

Cyclic and Polymeric Phosphazenes with Carbaborane Side Groups X-Ray Crystal Structure of a Carbaborane-substituted Cyclophosphazene

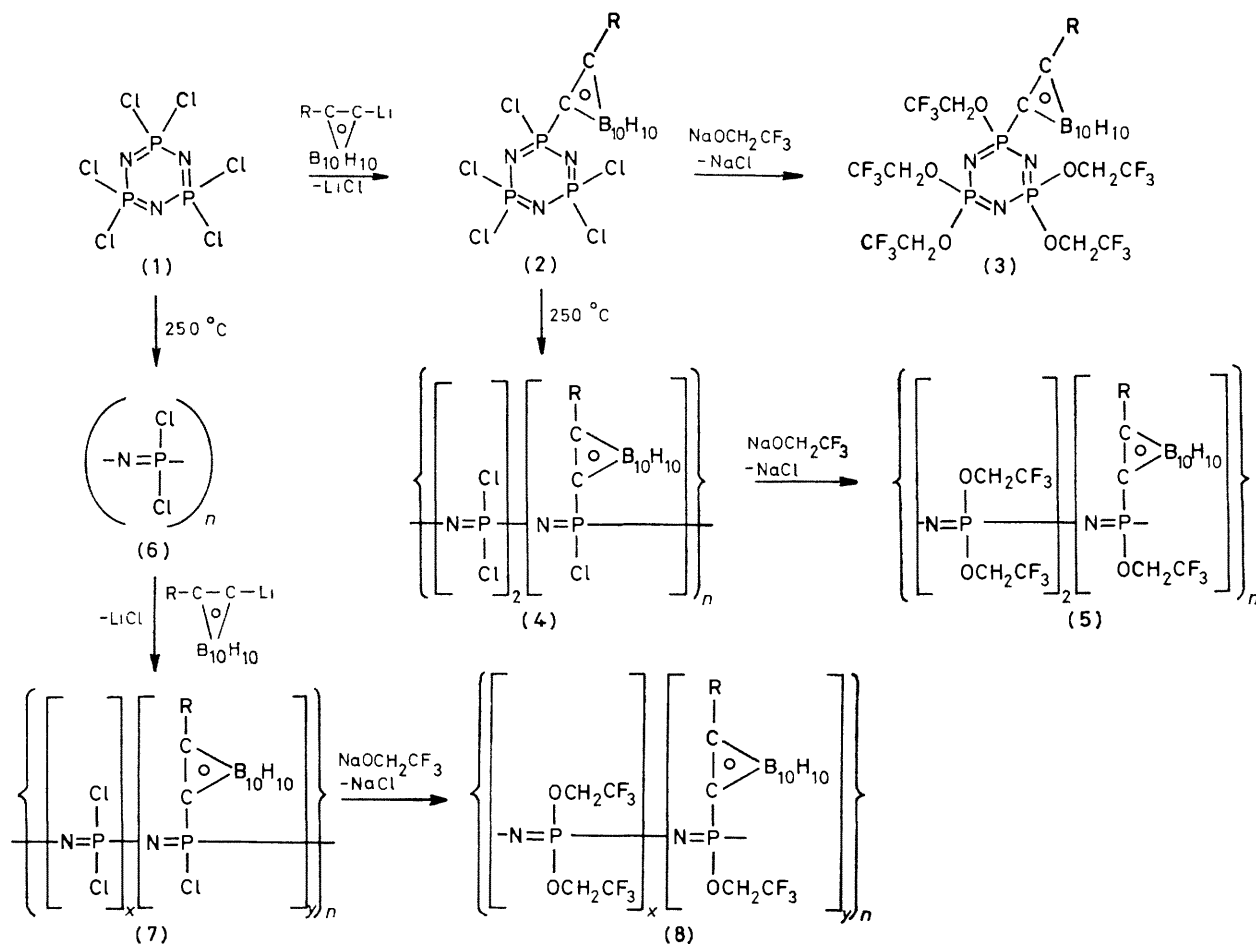
By ANGELO G SCOPELIANOS, JOHN P O'BRIEN, and HARRY R ALLCOCK*

(Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802)

Summary The syntheses of the first cyclic and polymeric phosphazenes with carbaborane side groups are reported

We report here the synthesis of carbaborane-substituted cyclophosphazenes (2) and (3) together with the preparation, by two different methods of the first carbaborane-

substituted phosphazene linear high polymers (4), (5), (7), and (8). These species are prototypes for a wide range of carbaborane-phosphazene rings and polymers that are of broad theoretical and practical interest as high temperature materials or as species with unusual electrical behaviour. The synthetic routes employed are summarized in the Scheme.



SCHEME R = Me or Ph

Compound (2) was prepared, by the interaction of the lithio-derivative of methyl- or phenyl-*o*-carbaborane with hexachlorocyclotriphosphazene (1). Specifically, the lithio-carbaboranes were prepared by the reaction of the appropriate carbaborane with *n*-butyl-lithium in diethyl ether at 25 °C. To each of these solutions was added a solution of (1) in diethyl ether. After reaction for 12 h at 25 °C, removal of the solvent, fractional sublimation of the residues, and recrystallization from heptane, the products corresponding to structure (2) were obtained (m.p. for R = Me, 93 °C; for R = Ph, 133 °C). The reactivity of (2) to nucleophilic substitution was confirmed by a reaction with sodium trifluoroethoxide^{1,2} to yield (3).†

The structures of (2; R = Me or Ph) were deduced by elemental microanalysis, i.r.,‡ mass spectrometric,§ and n.m.r.¶ techniques. A single crystal *X*-ray structure determination confirmed the structure for species (2) where R = Ph. For this compound the space group was $P2_1/n$, with $a = 9.476(3)$, $b = 12.984(2)$, $c = 18.726(3)$ Å, $\beta = 100.11(3)^\circ$, $V = 2268.2(3)$ Å³, and $Z = 4$. Data (Mo-K α) were collected on an Enraf Nonius CAD-4 diffractometer at room temperature. The structure was solved by standard Patterson and Fourier techniques. The final *R* factor was 0.0418 (2288 reflections).**

The molecular structure is illustrated in the Figure together with pertinent bond distances and angles. The structure is consistent with the synthetic route employed. A carbon atom C(2A) of the ortho-carbaboranyl unit is bonded to a phosphorus P(2) of the cyclotriphosphazene ring. All features of the molecule were identified, including the hydrogen atoms attached to boron.

The utility of (2) as an intermediate for the synthesis of macromolecules was established by the thermal polymerization of (2; R = Me or Ph) to (4) at 250 °C during 120 h. Because chlorophosphazene high polymers are extremely sensitive to moisture,³ the species of formula (4) were subjected to halogen replacement by reaction with sodium trifluoroethoxide in boiling tetrahydrofuran (THF) to yield (5). The i.r., microanalytical, and n.m.r. data were compatible with the structure shown for (5). The g.p.c. molecular weights were 1×10^5 (R = Ph) and 1×10^6 (R = Me).

The authenticity of the polymeric structure was confirmed by the synthesis of related polymers from linear,

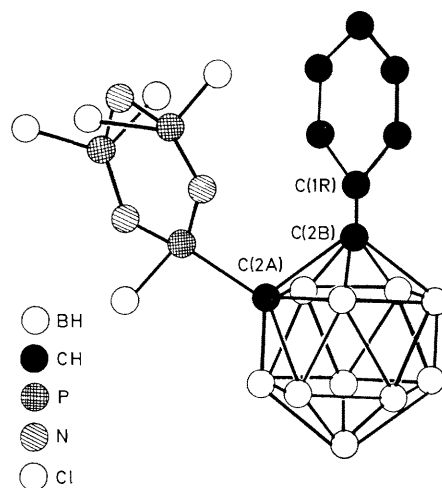


FIGURE. Molecular structure of (2); R = Ph. Bond distances and angles of particular interest are: P...N = 1.574(3) Å, P-C1 = 1.982(2) Å, P-C(2A) = 1.820(4) Å, C(2A)-C(2B) = 1.709(5) Å, C(2A)-B = C(2B)-B = 1.721(5) Å, P-N-P = 119.2°, C1-P-C1 = 108.5°, C1-P-C(2A) = 102.4°, and P-C(2A)-C(2B) = 118.5°.

high polymeric poly(dichlorophosphazene) (6).^{1,2,3} Two separate solutions of (6) in dry THF were added slowly to solutions of the two lithiocarbaboranes (R = Me and Ph) at 25 °C and were allowed to react for 1 h. Subsequent treatment with excess sodium trifluoroethoxide in THF yielded the two polymers of formula (8). Microanalysis and ³¹P integration suggested that the ratio of *x*:*y* in these polymers was 19:1 (R = Me) and 13:1 (R = Ph). The g.p.c. molecular weights were 3×10^5 (R = Ph) and 1×10^6 (R = Me).

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† Elemental analyses were consistent with the formulations shown.

‡ The i.r. spectra of both products showed peaks at 1200 cm⁻¹ (br, KBr disc) (P...N), 2600 (br) (B-H), 3100–2900 (w) (C-H), and 1500 cm⁻¹ (m) (C=C).

§ The mass spectrum of (2) (R = Ph) showed a parent peak at $m/e = 532$ ($M = 532$), and where R = Me at $m/e = 470$ ($M = 470$) with peaks corresponding to the successive loss of five chlorine atoms.

¶ The ³¹P n.m.r. spectra of both derivatives showed an AB₂ pattern centred at 19 p.p.m.

** The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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