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Complexes of Hexamethylbenzene with Chloro- and Dimethylamino-cyclophosphazenes. Some Alternation of Properties with Change in Ring Size

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AMINOCYCLOPHOSPHAZENES are strong electron donors to protonic and Lewis acids.^{1,2} Recently we used phase diagrams to demonstrate complex formation between various amino- and chloro-cyclophosphazenes.³ This technique is now extended to a study of compound formation between hexamethylbenzene, a typical strong π -donor, and chloro- and dimethylamino-cyclophosphazenes having six-, eight-, ten-, and twelve-membered rings. The results are summarized in the Table.

each form one complex; the cyclo-tetra- and -hexa-phosphazenes each form two complexes.

Dimethylaminocyclophosphazenes are strong donors. It is of particular interest that the cyclo-tetra- and -hexa-phosphazenes behave also as electron-acceptors and both form complexes with hexamethylbenzene. Complexes of cyclo-tri- and -penta-phosphazenes are not observed under similar conditions.

These are believed to be the first examples of

TABLE
Composition of Complexes

n	$C_6Me_6:N_nP_nCl_{2n}$	M.p. (°C)	$C_6Me_6:N_nP_n(NMe_2)_{2n}$	M.p. (°C)
3	2:1	149	—	—
4	2:1	152	2:1	156
	1:1	136		
5	2:1	141	—	—
6	1:1	125	1:1	178
	1:2	110		

Chlorocyclophosphazenes are weak or negligible donors towards protons or iodine,^{2,4} but strong acceptors which form complexes with hexamethylbenzene. The cyclo-tri- and -penta-phosphazenes

properties of cyclophosphazenes alternating with ring size. These phase diagrams give indications only of behaviour in the solid state, and the work is being extended to solution.

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¹ S. K. Ray and R. A. Shaw, *Chem. and Ind.*, 1961, 1173; D. Feakins, W. A. Last, and R. A. Shaw, *Chem. and Ind.*, 1962, 510; *J. Chem. Soc.*, 1964, 4464.

² S. K. Das, R. A. Shaw, B. C. Smith, W. A. Last, and F. B. G. Wells, *Chem. and Ind.*, 1963, 866.

³ S. K. Das, R. A. Shaw, and B. C. Smith, *Chem. Comm.*, 1965, 176.

⁴ D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Shaw, *J. Chem. Soc.*, 1965, 2804.