (−7.0 ppm) found for the homopolymer, [NP-(OCH$_2$CF$_3$)$_2$]$_n$. Thus, the peaks at 7.4 and 7.2 ppm were assigned to the two types of carboranyl-P-OCH$_2$CF$_3$ units. The infrared spectra of VII were very similar to the spectrum of [NP-(OCH$_2$CF$_3$)$_2$]$_n$, with additional peaks being detected at 2600 cm^{-1} (B–H) and at 1580 cm^{-1} (aryl) for the system where R = C$_6$H$_5$. The GPC molecular weights of VII (both R = CH$_3$ and C$_6$H$_5$) were in the region of 1 × 10^6.

Interaction of Poly(dichlorophosphazene) (VIII) with the Lithiocarboranes. The decline in average chain length of a macromolecule is a sensitive monitor of skeletal cleavage reactions. Conventional organometallic reagents such as Grignard or organolithium reagents react with (NPCl$_2$)$_n$ high polymer VIII to bring about concurrent halogen replacement and skeletal cleavage.[7] The two lithiocarboranes behaved in the same way. Substitution occurred to yield macromolecules of type IX, but the attachment of increasing numbers of carborane residues to the phosphazene chain was accompanied by a progressive decrease in the average chain length. As shown in Figure 3, a linear relationship exists between these two processes. The greater tendency shown by the methylcarboranyllithium reagent to cleave the chains may perhaps be ascribed to its higher nucleophilicity. It is clear from Figure 3 that high polymers can be obtained only if less than 15% of the halogen atoms are replaced by carborane residues. Hence, this method provides no synthetic advantage over the one that involves the polymerization of IV. The skeletal cleavage process with

Table III.[a] Selected Bond Distances (Å) and Angles (Deg)

Bond Distances

P(1)	C(11A)	1.976 (2)	C(5R)	C(6R)	1.383 (5)
P(1)	C(11B)	1.982 (1)	C(5R)	H–C(5)	0.900 (34)
P(1)	N(12)	1.573 (3)	C(6R)	H–C(6)	0.948 (35)
P(1)	N(13)	1.570 (3)	B(1)	B(2)	1.793 (6)
P(2)	C(2A)	1.820 (3)	B(1)	B(3)	1.754 (6)
P(2)	Cl(2B)	2.022 (2)	B(1)	B(4)	1.769 (6)
P(2)	N(12)	1.578 (3)	B(1)	H–B(1)	1.062 (33)
P(2)	N23	1.574 (3)	B(2)	B(3)	1.758 (7)
P(3)	Cl(3A)	1.969 (2)	B(2)	B(7)	1.779 (6)
P(3)	Cl(3B)	1.978 (2)	B(2)	B(8)	1.775 (7)
P(3)	N(23)	1.578 (3)	B(2)	H–B(2)	1.096 (33)
P(3)	N13	1.569 (3)	B(3)	B(4)	1.757 (6)
C(2A)	C(2B)	1.709 (5)	B(3)	B(6)	1.766 (7)
C(2A)	B(1)	1.733 (5)	B(3)	B(7)	1.765 (7)
C(2A)	B(2)	1.712 (5)	B(3)	H–B(3)	1.007 (35)
C(2A)	B(8)	1.704 (5)	B(4)	B(5)	1.763 (7)
C(2A)	B(9)	1.718 (5)	B(4)	B(6)	1.755 (7)
C(2B)	C(1R)	1.498 (5)	B(4)	H–B(4)	1.013 (33)
C(2B)	B(1)	1.744 (5)	B(5)	B(6)	1.767 (7)
C(2B)	B(4)	1.717 (5)	B(5)	B(9)	1.776 (6)
C(2B)	B(5)	1.702 (5)	B(5)	B(10)	1.760 (7)
C(2B)	B(9)	1.740 (5)	B(5)	H–B(5)	1.130 (33)
C(1R)	C(2B)	1.498 (5)	B(6)	B(7)	1.753 (7)
C(1R)	C(6R)	1.381 (5)	B(6)	B(10)	1.764 (7)
C(2R)	C(3R)	1.377 (6)	B(6)	H–B(6)	1.047 (32)
C(2R)	H–C(2)	0.873 (34)	B(7)	B(8)	1.770 (6)
C(3R)	C(4R)	1.352 (6)	B(7)	B(10)	1.775 (7)
C(3R)	H–C(3)	0.806 (37)	B(7)	H–B(7)	1.127 (35)
C(4R)	C(5R)	1.369 (6)	B(8)	B(9)	1.774 (6)
C(4R)	H–C(4)	0.920 (36)	B(8)	B(10)	1.775 (7)
			B(8)	H–B(8)	1.073 (33)
			B(9)	B(10)	1.771 (6)
			B(9)	H–B(9)	1.062 (34)
			B(10)	H–B(10)	1.021 (34)

Bond Angles

Cl(1A)	P(1)	Cl(1B)	101.42 (07)	C(2A)	C(2B)	C(1R)	121.74 (27)
Al(1A)	P(1)	N(12)	108.73 (13)	C(2A)	C(2B)	B(1)	60.23 (21)
Cl(1A)	P(1)	N(13)	109.04 (15)	C(2A)	C(2B)	B(4)	108.37 (26)
Cl(1B)	P(1)	N(12)	109.38 (13)	C(2A)	C(2B)	B(5)	108.68 (28)
Cl(1B)	P(1)	N(13)	108.80 (15)	C(2A)	C(2B)	B(9)	59.75 (21)
N(12)	P(1)	N(13)	118.16 (17)	C(1R)	C(2B)	B(1)	120.33 (30)
C(2A)	P(2)	Cl(2B)	102.42 (12)	C(1R)	C(2B)	B(4)	121.73 (30)
C(2A)	P(2)	N(12)	109.05 (16)	C(1R)	C(2B)	B(5)	119.49 (31)
C(2A)	P(2)	N(23)	109.56 (16)	C(1R)	C(2B)	B(9)	117.32 (30)
Cl(2B)	P(2)	N(12)	108.21 (13)	B(1)	C(2B)	B(4)	61.49 (23)
Cl(2B)	P(2)	N(23)	109.05 (14)	B(1)	C(2B)	B(5)	112.35 (29)
N(12)	P(2)	N(23)	117.49 (17)	B(1)	C(2B)	B(9)	111.54 (28)
Cl(3A)	P(3)	Cl(3B)	102.50 (09)	B(4)	C(2B)	B(5)	62.10 (25)
Cl(3A)	P(3)	N(23)	108.83 (14)	B(4)	C(2B)	B(9)	112.37 (29)
Cl(3A)	P(3)	N(13)	108.17 (16)	B(5)	C(2B)	B(9)	62.13 (25)
Cl(3B)	P(3)	N(23)	108.81 (14)	C(2B)	C(1R)	C(2R)	119.66 (34)
Cl(3B)	P(3)	N(13)	108.80 (15)	C(2B)	C(1R)	C(6R)	121.46 (34)
N(23)	P(3)	N(13)	118.53 (17)	C2R	C(1R)	C(6R)	118.66 (36)
P(1)	N(12)	P(2)	119.57 (19)	C(1R)	C(2R)	C(3R)	120.06 (40)
P(2)	N(23)	P(3)	118.43 (20)	C(1R)	C(2R)	H–C(2)	121.85 (252)
P(1)	N(13)	P(3)	121.28 (20)	C(3R)	C(2R)	H–C(2)	117.99 (251)
P(2)	C(2A)	C(2B)	118.46 (22)	C(2R)	C(3R)	C(4R)	121.12 (44)
P(2)	C(2A)	B(1)	116.10 (23)	C(2R)	C(3R)	H–C(3)	115.59 (308)
P(2)	C(2A)	B(2)	119.58 (25)	C(4R)	C(3R)	H–C(3)	123.28 (306)
P(2)	C(2A)	B(8)	121.71 (25)	C(3R)	C(4R)	C(5R)	119.62 (42)
P(2)	C(2A)	B(9)	118.67 (24)	C(3R)	C(4R)	H–C(4)	121.39 (245)
C(2B)	C(2A)	B(1)	60.87 (21)	C(5R)	C(4R)	H–C(4)	118.92 (217)
C(2B)	C(2A)	B(2)	111.28 (27)	C(4R)	C(5R)	C(6R)	120.34 (42)
C(2B)	C(2A)	B(8)	110.88 (27)	C(4R)	C(5R)	H–C(5)	145.15 (108)
C(2B)	C(2A)	B(9)	61.02 (22)	C(6R)	C(5R)	H–C(5)	120.17 (243)
B(1)	C(2A)	B(2)	62.72 (23)	C(1R)	C(6R)	C(5R)	120.17 (39)
B(1)	C(2A)	B(8)	113.86 (28)	C(1R)	C(6R)	H–C(6)	122.35 (223)
B(1)	C(2A)	B(9)	113.16 (28)	C(5R)	C(6R)	H–C(6)	117.43 (223)
B(2)	C(2A)	B(8)	62.64 (25)	C(2A)	B(1)	C(2B)	58.90 (21)
B(2)	C(2A)	B(9)	114.19 (30)	C(2A)	B(1)	B(2)	58.06 (22)
B(8)	C(2A)	B(9)	62.43 (24)	C(2A)	B(1)	B(3)	103.91 (32)

Table III *(Continued)*

C(2A)	B(2)	B(1)	59.22 (23)	C(2A)	B(1)	B(4)	104.98 (30)
C(2A)	B(2)	B(3)	104.60 (31)	C(2A)	B(1)	H–B(1)	119.92 (183)
C(2A)	B(2)	B(7)	104.58 (31)	C(2B)	B(1)	B(2)	105.98 (30)
C(2A)	B(2)	B(8)	58.46 (23)	C(2B)	B(1)	B(3)	105.16 (31)
C(2A)	B(2)	H–B(2)	118.14 (177)	C(2B)	B(1)	B(4)	58.50 (22)
C(2B)	B(4)	B(1)	60.01 (22)	C(2B)	B(1)	H–B(1)	122.49 (188)
C(2B)	B(4)	B(3)	106.18 (30)	C(2A)	B(9)	C(2B)	59.23 (20)
C(2B)	B(4)	B(5)	58.53 (23)	C(2A)	B(9)	B(5)	104.91 (30)
C(2B)	B(4)	B(6)	106.07 (31)	C(2A)	B(9)	B(8)	58.37 (23)
C(2B)	B(4)	H–B(4)	113.39 (200)	C(2A)	B(9)	B(10)	104.86 (33)
C(2B)	B(5)	B(4)	59.37 (23)	C(2A)	B(9)	H–B(9)	119.61 (186)
C(2B)	B(5)	B(6)	106.17 (33)	C(2B)	B(9)	B(5)	57.87 (23)
C(2B)	B(5)	B(9)	60.00 (23)	C(2B)	B(9)	B(8)	106.24 (31)
C(2B)	B(5)	B(10)	107.05 (32)	C(2B)	B(9)	B(10)	104.91 (32)
C(2B)	B(5)	H–B(5)	114.56 (175)	C(2B)	B(9)	H–B(9)	119.02 (185)
C(2A)	B(8)	B(2)	58.90 (23)				
C(2A)	B(8)	B(7)	105.30 (32)				
C(2A)	B(8)	B(9)	59.19 (23)				
C(2A)	B(8)	B(10)	105.29 (32)				
C(2A)	B(8)	H–B(8)	118.08 (184)				

[a] P(2) is the phosphorus atom linked to the carborane cage. Cl(B) are chlorine atoms on the side of the phosphazene ring closest to the phenylcarborane unit. Cl(A) species point away from the carborane structure. Cl(3A) is a chlorine atom attached to phosphorus P(3). N(23) is the nitrogen atom that links P(2) to P(3).
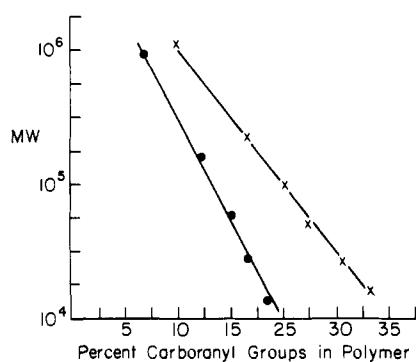

Figure 3. The variation in GPC average molecular weight for [NP-$(C_2B_{10}H_{10}R)_x(OCH_2CF_3)_y]_n$ vs. the percentage of methylcarboranyl groups (●) or phenylcarboranyl groups (✕) attached to the backbone.

Grignard or conventional organolithium reagents has been ascribed to the opportunities that exist for the metallic cation to coordinate to the backbone nitrogen atoms.[19] Apparently, the steric bulk of the bound carborane residues does not appreciably retard this process.

The polymers of type IX were hydrolytically unstable because of the presence of residual phosphorus–chlorine bonds. However, replacement of these by trifluoroethoxy groups to yield X stabilized the polymers against hydrolysis. The structure of these macromolecules was deduced by a combination of elemental analysis, ^{31}P NMR spectroscopy, infrared techniques, and gel permeation chromatography. Of course, the principal difference between polymers of type X and those of type VII is that the latter possesses a fixed ratio of the two types of repeating units, whereas the former do not.

The microanalytical data (see Table IV) allowed an estimate to be made of the degree of carboranyl substitution. The ^{31}P NMR spectra showed two broad peaks at approximately 4.0 and –8.0 ppm, with the peak areas proportional to the degree of carboranyl substitution. The peaks at –8.0 ppm were assigned to P(OC-H$_2$CF$_3$)$_2$ units and those at 4.0 ppm to phosphorus atoms connected to the methyl- or phenylcarboranyl units. However, the peaks were too broad to allow a distinction to be made between geminal and nongeminal substitution patterns. The infrared spectra of these polymers were very similar to the spectrum of [NP(OCH$_2$CF$_3$)$_2$]$_n$, with an additional band being detected at 2600 cm^{-1} (B–H). The intensity of this peak was dependent on

(19) Allcock, H. R.; Evans, T. R.; Patterson, D. B. *Macromolecules* **1980**, *13*, 201.

(20) Schaeffer, R. *J. Am. Chem. Soc.* **1957**, *79*, 1006.

Table IV. Composition and Molecular Weights for Polymers of Type X

reaction time, h	R = C$_6$H$_5$			R = CH$_3$		
	% B	% carboranyl groups[a]	mol wt[b]	% B	% carboranyl groups[a]	mol wt
0.4	4.0	10.6	1×10^6	3.1	5.2	$>1 \times 10^6$
1.0	7.6	17.2	3×10^5	5.3	8.7	1×10^6
1.5	9.1	20.3	1×10^5	7.8	13.0	2×10^5
2.0	10.4	22.4	6×10^4	9.3	15.5	8×10^4
2.5	10.6	26.0	3×10^4	10.0	16.6	4×10^4
3.0	12.8	28.6	9.5×10^3	10.9	18.1	1.2×10^4
3.5	13.3	29.6	$<8 \times 10^3$	11.1	18.5	$<1.0 \times 10^4$
4.0	13.9	31.1	$<8 \times 10^3$	12.9	21.4	$<1.0 \times 10^4$
7.5	17.7	39.7	$<8 \times 10^3$	16.3	27.1	$<1.0 \times 10^4$

[a] The percent of carboranyl groups (of the total number of side groups) was determined in terms of boron content per phosphazene repeating unit. [b] By gel permeation chromatography.

the number of carboranyl groups in the polymer.

Depending on the reaction conditions (see Experimental Section), it was possible to replace up to 40% of the chlorine atoms in VIII by phenylcarboranyl residues. Up to 25% replacement was achieved with the methylcarboranyl system.

Experimental Section

Materials. Decaborane and *o*-carborane (Alfa) were sublimed before use. Propargyl bromide, magnesium, phenylacetylene, and *n*-butyllithium (1.6 molar in hexane) were obtained from Aldrich and were used as received. Diethyl ether, acetonitrile, and benzene (Fisher) were dried by distillation from calcium hydride. Tetrahydrofuran (Baker) was dried by distillation from sodium benzophenone ketyl. Hexachlorocyclotriphosphazene (Ethyl Corp.) was sublimed and recrystallized from hexane. Methyl iodide, hexane, and sodium (Fisher) were used as received. Trifluoroethanol was obtained from Halocarbon Products and was dried over molecular sieves before use.

Poly(dichlorophosphazene) (VIII) was prepared by the polymerization of [NPCl$_2$]$_3$ (III) at 250 °C. An average of 30–40% conversion to the linear polymer was obtained. Sodium trifluoroethoxide was obtained by the reaction of sodium with trifluoroethanol in THF solution. All manipulations of poly(dichlorophosphazene) were performed under a nitrogen atmosphere with the use of a glovebag.

Analytical Equipment. Infrared spectra were recorded on a Perkin-Elmer 580 grating spectrometer. ^{31}P NMR spectra were obtained with the use of a JEOL PS-100 FT NMR spectrometer. Gel permeation chromatography was carried out with Waters Associates instruments (ALC/GPC) with 500, 10^3, 10^4, 10^5, and 10^6 microstyragel columns for tetrahydrofuran solutions. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Bis(acetonitrile)decaborane.[13] A solution of decarborane (20 g, 1.64 × 10⁻¹ mol) in acetonitrile (150 mL) was boiled at reflux for 2 h. A white precipitate of bis(acetonitrile)decaborane deposited from the solution after being cooled. This was filtered and was washed with a small amount of acetonitrile.

Phenyl-*o*-carborane.[13] Phenylacetylene (8.3 g, 8.13 × 10⁻² mol) and bis(acetonitrile)decaborane (13.6 g, 6.73 × 10⁻² mol) in 140 mL of benzene were boiled at reflux for 4 h. After the solution was cooled and filtered, the filtrate was treated with trimethylamine. The resulting mixture was filtered, the filtrate was evaporated, and the solid residue was sublimed (62 °C (0.05 torr)) to yield phenylcarborane in 70% yield; mp 66–68 °C.

(Bromomethyl)carborane. (Bromomethyl)carborane was prepared by using methods described elsewhere.[14]

(1-Carboranylmethyl)magnesium Bromide.[14] A 50-mL flask was charged with magnesium turnings (0.10 g, 0.004 mol) and anhydrous ether (10 mL) under nitrogen. A solution of 1-(bromomethyl)carborane (1.00 g, 0.004 mol) in anhydrous ether (9 mL) was added to the flask dropwise. A crystal of iodine was used to initiate the reaction. After the addition was complete (2.5 h), the mixture was boiled at reflux for an additional hour. The solution was used in situ for the following experiment.

Methyl-*o*-carborane.[14] To a solution of (1-carboranylmethyl)magnesium bromide prepared from 1-(bromomethyl)carborane (2.60 g, 0.011 mol) was added dropwise an excess of 5% HCl at 0–15 °C. The resultant solution was transferred to a separatory funnel, and the ether layer was drawn off and evaporated to dryness. The residue was heated in pentane, filtered hot, evaporated to dryness, and sublimed (70 °C (0.05 torr)) to yield methyl-*o*-carborane (1.5 g, 87.8%) as white crystals, mp 211–215 °C.

Methyl- and Phenyllithiocarboranes. To separate solutions of methyl- and phenylcarboranes (6.32 × 10⁻³ mol) in anhydrous ether (10 mL) was added *n*-butyllithium (3.95 mL, 6.32 × 10⁻³ mol) slowly over a period of 15 min, with stirring at 0 °C. The reaction mixtures were stirred for an additional 1 h, during which time an oily layer separated from the ether solutions. These solutions were used in situ for the following experiments.

Reactions of Lithiocarboranes with (NPCl₂)₃. To the separate methyl- or phenyllithiocarborane solutions, prepared as described above, was added (NPCl₂)₃ (6.3 × 10⁻³ mol) dissolved in anhydrous ether (15 mL) dropwise with stirring at 0 °C during 15 min. The mixtures were warmed slowly to room temperature and were stirred for an additional 12 h. The solvents were removed and the most volatile components were removed in a sublimator at 60 °C (0.05 torr). A temperature increase to 100 °C then yielded a sublimate of crystalline IV. Purification of both compounds was effected by recrystallization from hexane–chloroform mixed solvent systems (mp for R = CH₃, 93 °C, and for R = C₆H₅, 133 °C). Typical yields obtained were 40% for R = C₆H₅ and 25% for R = CH₃. The mass spectra of these compounds showed parent peaks at *m/e* 532 and 470 for R = C₆H₅ (mol wt = 532) and R = CH₃ (mol wt = 470), respectively. Major peaks corresponding to the successive loss of five chlorine atoms were also observed.

Anal. Calcd for $C_3H_{13}B_{10}Cl_5N_3P_3$ (IV, R = CH₃): B, 23.08; C, 7.67; H, 2.77; P, 19.79; N, 8.95; Cl, 37.76. Found: B, 23.15; C, 7.59; H, 2.72; P, 19.89; N, 8.87; Cl, 37.79. Anal. Calcd for $C_8H_{15}B_{10}Cl_5N_3P_3$ (IV, R = C₆H₅): B, 20.36; C, 18.07; H, 2.82; P, 17.49; N, 7.90; Cl, 33.36. Found: B, 20.53; C, 17.95; H, 2.73; P, 17.61; N, 7.85; Cl, 33.36.

Reaction of (Methylcarboranyl)- or (Phenylcarboranyl)pentachlorocyclotriphosphazene (IV) with Sodium Trifluoroethoxide. A solution of IV (1.87 × 10⁻³ mol) dissolved in dry THF was treated with a solution of sodium trifluoroethoxide (2.80 × 10⁻² mol) in THF (20 mL) for 28 h at 66 °C. The mixture was cooled, concentrated, and neutralized to litmus with hydrochloric acid. The resultant oil was extracted with benzene and was dried over magnesium sulfate. After filtration and removal of the solvent, the products were obtained as oils. Typical yields were 60% for R = C₆H₅ and 70% for R = CH₃. The mass spectra of V (R = C₆H₅) showed a parent peak at *m/e* 850 (mol wt = 850) and for R = CH₃ at *m/e* 788 (mol wt = 788) with peaks corresponding to the successive loss of five trifluoroethoxy groups.

Thermal Polymerization of (Methylcarboranyl)- or (Phenylcarboranyl)pentachlorocyclotriphosphazene (IV). A 2-g portion of IV was placed in a 10 × 1 cm constricted Pyrex tube. Air was removed on a vacuum line for 1 h at 0.05 torr, and the contents were subjected to a melt–freeze–evacuate cycle before the tube was sealed. The tube was then encased in a wire screen jacket and was heated in a thermoregulated oven at 250 °C for 120 h. The mixture of polymer and unchanged trimer was then subjected to vacuum sublimation at 90 °C to remove the trimer. The residual polymer was stored in vacuo until used in the halogen-substitution step. An average of 60–70% conversion to linear polymer was obtained.

Synthesis of VII. The (phenylcarboranyl)- or (methylcarboranyl)-chlorophosphazene polymer (VI) (1.87 × 10⁻³ mol) was dissolved in dry THF (15 mL) and was treated with a solution of sodium trifluoroethoxide (1.40 × 10⁻² mol) in THF for 120 h at 66 °C. The mixture was concentrated and neutralized to litmus with hydrochloric acid. The precipitate was filtered off, washed with water, and dried. The high polymers were obtained by fractional precipitation of a THF solution of the products into benzene to give VII. An average of 80% yield was obtained.

Anal. Calcd for R = C₆H₅ for formula $[N_3P_3(OCH_2CF_3)_5-(C_8H_{15}B_{10})]_n$: B, 12.74; C, 25.43; H, 2.94; P, 10.95; N, 4.94; O, 9.42; F, 33.56. Found: B, 12.90; C, 25.66; H, 2.81; P, 11.01; N, 4.76; O, 9.38; F, 33.51. Anal. Calcd for R = CH₃ for formula $[N_3P_3(OCH_2CF_3)_5-(C_3H_{13}B_{10})]_n$: B, 13.74; C, 19.81; H, 2.92; P, 11.81; N, 5.33; O, 10.16; F, 36.20. Found: B, 13.78; C, 19.97; H, 2.96; P, 12.12; N, 5.31; O, 10.00; F, 36.05.

Synthesis of (Methylcarboranyl)- or (Phenylcarboranyl)(trifluoroethoxy)phosphazene Polymers. The following procedure is typical. Methyl or phenyllithiocarborane was prepared from *n*-butyllithium (1.5 × 10⁻² mol) and the carborane (1.4 × 10⁻² mol) in THF solutions. The freshly prepared solution was added dropwise to a solution of poly(dichlorophosphazene) (1.83 g, 1.58 × 10⁻² mol) in THF (50 mL) at 25 °C. Reactions were carried out at 25 °C for 25 min and 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 7.5 h. After these reactions times, trifluoroethanol (5 mL) was added to quench the unreacted lithiocarborane reagent. Sodium trifluoroethoxide, prepared from sodium (2.18 g, 0.0948 mol) and trifluoroethanol (20.6 mL, 0.2844 mol) in THF (25 mL), was added over 15 min to the reaction mixture. The mixture was then boiled at reflux for 120 h. The mixture was cooled, concentrated, and precipitated into dilute hydrochloric acid. Further precipitation was carried out by precipitation from THF into water twice and from THF into benzene twice. The infrared spectra showed the characteristic absorption bands for trifluoroethoxy groups and for carboranyl and phosphazene groups, as follows (in cm⁻¹): 3020 (w) (C—H), 2600 (s) (B—H), 1580 (w) (C=C, R = C₆H₅), 1120 (P—O—C), 1280 (s) (P—N), 965, 880 (P—O—C), 750 (vw) (P—N). The molecular weights of these polymers were estimated by gel permeation chromatographic analysis in THF, and the degree of substitution was determined by elemental boron analysis. The results are listed in Table IV.

X-ray Structure Determination Technique. Cyrstals of IV (R = C₆H₅) suitable for X-ray diffraction examination were grown from hexane solution at 25 °C. A clear crystal, 0.15 × 0.25 × 0.20 mm, was mounted on a glass fiber which was then transferred to a eucentric goniometer head and was attached to an Enraf-Nonius CAD-IV diffractometer.

Unit-cell dimensions determined from 25 reflections of moderate intensity suggested a monoclinic cell of dimensions a = 9.476 (3) Å, b = 12.984 (2) Å, c = 18.726 (3) Å, and β = 100.11 (3)° with V = 2268.2 (3) Å³. The observed volume is consistent with that expected for Z = 4 and a D(calcd) = 1.5 g/mL. The observed absences of $h0l$ for $h + l$ = $2n + 1$ and $0k0$ for $k = 2n + 1$ defined the space group as $P2_1/n$.

A graphite crystal incident beam monochromator was used with Mo Kα radiation (λ Mo Kα_1) = 0.709 30 Å) with data collected at a take-off angle of 2.80°. The crystal to incident beam collimator distance was 48 mm, and the crystal to aperture distance was 173 mm. A θ–2θ scan method was used with a variable scan rate ranging from 20°/min for the most intense reflections to 1°/min for the weak ones. The ω (angular) scan width was variable and amounted to 0.60° below 2θ (Mo Kα) and (0.60 + 0.347 tan θ) after 2θ (Mo Kα_2). Right and left backgrounds were each scanned for 25% of the total scan time. During data collection, three "standard" reflections were recorded after every 4 h of actual X-ray exposure time and were used to monitor crystal stability. (The change in intensities of the standards over the entire data set was ±3%.) A total of 7072 reflections were collected out to 2θ = 70°; of these 2288 had intensities with $I > 3\sigma(I)$ and were considered observed. (Here $\sigma(I)$ = $[S^2(C + R^2B) + (\rho I)^2]^{1/2}$ and $I = S(C - RB)$, where S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, and ρ = 0.05.) These data were corrected for Lorentz and polarization factors[21] and were used in the refinement of the structure.

The solution and refinement of the structure was accomplished in the following way. The starting positions for four chlorine and three phosphorus atoms were obtained from a Multan E map synthesis where E_{min} = 2.00. Refinement was carried out by the full-matrix least-squares method and yielded isotropic R_1 = 0.456 and R_2 = 0.475. A difference Fourier phased on this model located the remaining nonhydrogen atoms. Isotropic least-squares values at this stage were R_1 = 0.145 and R_2 = 0.145.

(21) All the programs used for this study were part of the Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975; revised 1977 and implemented on a PDP 11/34 computer.

The hydrogen atoms were located from a difference Fourier. Anisotropic refinement of all nonhydrogen atoms and hydrogen positional parameters (isotropic B value at one more than average value of ring carbons and boron atoms) yielded a final $R_1 = 0.0428$ and $R_2 = 0.0408$. (Convergence was considered complete when all the shifts were less than one-tenth their standard deviation.) Here $R_1 = \sum/|F_o| - |F_c|/\sum|F_o|$, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/\sigma(F_o)^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $F_o^2 = F^2/Lp$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.25F^2)^2]^{1/2}/Lp$.

The function minimized was $\sum w(|F_o| - |F_c|)^2$. Atomic scattering factors for all atoms were taken from the compilation of Cromer and Waber[22] and were corrected for anomalous dispersion (both real and imag-

(22) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography": The Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2 B and 2.31.

inery parts).[22]

Final positional and thermal parameters are presented in Table 1. A table of observed and calculated structure factors is available as supplementary material (Table V). Inclusion of the unobserved reflections had little or no effect on the bond distances and angles. The final difference map was relatively smooth with maxima of ±0.345 e/Å³ in the region of the P–N bonds.

Structures of [(CH₃)₂(t-BuN)W]₂(μ-t-BuN)₂ and [((CH₃)₂N)₂Ti]₂(μ-t-BuN)₂. A Molecular Orbital Explanation of the Existence of Unsymmetrically or Symmetrically Bridging Organoimido Ligands
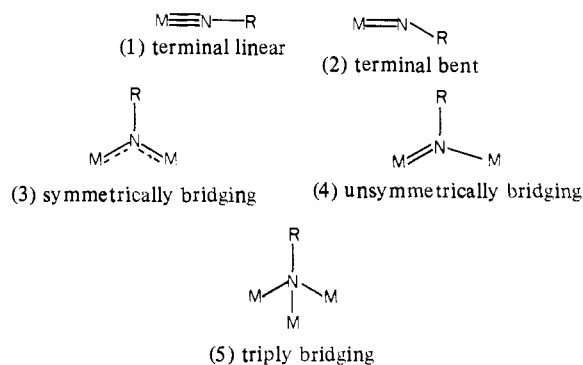
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Abstract: The crystal structures of the unsymmetrically bridging imido complex [(CH₃)₂(t-BuN)W]₂(μ-t-BuN)₂ (Ib) and the symmetrically bridging imido complex [((CH₃)₂N)₂Ti]₂(μ-t-BuN)₂ (IIb) have been determined. Both compounds Ib and IIb crystallize in the space group $P2_1/n$ with two molecules in the unit cell. Compound Ib has the cell dimensions (at −100 °C) $a = 12.987$ (2) Å, $b = 9.477$ (2) Å, $c = 11.252$ (2) Å, $\beta = 103.85$ (1)°, $V = 1345$ Å³, and $\rho_{calcd} = 1.759$ g cm⁻³; compound IIb has the cell dimensions (at −20 °C) $a = 9.434$ (2) Å, $b = 15.984$ (4) Å, $c = 8.795$ (2) Å, $\beta = 115.55$ (2)°, $V = 1197$ Å³, and $\rho_{calcd} = 1.150$ g cm⁻³. Final conventional and weighted agreement indices on F_o for $F_o^2 > 3\sigma(F_o^2)$ are 0.033 and 0.031 for Ib and 0.040 and 0.037 for IIb. Molecular orbital calculations suggest that the unsymmetrical bridging mode in Ib, and in the previously studied Mo analogue Ia, is a manifestation of an "antiaromatic" electronic structure and that the symmetrical bridging mode in IIb and in the previously examined Zr analogue IIa is consistent with an "aromatic" electronic structure.

Transition-metal imido (NH and NR) species are ubiquitous intermediates in industrial[1] and laboratory[2] organic synthesis. Nevertheless, our systematic understanding of the chemistry of imido compounds is limited, particularly with regard to the relationship between structure and reactivity.[3] Structural studies in these laboratories[4] and elsewhere[3] have established that five different bonding modes (1–5) can be present in these complexes. An understanding of the electronic differences reflected by modes

(1) terminal linear   (2) terminal bent

(3) symmetrically bridging   (4) unsymmetrically bridging

(5) triply bridging

1–5 should provide insight into the chemistry of the respective complexes. Moreover such an investigation should also shed light on structure-reactivity trends in the related alkylidene[5] and oxo[6] transition-metal complexes.

Recently we have isolated and structurally characterized the imido-bridged dimeric compound [(CH₃)₂(t-BuN)Mo]₂(μ-t-BuN)₂ (Ia),[4f] drawn below. The distinctly asymmetric structure in the bridging region of Ia[4f] is remarkably different from the symmetrical structure of the imido-bridged dimer [((CH₃)₂N)₂Zr]₂(μ-t-BuN)₂ (IIa).[4d] This difference has prompted us to determine the structures and establish the mode of bridge bonding in the

(1) Examples of such reactions and relevant literature include the following. (a) Ammoxidation of propylene to acrylonitrile: Burrington, J. D.; Grasselli, R. K. *J. Catal.* **1979**, *59*, 79–99. (b) Hydrogenation of nitriles: Andrews, J. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1977**, *99*, 6763–6765. (c) Haber ammonia synthesis: Jones, A.; McNicol, B. D. *J. Catal.* **1977**, *47*, 384–388; Irgranova, E. G.; Ostrovskii, V. E.; Temkin, M. 1. *Kinet. Katal.* **1976**, *17*, 1257–1262.

(2) Examples include the following. (a) Osmium-catalyzed oxyamination of olefins: Sharpless, K. B.; Chong, A. O.; Oshima, K. *J. Org. Chem.* **1976**, *41*, 177–179; Herranz, E.; Sharpless, K. B. *Ibid.* **1978**, *43*, 2544–2548; Herranz, E.; Biller, S. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1978**, *100*, 3596–3598. (b) Electrochemical tosylamidation at a vanadium anode: Breslow, R.; Kluttz, R. Q.; Khanna, P. L. *Tetrahedron Lett.* **1979**, 3273–3274. (c) Reduction of organic azides: Ho, T.-L.; Henninger, M.; Olah, G. A. *Synthesis* **1976**, 815–816; Kwart, H.; Kahn, A. A. *J. Am. Chem. Soc.* **1967**, *89*, 1950–1950.

(3) For a review on organoimido and related complexes of transition metals see: Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175.

(4) (a) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 579–580. (b) *Ibid.* **1979**, 342–343. (c) *Ibid.* **1979**, 1105–1106. (d) *Inorg. Chem.* **1979**, *18*, 2030. (e) *Ibid.* **1980**, *19*, 777–779. (f) *J. Am. Chem. Soc.* **1980**, *102*, 1759–1760. (g) Nugent, W. A.; Harlow, R. L.; McKinney, R. J. *Ibid.* **1979**, *101*, 7265–7268.

(5) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

(6) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459–517.