Cyclophosphazenes as Nucleophiles: the Addition of Copper(I) Cyclophosphazenes to Aldehydes and Ketones

Pieter L. Buwalda and Johan C. van de Grampel*

Department of Inorganic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Novel *gem*-alkyl(hydroxyalkyl)tetrachlorocyclophosphazenes $(NPCl_2)_2NPR^1[C(OH)R^2R^3]$ have been prepared by nucleophilic addition of copper(I) cyclophosphazenes to aldehydes or ketones, followed by acid hydrolysis.

The formation of transient copper(I) cyclophosphazenes by the reaction of $(NPCl_2)_3$ (**1**) with RMgCl in the presence of $[Bu^n{}_3PCuI]_4$[1,2] offers a unique opportunity of performing nucleophilic substitutions and additions using cyclophosphazenes as nucleophilic agents. The substitution of halide in alkyl halides, leading to a broad range of *gem*-dialkylcyclophosphazenes has been described by Allcock and coworkers.[2] Here we report some examples of a nucleophilic addition involving aldehydes and ketones, as shown in Scheme 1.

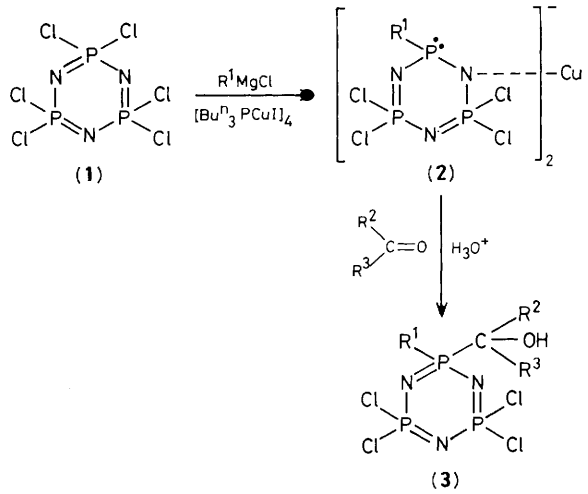
Metallophosphazene (**2**) was prepared in essentially the same way as described in the literature.[1] Then 4 equiv. of aldehyde or ketone were added (except for acetone where 40 equiv. were used). The resulting mixture was stirred for 2 hours to 10 days under dry nitrogen. After hydrolysis of the reaction mixture by a saturated aqueous NH_4Cl solution, products (**3**) could be obtained in a pure state by flash chromatography (silica column, tetrahydrofuran–hexane mixtures as eluant) and subsequent recrystallization from pentane (yields varying from 50 to 75%). Characterization took place by spectroscopic methods (i.r., n.m.r., and mass) and by elemental analysis. The various products (**3**) obtained are given in Table 1, together with their ^{31}P n.m.r. data.

As expected aldehydes appear to be more reactive than ketones (reaction time 2 *vs.* 10 days), whereas chloroacetone reacts within 2 hours. It is noteworthy that in the case of crotonaldehyde the 1,2-addition competes successfully with the 1,4-route, as no $-CH(Me)CH_2CHO$ derivative could be detected in the reaction mixture.

Table 1. Compounds $(NPCl_2)_2NPR^1[C(OH)R^2R^3]$ (**3**); $^{31}P\{^1H\}$ n.m.r. data.[a]

			δ(^{31}P)/p.p.m.			$^2J_{PP}$/Hz		
R^1	R^2	R^3	P(organosubst.)	PCl_2(A)	PCl_2(B)	AX	BX	AB
Me	Me	H	39.3	19.0		[d]	[d]	[d]
Me	Me	Me[b]	43.8	18.1		[d]	[d]	[d]
Me	Ph	H	37.1	19.0		[d]	[d]	[d]
Pr^i	Me	H	49.3	19.3		[d]	[d]	33.7
Pr^i	Ph	H	47.3	19.3		[d]	[d]	32.6
Bu^t	Me	H	50.0	18.1	19.5	14.4	10.2	32.4
Bu^t	Me	Me	51.8	18.1		17.4		
Bu^t	CH_2Cl	Me	49.5	18.6[c]		15.0		
Bu^t	CH=CHMe	H	48.9	18.3	19.6	17.0	15.2	31.5
Bu^t	Ph	H	49.0	18.0	19.5	14.9	12.6	31.4
Bu^t	*p*-$NO_2C_6H_4$	H	45.3	19.3	19.9	[d]	[d]	34.0

[a] Solvent $CDCl_3$, external reference $(NPCl_2)_3$, δ(^{31}P) = 19.9 p.p.m. [b] Liquid. [c] A_2X type spectrum. [d] Coupling unresolved.



Scheme 1

The presence of an asymmetric $C(OH)R^2R^3$ moiety in compound (**3**) can lead to ABX type $^{31}P\{^1H\}$ n.m.r. spectra caused by the diastereotopic nature of the PCl_2 groups.

The nucleophilic addition reactions are not restricted to the NP system only, as the cyclothiaphosphazene $NSOPh(NPCl_2)_2$ gives similar results.

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References

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