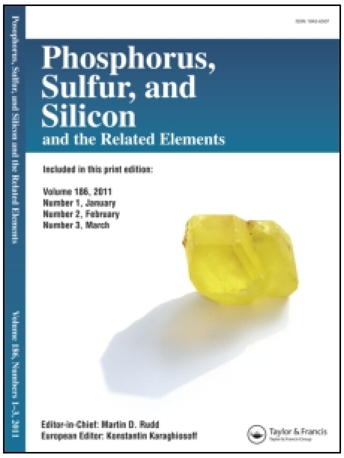


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Novel Phosphazene-Substituted Siloxanes and Silanes

J. C. van De Grampel[a]; A. P. Jekel[a]; R. Puyenbroek[a]; T. J. Arling[a]; M. C. Faber[a]; W. Fransen[a]; A. Meetsma[a]; J. H. Wübbels[a]
[a] Department of Polymer Chemistry, University of Groningen, AG Groningen, The Netherlands

To cite this Article van De Grampel, J. C. , Jekel, A. P. , Puyenbroek, R. , Arling, T. J. , Faber, M. C. , Fransen, W. , Meetsma, A. and Wübbels, J. H.(1993) 'Novel Phosphazene-Substituted Siloxanes and Silanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 76: 1, 215 — 218

To link to this Article: DOI: 10.1080/10426509308032397
URL: http://dx.doi.org/10.1080/10426509308032397

Phosphorus, Sulfur, and Silicon, 1993, Vol. 76, pp. 215–218

NOVEL PHOSPHAZENE-SUBSTITUTED SILOXANES AND SILANES

J.C. VAN DE GRAMPEL, A.P. JEKEL, R. PUYENBROEK, T.J. ARLING, M.C. FABER, W. FRANSEN, A. MEETSMA, and J.H. WÜBBELS

Department of Polymer Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

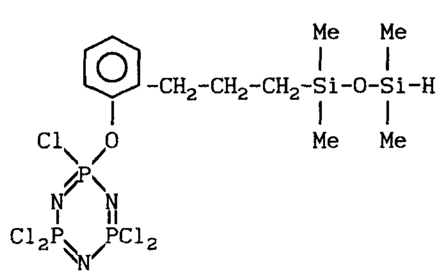
Abstract Cyclophosphazene-substituted siloxanes and silanes are prepared by the method of hydrosilylation, starting from allyl-derivatized cyclophosphazenes and hydrosiloxanes or hydrosilanes in the presence of a platinum catalyst. Steric and electronic effects govern the course of the reaction.

INTRODUCTION

Hydrosilylation appears to be a very effective and useful method to induce coupling between a Si-H and an alkenyl residue. For instance, the reaction between Cl_2MeSiH and allylbenzene in the presence of a platinum catalyst leads to a high yield of $Cl_2MeSiCH_2CH_2CH_2Ph$. In the scope of our research on polymeric systems with inorganic side groups[1] we used this method to prepare cyclophosphazene-substituted siloxanes and silanes, starting from allyl-derivatized cyclophosphazenes and hydrosiloxanes or hydrosilanes.

RESULTS AND DISCUSSION

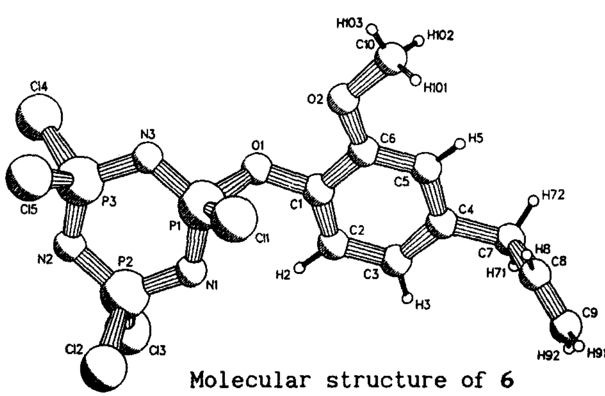
Hydrosilylation of tetramethyldisiloxane (**1**) with one equivalent of *o*-allylphenoxypentachloro-cyclotriphosphazene (**2**) in the presence of Karstedt catalyst gave the disiloxane (**3**) almost quantitatively.



3

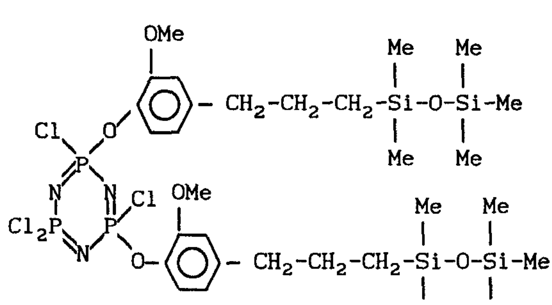
When raising the amount of the phosphazene in the reaction mixture the corresponding disubstituted tetramethyldisiloxane (**4**) was formed. Reaction of **2** with the polysiloxane, $Me_3SiO[(SiMe_2O)_x(SiMeHO)_y]SiMe_3$ ($x = 0$, $y = 35$) did not lead to a complete hydrosilylation. Only the so-called diluted systems ($x \neq 0$) showed reactions at all SiH centres. For the phenoxy analogue of **2**, $[NP(OPh)_2]_2NP(OPh)OC_6H_4$-*o*-$CH_2CH{=}CH_2$ (**5**), even the diluted systems did not show a complete hydrosilylation[2]. This means that obviously steric hindrance, exerted by the phosphazene moiety, plays an important role during the hydrosilylation. Therefore another allylphenoxy derivative was introduced, now with the reactive organic side on *p*-position, viz. $(NPCl_2)_2NPClOC_6H_3$(*o*-OMe)*p*-$CH_2CH{=}CH_2$ (**6**). Both on small molecule [tetra- or pentamethyldisiloxane, (**1**), (**7**)] as on polymer scale complete hydrosilylation took place.

The structure of **6** clearly shows the C=C moiety being at the outside of the molecule which corresponds with the reactivity observed.



Molecular structure of **6**

The compound, *cis*-$NPCl_2[NPClOC_6H_3$(*o*-OMe)*p*-$CH_2CH{=}CH_2]_2$ (**8**), exhibits

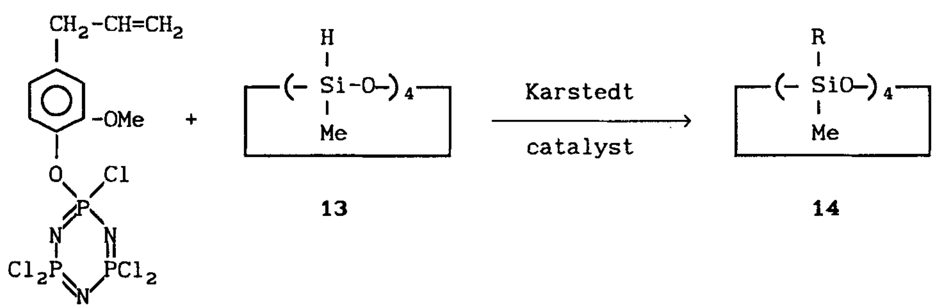


9

similar structural features and hence a comparable reactivity. Hydrosilylation of **7** with **8** gave smoothly the expected addition product (**9**).

Polyhydrosilylation can be induced when **8** or other bifunctional phosphazenes with allyl residues, e.g. $(NPCl_2)_2NPClN(CH_2CH{=}CH_2)_2$ (**10**), $NPCl_2[NPCl(NHCH_2CH{=}CH_2)]_2$ (**11**), or $(NPCl_2)_2NP(OC_6H_4$-*o*-$CH_2CH{=}CH_2)_2$ (**12**) are allowed to react with **1**. Preliminary results showed indeed the formation of low-molecular weight oligomers.

Also cyclosiloxanes are accessible to hydrosilylation with **6**, which is demonstrated by the reaction given below.



6 **13** **14**

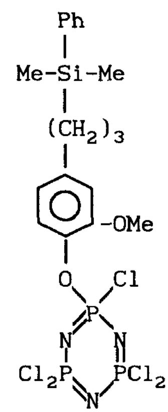
$R = (NPCl_2)_2NPClOC_6H_3(OMe)(CH_2)_3$

Besides the formation of **14** considerable isomerization of **6** to $(NPCl_2)_2NPOC_6H_3(OMe)CH{=}CHCH_3$ (**15**) was observed.

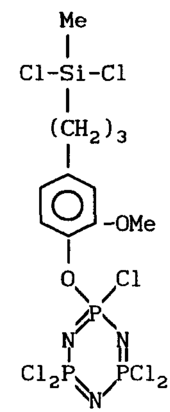
With respect to other side reactions it has to be mentioned that in general pentamethyldisiloxane (**7**) offers less complicated reaction mixtures than its tetramethyl analogue (**1**).

Compared with siloxanes, silanes exhibited a similar reactivity towards alkenyl-substituted cyclophosphazenes. For instance, compounds (**16**) and (**17**) could be prepared in very high yields from **6** in combination with $PhMe_2SiH$ (**18**) and $MeHSiCl_2$ (**19**), respectively.

In addition to steric effects reactivity in hydrosilylation is governed by the electron density of the unsaturated ligand-site. This means that an insulating spacer between the electron-withdrawing phosphazene ring and the C=C bond plays an important role.



16



17

To reveal to some extent the directing effect of the spacer reactions were carried out with **18** as "SiH" reagent and some organo-substituted cyclophosphazenes, differing from each other by the nature of the spacer. Karstedt's compound was used as catalyst. The electron density of the C=C moiety was correlated to the ^{13}C chemical shift of $=CH_2$ group, as lower the value of δ ^{13}C as higher the electron density. It turned out that compounds $(NPCl_2)_2NPCl[spacer]CH_2CH=CH_2$ (spacer = $OC_6H_{3,4}$, N, or O) and the compound $(NPCl_2)_2NPMe(CH_2CH=CH_2)$ with δ $^{13}C(=CH_2)$ values ranging from 116 to 122 ppm were reactive in hydrosilylation, whereas $(NPCl_2)_2NP^iPrCH(Me)OC(O)C(Me)=CH_2$ [δ $^{13}C(=CH_2)$ = 127 ppm] appeared to be not active under the reaction conditions applied.

Investigations to the behaviour in hydrosilylation reactions of the disilane $Me_2HSiSiHMe_2$ and the polysilane $Me_3Si-[MeSiH]_n-SiMe_3$ are currently underway.

REFERENCES

1. J. C. van de Grampel, G. O. R. Alberda van Ekenstein, J. Baas, P. L. Buwalda, A.P. Jekel and G.E. Oosting, Phosphorus Sulfur Silicon, 64, 91 (1992).
2. R. Puyenbroek, A. P. Jekel and J. C. van de Grampel, J. Inorg. Organomet. Polym., 1, 105 (1991).