Phosphazene Carbanions as Synthetic Intermediates: Silicon, Germanium, and Tin Derivatives

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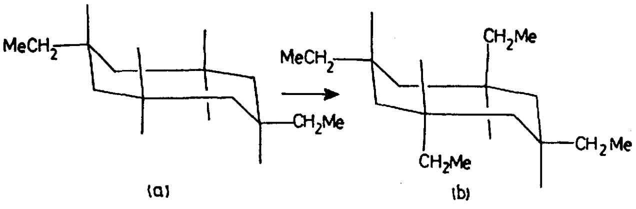
Summary The tetra-carbanion formed from methyllithium and octamethylcyclotetraphosphazene reacts with methyl iodide and with the chlorides Me_3XCl (X = Si, Ge, Sn) to give $N_4P_4Me_4(CH_2R)_4$ (R = Me, XMe_3).

Although there have been many investigations of the effect of different substituents on the reactivity of cyclic phosphazenes, the reactivity of the substituent itself has been less studied. We have found that octamethylcyclotetraphosphazene $N_4P_4Me_8$ can be deprotonated by methyllithium in diethyl ether. The novel carbanion $N_4P_4Me_4(CH_2^-)_4$ so formed has been identified through its reaction with methyl iodide, which gives $N_4P_4Me_4Et_4$ (**1**) with a small amount of the diethyl derivative, isolated as its dihydrochloride $N_4P_4Me_6Et_2 2HCl$ (**2**). All four phosphorus atoms in (**1**) are equivalent [δ_P ($CDCl_3$, upfield of ext. P_4O_6) 89·4], each phosphorus atom carrying a methyl and an ethyl group [δ_H ($CDCl_3$, int. Me_4Si) 1·41 MeP, 1·10 *Me*CH_2P; 1·65 MeCH*$_2$*P; J_{PH} MeP, 11·5; *Me*CH_2P, 17·0 Hz]. The carbanion reacts similarly with Me_3XCl(X = Si, Ge, Sn) to form the air-stable, crystalline compounds $N_4P_4Me_4(CH_2XMe_3)_4$ in high yields.†

A crystal structure determination shows that the ethyl groups in (**2**) lie in equatorial positions of a centrosymmetric chair-shaped cation (a). The Raman and i.r. spectra of (**1**) are consistent with the centrosymmetric structure (b), though, because of possible accidental degeneracies, they do not entirely exclude the alternative *cis*, *-cis*, *-cis*, *-trans*-configuration. Activation of methyl[1] and methylene[2] groups attached to a phosphoryl group has often been attributed to *d*-orbital interactions, and a phosphazo-group may well act similarly; the stability of the carbanion would be enhanced by conjugation with the ring π-system, as in the anions formed from methylpyridines;[3] a similarly large formal charge is found in the carbanion $(SCH^-)_4$,[4] which owes its stability to the known acceptor properties of divalent sulphur.



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† Correct analyses were obtained for all compounds.

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