An Unusually Complex Phosphazene arising from the Reaction of Hexachlorocyclotriphosphazatriene with Diphenylmagnesium in 1,4-Dioxan

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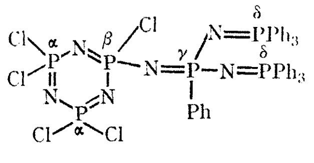
WE recently reported the isolation of a two-ring phosphazene assembly, $N_6P_6Ph_2Cl_8$,[1] from the reaction of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with diphenylmagnesium in 1,4-dioxan. The major product (41%) is compound (I), m.p. 152°, whose elemental analysis and molecular weight indicate the formula $N_6P_6Ph_7Cl_5$. Compound (I) has a pronounced tendency to crystallise with the inclusion of solvent, *e.g.* benzene, diethyl ether, or n-hexane It can however be obtained free of solvent by heating to 155° or by recrystallisation from nitromethane or ethyl alcohol. Acid degradation of compound (I) yields triphenylphosphine oxide, $Ph_3P{:}O$ (2 mol.), phenylphosphonic acid, $PhP({:}O)(OH)_2$ (1 mol.), and phosphoric acid, H_3PO_4 (3 mol.). The ^{31}P spectrum of this compound (I) has been studied with a nuclear–electron double resonance spectrometer operating at 12,500 G. Comparison of the ^{31}P spectrum of compound (I) with those of reference compounds (studied by means of the above technique)[2] such as $N_3P_3Cl_6$, $N_4P_4Cl_8$, *gem*-$N_3P_3Cl_4Ph(NPPh_3)$,[3] $N_3P_3Cl_5(NPPh_3)$,[3,4] and $N_4P_4Cl_7(NPPh_3)$,[4] strengthens the above assignments. We suggest 2,2,4,4,6-pentachloro-6-[2,4,4,4-tetraphenyl-2-(2,2,2-triphenylphosphazen-1-yl)diphosphazadien-1-yl]cyclotriphosphazatriene, $N_3P_3Cl_5[NPPh_3)_2]$, as structure for compound (I).

TABLE

^{31}P Chemical shift from external P_4O_6 (p.p.m.)	Enhancement	Line width (Hz)	Splitting (Hz)	Relative area	Assignment
$+\ 93{\cdot}2 \pm 0{\cdot}5$	+1	20	40 ± 2	2	P_α
$+105{\cdot}4 \pm 0{\cdot}7$	0 or -ve	45	s	2	P_δ
$+118{\cdot}1 \pm 0{\cdot}5$	0 or -ve	45	s	1	P_γ
$+122{\cdot}6 \pm 1{\cdot}0$	0	20—30	t 1:2:1 40 ± 5	1	P_β



Reaction of compound (I) with an excess of the sodium salt of 2,2,2-trifluoroethanol affords the corresponding pentakis-(2,2,2-trifluoroethoxy)-derivative, $N_6P_6Ph_7(OCH_2CF_3)_5$. The ^{19}F n.m.r. spectrum (Varian HA 100 instrument) showed three different ^{19}F chemical environments in the ratio of 2:2:1, in agreement with the phosphorus–nitrogen skeleton proposed. The high yield of this product (I) arising from such apparently simple starting materials gives some indication of the complexity of this reaction.

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