Reactivity of Trimeric Chlorophosphazenes and Chlorothiaphosphazenes towards Alkyl-lithium Reagents

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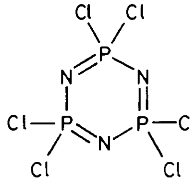
Reaction of cyclic chlorophosphazenes and chlorothiaphosphazenes with alkyl-lithium reagents and isopropyl alcohol affords hydrido-isopropoxy derivatives and cyclic alkylated species.

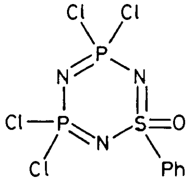
Reactions between $(NPCl_2)_3$ (**1**) and Grignard reagents, *i.e.* RMgCl and RMgCl–$(Bu^n{}_3PCuI)_4$ (R = alkyl), are well documented.[1—3] The predominant reaction pathway is presumed to be a metal–halogen exchange process leading to alkylated derivatives in excellent yields. Surprisingly little is known about the reactivity of (**1**) towards alkyl- and aryl-lithium reagents. Reactions of (**1**) with PhLi, $PhCH_2Li$, or MeLi have been reported to give extensive ring cleavage in addition to the formation of a very small amount of methylated cyclic derivatives in the case of MeLi.[4]

Here we report serendipitous results from the reaction of $(NPCl_2)_n(NSOPh)_{3-n}$ (n = 1,2,3) with RLi (R = Me, Bu^t).

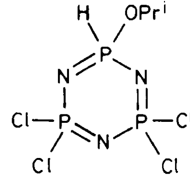
Reaction of *trans*-$NPCl_2(NSOPh)_2$ (**2**) with Bu^tLi (1 : 1) in tetrahydrofuran (THF) at −78 °C under dry nitrogen, followed by stirring at room temperature for two hours and subsequent treatment with a five-fold excess of Pr^iOH at 0 °C afforded a mixture of three cyclic products, which could be separated by means of h.p.l.c. (silica column, Et_2O–hexane–MeCN = 1 : 1 : 0.005), *viz*. $NPClBu^t(NSOPh)_2$ (**3**) (yield 38%, m.p. 166.0—168.0 °C), $NP(H)Bu^t(NSOPh)_2$ (**4**) (yield 8%, m.p. 125.0—127.0 °C), and $NP(H)OPr^i$-$(NSOPh)_2$ (**5**) (yield 30%, m.p. 77.5—79.5 °C). Structures could be assigned unambiguously on the basis of ^{31}P and ^1H n.m.r. spectroscopic (Table 1), mass spectrometric, and micro-analytical data.



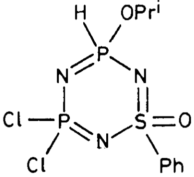
(**1**)



(**6**)



(**7**)



(**8**)

By analogy with the alkylation of (**1**) by RMgCl–$(Bu^n_3PCuI)_4$, the formation of (**4**) is assumed to proceed according to a metal–halogen exchange process and subsequent reactions with Bu^tLi and Pr^iOH.[2] Presumably, (**5**) is formed *via* the intermediate $NP(H)Cl(NSOPh)_2$; a simple nucleophilic substitution leads to the formation of (**3**). The elucidation of the complex reaction scheme, however, needs further investigation. The compounds $(NPCl_2)_2NSOPh$ (**6**) and (**1**) appeared to be less reactive than (**2**) towards Bu^tLi. Reaction mixtures contained the starting materials (40%) together with hydrido–isopropoxy derivatives (50—60%), $NP(H)OPr^iNPCl_2NSOPh$ (**8**) and $NP(H)OPr^i(NPCl_2)_2$ (**7**), respectively. In the case of (**6**) small amounts of alkylated species (10%) were also obtained.

In contradiction to literature results, reactions with MeLi did not lead to extensive ring degradation. For instance, reaction of (**1**) with MeLi (molar ratio 1 : 1) in THF at −78 °C, followed by stirring at −20 °C for four hours and subsequent

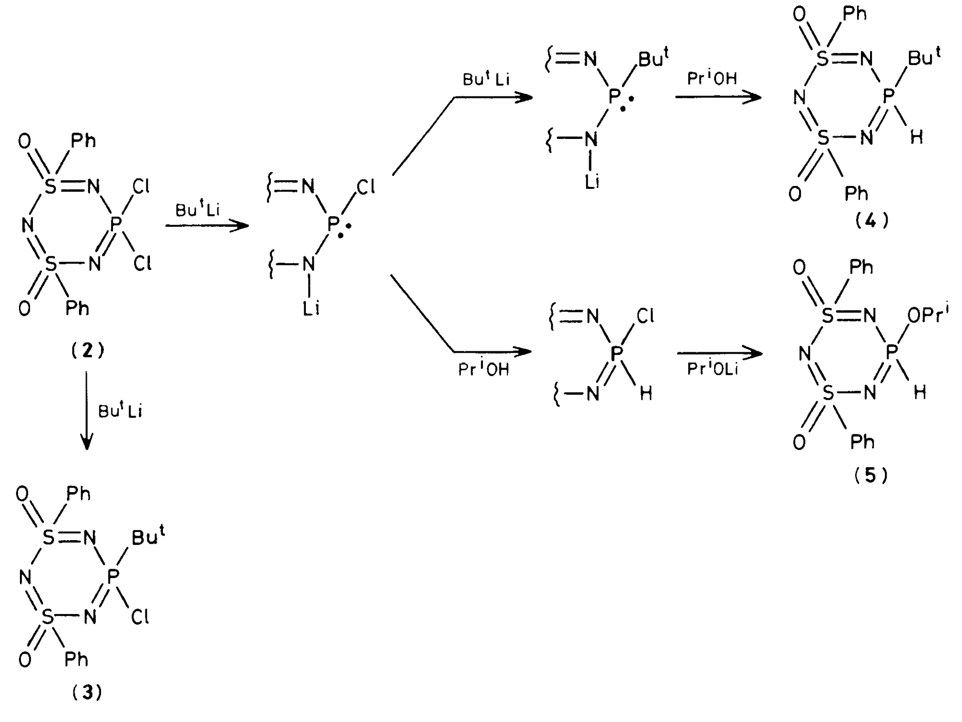


Table 1. ^{31}P N.m.r. (81.0 MHz) and ^1H n.m.r. (60 MHz) data ($CDCl_3$).

	$\delta(^{31}P)$/p.p.m.		$^2J_{PP}$/HZ	$^1J_{PH}$/Hz	$\delta(^1H)$			$^3J_{HH}$/Hz	$^3J_{PH}$/Hz
	PRR′	PCl_2			Me	CH	PH		
(**3**)	51.5				1.2				22.6
(**4**)	26.7			532.8	1.0		6.6		19.7
(**5**)	−1.0			731.6	1.0/1.2[a]	4.3	6.8	5.8	
(**7**)	2.5	20.9	26.0	719.0	1.3	4.5	6.4	5.8	
(**8**)	1.4	23.3	28.0	725.2	1.4	—	—	5.8	

[a] Two ^1H n.m.r. signals were observed due to the chirality of the ring system.

treatment with a five-fold excess of Pr^iOH at −20 °C, yielded a mixture of cyclic compounds. Extraction of the crude reaction mixture with pentane afforded a white oil (yield about 70%) consisting of (**1**) (15%) and (**7**) (85%) (based on ^{31}P n.m.r.). Purification of (**7**) by h.p.l.c. or distillation at reduced pressure failed because of its moisture sensitivity and thermal instability. After sublimation at 60 °C (0.1 mm Hg) and molecular distillation at 100 °C (0.1 mm Hg) a colourless oil could be obtained with a 96% purity of (**7**).

Under the same reaction conditions (**6**) provided a white oil (yield about 70%) consisting of (**6**) and (**8**) in a ratio of 3 : 7; in the case of (**2**) only the hydrido-isopropoxy derivative was formed in a yield of 50%.

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