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Synthesis of Alkoxysilyl Substituted Cyclophosphazenes and their Properties in the Sol-Gel Process

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Summary. Cyclophosphazenes with different alkoxysilyl substituents were synthesized as new starting compounds for material synthesis *via* the sol-gel process. Their hydrolysis was investigated by FT *Raman* spectroscopy, and the thermal stability of the hydrolyzed and condensed new cyclophosphazenes was determined *via* thermogravimetric analysis. The organopolysiloxane of the type $(N=P(CH_2SiO_{3/2})_2)_5$ is thermally stable up to 430°C in air. Cyclophosphazenes bearing 3-aminopropyltriethoxysilane (*APTES*) substituents were cocondensed with methacryloxypropyltrimethoxysilane, and some properties of coatings obtained from this composition were compared with the properties of a coating made from a mixture of tetraethoxysilane (*TEOS*) and methacryloxypropyltrimethoxysilane.

Keywords. Alkoxysilyl substituted cyclophosphazenes; Hydrolysis; Thermal stability; Coatings.

Synthese von alkoxysilylsubstituierten Cyclophosphazenen und ihre Eigenschaften im Sol-Gel-Prozeß

Zusammenfassung. Cyclophosphazene mit unterschiedlichen Alkoxysilylsubstituenten wurden als neue Ausgangsverbindungen für die Materialsynthese im Sol-Gel-Prozeß hergestellt. An den neuen Cyclophosphazenverbindungen wurde die Hydrolysereaktion mittels FT-*Raman*-Spektroskopie untersucht. Die thermische Stabilität der hydrolysierten und kondensierten Cyclophosphazene wurde mittels Thermogravimetrie bestimmt. Das Polysiloxan mit der Zusammensetzung $(N=P(CH_2SiO_{3/2})_{25}$ ist an Luft bis 430°C stabil. Cyclophosphazene mit 3-Aminopropyltriethoxysilan (*APTES*) als Substituent wurden mit Methacryloxypropyltrimethoxysilan kokondensiert. Die aus dem resultierenden Sol hergestellten Schichten wurden mit Schichten aus Tetraethoxysilan (*TEOS*) und Methacryloxypropyltrimethoxysilan verglichen.

Introduction

During the last years, sol-gel derived coatings have been well established for various applications. The sol-gel route, originally directed towards the synthesis of purely inorganic materials, is increasingly being extended to the preparation of inorganic/organic copolymers [1]. Starting from hydrolyzable molecular com-

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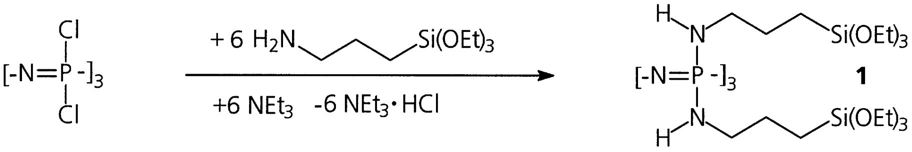
pounds *e.g.* *R*Si(OEt)$_3$, formation of a siloxane network is induced by reaction with water. Polymerizable or special functional groups *R* influence the chemical and physical properties of the resulting materials to a high degree [2]. In order to increase the field of applications for this type of material, new compositions are investigated world-wide with the aim to improve and tailor the desired material properties. Since the sol-gel process requires monomeric hydrolyzable alkoxysilyl compounds, new alkoxysilyl substituted cyclophosphazenes were synthesized with the goal to incorporate these thermally stable ring systems into organically modified polysiloxanes *via* sol-gel processing [3].

Results and Discussion

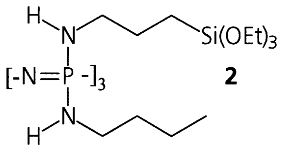
Synthesis of the precursor molecules

The incorporation of cyclophospazenes into organopolysiloxanes *via* sol-gel processing affords the synthesis of monomeric hydrolyzable alkoxysilyl substituted cyclophosphazenes as precursor molecules. The easiest way to introduce an alkoxysilyl group is the reaction between hexachlorocylotriphosphazene and 3-aminopropyltriethoxysilane (*APTES*). According to a general procedure developed by *Allcock* for the synthesis of aminosubstituted cyclophosphazenes [4], 3-aminopropyltriethoxysilane was reacted with hexachlorocyclotriphosphazene in toluene.



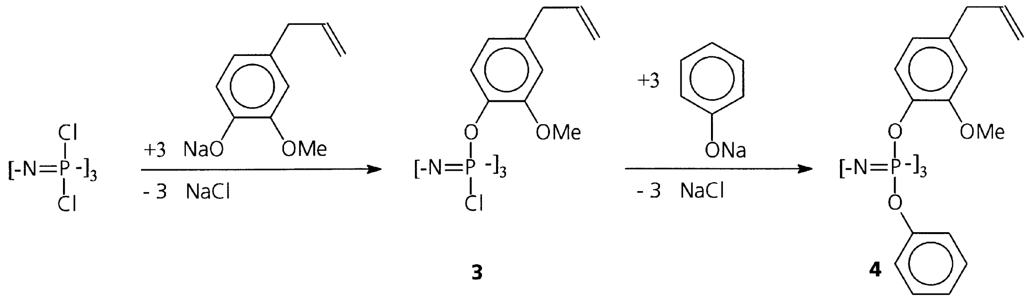
Scheme 1

This reaction provided **1** in 82% yield. In an analogous reaction using 6 equivalents of butylamine in the first step and 3 equivalents of 3-aminopropyltriethoxysilane as well as an excess of triethylamine in the second step, compound **2** was isolated as a mixture of geminal and non-geminal isomers.



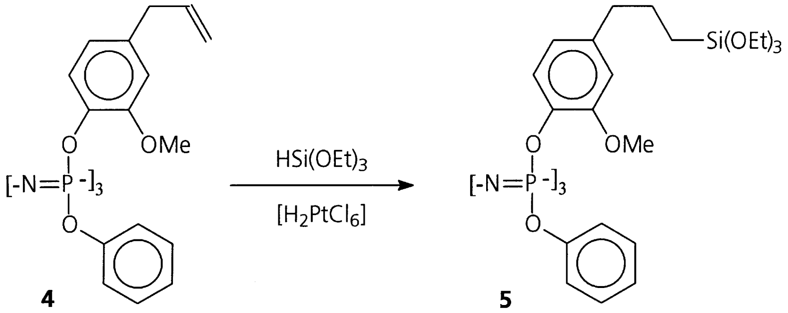
Scheme 2

Van den Grampel et al. introduced allylaryl substituents into cyclotriphosphazene for the purpose of hydrosilylation [5]. Following this route, three chlorine atoms in hexachlorocyclotriphosphazene were substituted by potassium-2-methoxy-4-allylphenolate, leading to the non-geminal product **3**. In the second step, the remaining chlorine atoms were replaced by a stoichiometric amount of sodium phenolate. Compound **4** was isolated in a yield of 49% calculated from the amount of hexachlorocyclotriphosphazene used. The substitution of all chlorine atoms is necessary due to the instability of the phosphorus-chlorine bond towards hydrolysis.



Scheme 3

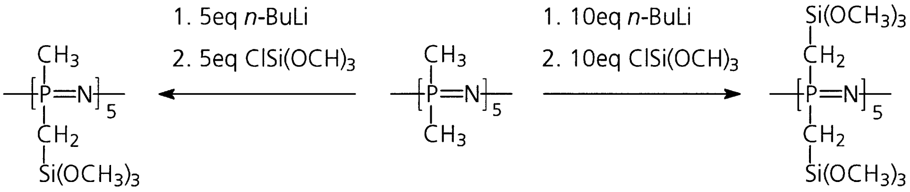
Hydrosilylation of **4** with triethoxysilane under catalysis of $[H_2PtCl_6]$/2-propanol in *THF* finally afforded the silylated compound **5** in 78% yield.



Scheme 4

In order to obtain cyclophosphazenes containing a direct phosphorus-carbon linkage without nitrogen or oxygen as heteroatom in the bridging unit between the phosphazene ring and the alkoxysilyl moiety, a different approach was necessary. The cyclophosphazene ring is formed by a thermal decomposition reaction of $(H_3C)_2BrP{=}NSi(CH_3)_3$. A modification of the pyrolysis reaction of the N-silyl-P-bromophosphinimine established by *Neilson et al.* [6] leads to decamethylcyclopentaphosphazene in a yield of 84%.

Complete or partial lithiation of decamethylcyclopentaphosphazene followed by the addition of chlorotrimethoxysilane results in the formation of the silylated compounds **6** and **7**.



Scheme 5

FT Raman spectroscopic investigations

Raman spectroscopy has proven to be a powerful tool for the investigation of the sol-gel process [7]. *Raman* data provide information about the hydrolysis reaction of the alkoxysilanes leading to the silsesquioxane network. In Fig. 1, the *Raman* spectra of **1** during the reaction with water are shown. After starting the hydrolysis using a stoichiometric amount of water with respect to the number of hydrolyzable alkoxysilyl groups and NH_4F as catalyst, the band at $650\,cm^{-1}$ diminishes. This band can be assigned to the $\nu(SiO_3)$ stretchting vibration of the $-Si(OEt)_3$ moiety [7] and shows the decrease of the unhydrolyzed compound **1** during formation of the siloxane network. The band at $884\,cm^{-1}$ assigned to the CO-stretching vibration of ethanol [8] appears during the reaction indicating the evolving of ethanol due to hydrolysis of **1**.

For the evaluation of the reaction kinetics, the intensities of the *Raman* bands at $650\,cm^{-1}$ and $884\,cm^{-1}$ were determined and plotted against the reaction time (Fig. 2).

Generally, the decrease of the $\nu(SiO_3)$ stretchting vibration goes along with the increase of the CO-stretching of ethanol as expected. The curves show that the decrease of the $-Si(OEt)_3$ moiety is complete after 120 min, whereas EtOH formation is nearly finished after about 200 min. This phenomenon is explained by the formation of partially hydrolyzed intermediate species (RSi(OH)(OEt)$_2$ and RSi(OH)$_2$OEt) which could not be identified due to their low intensities in this *Raman* experiment, but which also eliberate ethanol.

It turned out that the hydrolysis of **1** depends strongly on the catalyst used. As can be seen from Fig. 3, only NH_4F is significantly effective. The same behaviour is observed for **2**. Therefore, NH_4F is used as a catalyst in the following experiments with **1** and **2**.

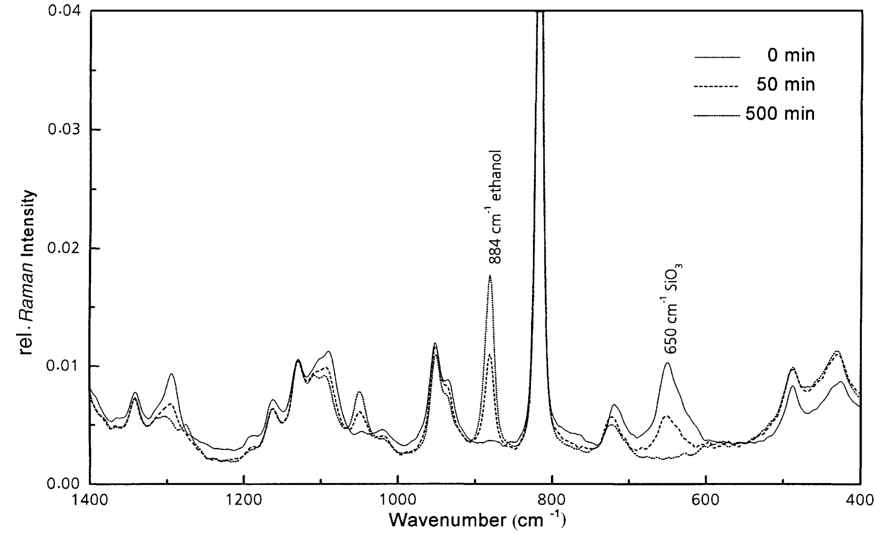


Fig. 1. *Raman* spectra of **1** during hydrolysis at 20°C with 0.1 *M* NH_4F as catalyst; the characteristic *Raman* bands are indicated in the plot; the plots are recorded 0 min (solid), 50 min (dashed), and 500 min (dotted) after start of the hydrolysis reaction

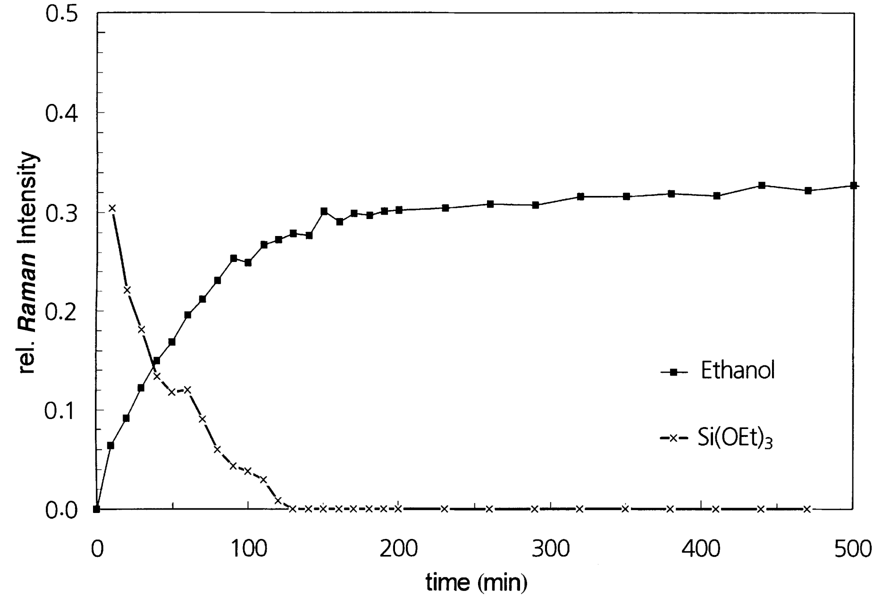


Fig. 2. Kinetic plot of the hydrolysis of 1; the curve indicated by squares represents the evolving of ethanol, the curve indicated by crosses represents the decrease of unhydrolyzed **1**

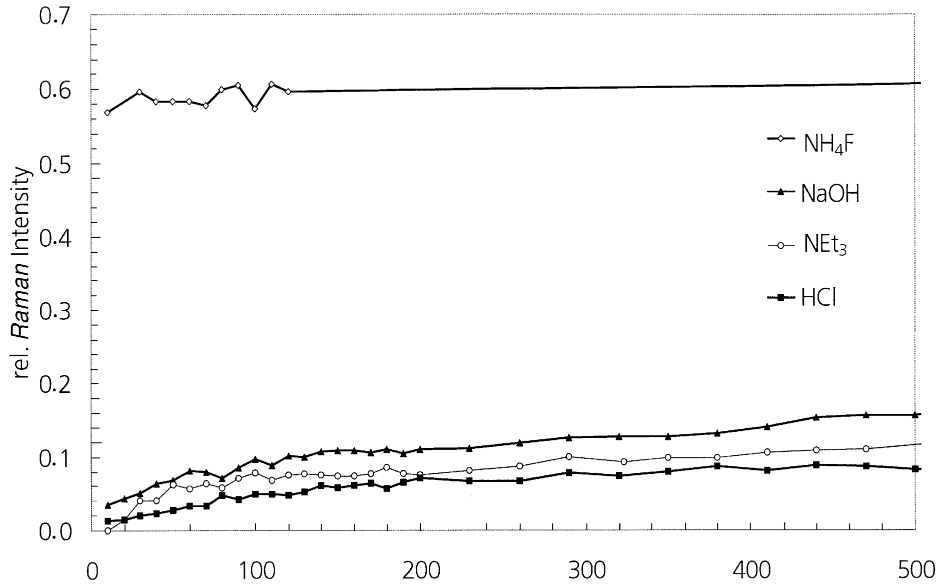


Fig. 3. Kinetic plot of EtOH formation from **1** (filled squares: catalysis with 0.1 *M* HCl, circles: 0.1 *M* NEt_3, triangles: 0.1 *M* NaOH, unfilled squares 0.1 *M* NH_4F)

A completely different behaviour was observed with **6** and **7**. The hydrolysis rate is four times faster than for **1** and **2** and independent from the catalyst used. In the present case, even the reaction without any catalyst proceeds in the same time as the catalyzed reaction. The effect is shown for **6** in Fig. 4. This behaviour is

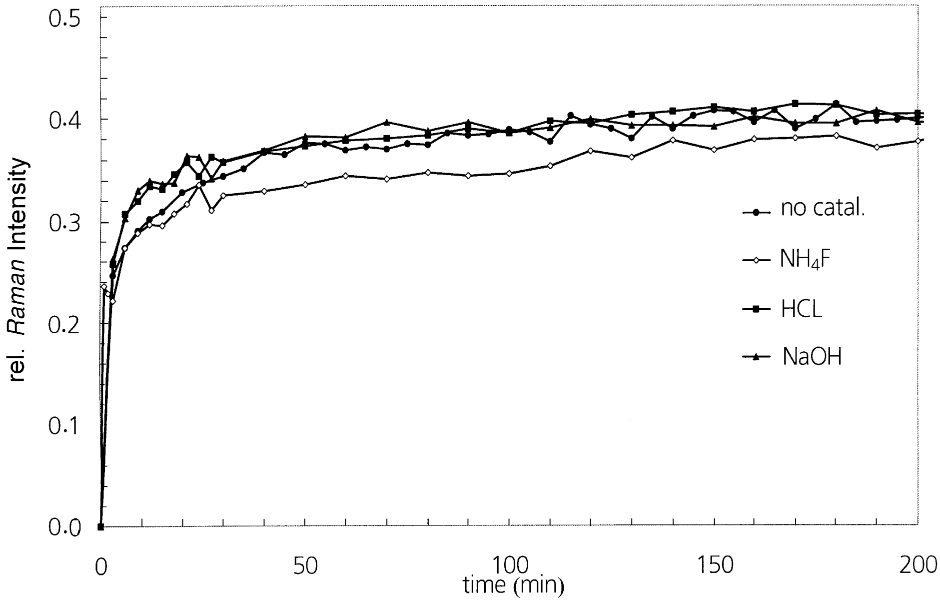


Fig. 4. Kinetic plot of EtOH formation from **6** (filled squares: 0.1 *M* HCl catalysis, circle: without catalysis, triangles: 0.1 *M* NaOH catalysis, unfilled squares: 0.1 *M* NH_4F catalysis)

partly attributed to the more reactive methoxy groups. It is also possible that a neighbouring group mechanism is operating and that the nitrogen atoms of the phosphazene ring act as a donor and a pentavalent intermediate is formed that stretches and weakens the Si–OMe bonds.

Thermal stability of cyclophosphazene modified organopolysiloxanes

The samples obtained from the hydrolysis experiments were dried for two hours at 120°C in an oven and submitted to TGA. The decomposition temperature measured in air was defined as the temperature where a weight loss of 5% had occurred [9]. The hydrolysis products derived from **1** and **2** are fairly instable and start to decompose around 220°C. Both the stabilizing influence of the phenyl group and the presence of an oxygen link to the phosphazene ring in the siloxane derivative of **5** increase significantly the stability up to 320°C. The highest thermal stability was measured for the hydrolysis products of **6** and **7** which exhibit decomposition temperatures of 345°C and 430°C, respectively. On the one hand, the direct P–C-linkage in **6** and **7** increases the stability of the resulting phosphazene siloxanes compared to derivatives with an oxygen or a nitrogen as bridging atom. On the other hand, the higher number of alkoxysilyl groups in **7** compared to **6** faciliates inorganic silicate-like crosslinking also leading to a higher thermal stability.

Coating properties

An important feature of the polysiloxane coating materials developed at the Fraunhofer Institute for Silicate Research known as ORMOCER®s (Trademark of the *Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V.*) is their hardness. Therefore, they are widely used as scratch resistant coatings on various substrates [10, 11]. In order to elucidate the properties of polysiloxanes containing cyclophosphazenes, the new alkoxysilanes **1** and **2** were cocondensed with methacryloxy-propyltrimethoxysilane (*MEMO*). The obtained sols were applied on glass and polycarbonate substrates and cured by UV induced polymerization of the methacrylic group using Irgacure 500® as photoinitiator. The resulting coatings were compared to a UV cured coating derived from tetraethoxysilane (*TEOS*) and *MEMO*. In preliminary investigations it turned out that the hardness of the coatings prepared from **1** (*MEMO*:**1** = 16:0.9) and **2** (*MEMO*:**2** = 16:1.8) was 256 N/mm^2 and 276 N/mm^2, respectively. Layers prepared from *MEMO* and TEOS (ratio:16:4) exhibit only 208 N/mm^2. This significant increase of hardness is remarkable since the amount of hydrolyzable and crosslinkable alkoxy groups in the sols derived from *TEOS*, **1** and **2** were equal. The higher hardness of the layers made from **1** and **2** can be attributed to the higher degree of three-dimensional inorganic crosslinking of the large silyl substituted cyclophosphazene. The higher hardness of the layer derived from **2** compared to that from **1** can be explained by the increased steric hindrance in **1** which possesses 18 alkoxy groups. This high steric hindrance will interfere with the hydrolysis reaction and on a larger scale with the condensation reaction. Thus, the formation of the silicate-like network is limited. This assumption is manifested by solid state ^{29}Si NMR experiments. The ^{29}Si CP/MAS spectra of the hydrolysis and condensation products derived from **1** show a smaller intensity of the T^3-peak than the spectra of the product derived from **2**. Therefore, the inorganic crosslinking in products derived from **2** is higher than in products derived from **1**.

Experimental

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a Bruker AMX 400 NMR spectrometer. Solid state ^{29}Si NMR spectra were obtained a Bruker DSX 400 instrument. IR spectra were measured using a Nicolet FTIR spectrometer Magna 750. *Raman* spectra were recorded in a tempered *Raman* cell attached to a Bruker RFS100 *Raman* spectrometer. Mass spectra were performed on a Finnigan MAT 8200. All reactions for the synthesis of phosphazene monomers were carried out under an atmosphere of dry argon in oven dried glassware. Hydrolysis reactions were conducted in ambient atmosphere. To the synthesized polysiloxanes 1% (w/w) Irgacure 500® (Ciba Geigy) was added, and the coatings solutions were applicated *via* knife coating on a glass or polycarbonate substrate and UV cured within 20 seconds. The universal hardness was determined by microindentation with a Fischerscope H100.

$(NP[NHCH_2CH_2CH_2Si(OEt)_3]_2)_3$ (**1**; $C_{54}H_{132}N_9O_{18}P_3Si_6$)

6.64 g (30 mmol) 3-aminopropyltriethoxysilane were added dropwise at 0°C to a solution of 1.78 g (5.0 mmol) hexachlorocyclotriphosphazene and 3.34 g (33 mmol) triethylamine in 100 ml toluene. After the addition, the reaction mixture was heated to reflux for 24 h. Filtration under argon followed by solvent removal left 5.97 g (82%) **1** as colourless viscous liquid.

^{1}H NMR (CDCl$_3$, δ, 400 MHz): 0.73 (t, CH$_2$Si, 12H), 1.14 (t, OCH$_2$CH_3, 54H), 1.75 (m, CH$_2$CH_2CH$_2$, 12H), 3.07 (t, NCH$_2$, 12H), 3.75 (q, OCH_2CH$_3$, 36H) ppm; ^{13}C NMR (CDCl$_3$, δ, 100 MHz): 8.09 (CH$_2$Si), 18.5 (OCH$_2$$CH_3$), 26.6 (CH$_2$$CH_2CH_2$), 44.7 (NCH$_2$, 12H), 58.4

($O\mathit{CH}_2CH_3$) ppm; ^{31}P NMR ($CDCl_3$, δ, 162 MHz): 17.9 ppm; IR (Film): $\nu = 1183$–$1195\,cm^{-1}$ (P=N).

$(NP[NHCH_2CH_2CH_2Si(OEt_3)][NHCH_2CH_2\ CH_2CH_3])_3$ (**2**; $C_{39}H_{96}N_9O_9P_3Si_3$)

6.32 g (86.4 mmol) *n*-butylamine were added dropwise at 0°C to a solution of 5.0 g (14.4 mmol) hexachlorocyclotriphosphazene in 100 ml toluene. After the addition, the reaction mixture was heated to reflux for 24 h. The solution was decanted from the precipitate. 9.56 g (43.2 mmol) 3-aminopropyltriethoxysilane were added to the obtained solution. The resulting mixture was refluxed for 30 h. Filtration under argon followed by solvent removal left 12.7 g (82%) **2** as a mixture of isomers. **2** was a colourless highly viscous liquid.

^{1}H NMR ($CDCl_3$, δ, 400 MHz): 0.73 (t, CH_2Si, 6H), 0.93 (t, $CH_2CH_2CH_2\mathit{CH}_3$, 9H), 1.14 (t, $OCH_2\mathit{CH}_3$, 27H), 1.63 (m, $CH_2CH_2\mathit{CH}_2CH_3$, 6H), 1.71 (m, $CH_2\mathit{CH}_2CH_2CH_3$, 6H), 1.75 (m, $CH_2\mathit{CH}_2CH_2$, 6H), 3.07 (t, NCH_2, 5H), 3.11–3.19 (m, (($NH\mathit{CH}_2$)($NHCH_2\mathit{CH}_2CH_2CH_3$)), 12H), 3.26 (t, $NH\mathit{CH}_2CH_2CH_2CH_3$), 3.75 (q, $O\mathit{CH}_2CH_3$, 18H) ppm; ^{13}C NMR ($CDCl_3$, δ, 100 MHz): 8.09 (CH_2Si), 10.2 ($CH_2CH_2CH_2\mathit{C}H_3$), 18.9 ($OCH_2\mathit{C}H_3$), 22.5 ($CH_2CH_2\mathit{C}H_2CH_3$), 25.7 ($CH_2\mathit{C}H_2CH_2CH_3$), 26.6 ($CH_2\mathit{C}H_2CH_2$), 44.7 ($NCH_2$), 58.4 ($O\mathit{C}H_2CH_3$) ppm; ^{31}P NMR ($CDCl_3$, δ, 162 MHz): 14.2 (d, $P(NHBu)_2$, $J_{PNP} = 22$ Hz), 16.3 (dd, P(NHBu)(*AMEO*), $J_{PNP} = 17$ Hz, 22 Hz), 18.4 (dd, P((*AMEO*)$_2$, $J_{PNP} = 17$ Hz, 22 Hz) ppm; IR (Film): $\nu = 1192$–$1196\,cm^{-1}$ (P=N).

$(NP[O(C_6H_3)(OMe)CH_2CHCH_3]Cl)_3$ (**3**; $C_{30}H_{33}Cl_3N_3O_6P_3$)

A solution prepared from 9.85 g (60 mmol) 4-allyl-2-methoxyphenol and 1.44 g (60 mmol) sodium hydride in 100 ml *THF* was added dropwise at 0°C to 6.96 g (20.0 mmol) hexachlorocyclotriphosphazene in 60 ml *THF*. The reaction mixture was stirred for 12 h at 20°C and subsequently heated to reflux for 4 h. The solvent was removed *in vacuo*. The obtained liquid was dissolved in 50 ml diethylether, washed with water, dried over Na_2SO_4, and the solvent was removed *in vacuo*. Traces of 4-allyl-2-methoxyphenol were removed at 120°C (0.4 mbar), and 10.1 g (13.8 mmol) of **3** was isolated as a slightly yellow solid.

^{1}H NMR ($CDCl_3$, δ, 400 MHz): 3.36 (d, $ArCH_2$, 6H), 3.87 (s, OCH_3, 9H), 5.11 (m, $=CH_2$, 6H), 5.85 (m, $CH_2\mathit{CH}CH_2$, 3H), 7.03 (m, ArH, 9H) ppm; ^{31}P NMR ($CDCl_3$, δ, 162 MHz): 13.3 (P(OAr)(Cl)) ppm; IR (CCl_4): $\nu = 1235$–1242 (P=N) cm^{-1}.

$(NP[O(C_6H_3)(OMe)CH_2CHCH_2]OPh)_3$ (**4**; $C_{45}H_{42}N_3O_6P_3$)

A solution prepared from 3.78 g (40.2 mmol) phenol and 0.96 g (40.2 mmol) sodium hydride in 50 ml *THF* was added to a solution of 8.60 g **3** in 50 ml THF. The mixture was heated to reflux for 24 h. *THF* was removed *in vacuo*. 30 ml water and 1 ml 0.1 *M* HCl were added to the crude product. The aqueous solution was extracted with $CHCl_3$. The combined organic layers were dried over Na_2SO_4, and the solvent was removed *in vacuo*. The liquid was dissolved in 20 ml pentane and purified *via* flash chromatography (silica gel 50, 30–70 mesh, petroleum 40–60:ethylacetate = 4:1). After evaporation of the solvent *in vacuo*, 7.74 g (71%) of **4** were obtained as a colourless viscous liquid.

^{1}H NMR ($CDCl_3$, δ, 400 MHz): 3.34 (d, $ArCH_2$, 6H), 4.97 (m, $=CH_2$, 6H), 5.72 (m, $CH_2\mathit{CH}CH_2$, 3H), 7.22–7.28 (m, ArH, 27H) ppm; ^{31}P NMR ($CDCl_3$, δ, 162 MHz): 8.82 (P(OAr)(OPh)) ppm; IR (CCl_4): $\tilde{\nu} = 1235$–1242, 1254–1272 (P=N) cm^{-1}.

$(NP[O(C_6H_3)(OMe)CH_2CH_2CH_2Si(OEt)_3]OPh)_3$ (**5**; $C_{63}H_{90}N_3O_{15}Si_3$)

4.53 g (5.00 mmol) **4** were dissolved in 15 ml *THF* and 0.5 ml of a 10^{-6} *M* solution of H_2PtCl_6 in 2-propanol were added. After stirrig for 1 h at 20°C, 2.4 g (15.0 mmol) triethoxysilane were added and heated to reflux for 24 h. Volatile substances were removed *in vacuo*. The crude yellow product was dispersed in 30 ml heptane and filtered over a 3 cm layer of silica gel 60. The filtrate was concentrated to provide 5.45 g (78%) **5** as a colourless liquid.

^{1}H NMR ($CDCl_3$, δ, 400 MHz): 0.59 (t, CH_2Si, 6H), 1.13 (t, OCH_2CH_3, 27H), 1.53 (m, $CH_2CH_2CH_2$, 6H), 3.32 (t, $ArCH_2$, 6H), 3.81 (q, OCH_2CH_3, 18H), 3.89 (s, OCH_3, 9H) 7.22–7.28 (m, ArH, 24H) ppm; ^{31}P NMR ($CDCl_3$, δ, 162 MHz): 8.93 (P(OAr)(OPh)) ppm; IR (CCl_4): $\tilde{\nu} = 1235$–1242, 1262–1274 (P=N) cm^{-1}.

[NP(CH$_3$)$_2$]$_5$ ($C_{10}H_{30}N_5P_5$)

32.7 g (143 mmol) P-bromo-P,P-dimethyl-N-silylphosphinimine were heated for 2 h to 160°C in a round bottom flask equipped with a reflux condenser and a liquid separator. The trimethylbromosilane formed during the reaction was continuously removed *via* the liquid seperator. To complete the reaction, the temperature was slowly rised to 200°C. After 5 h the reaction was completed. Sublimation of the obtained white needles yielded 9.02 g (84%) $[NP(CH_3)_2]_5$.

^{1}H NMR ($CDCl_3$, δ, 400 MHz): 1.45 ($P(CH_3)_2$, $^3J_{PH} = 12$ Hz) ppm; ^{31}P NMR ($CDCl_3$, δ, 162 MHz): 19.25 ($P(CH_3)_2$) ppm; El-MS: $m/z = 375.3$ (M^+, 19%), 360.1 (M^+-CH_3, 57%), 300.0 (M^+-$NP(CH_3)_2$, 58%), 285.1 (M^+-$NP(CH_3)_2$-CH_3, 100%), 225.1 (M^+-2 $NP(CH_3)_2$, 5%), 210.1 (M^+-2 $NP(CH_3)_2$-CH_3, 57%).

(NP[CH$_3$][CH$_2$Si(OMe)$_3$])$_5$ (**6**; $C_{25}H_{70}N_5O_{15}P_5Si_5$)

40 ml of a 2 *M* solution of *n*-BuLi in heptane were added dropwise to an ice-cooled solution of 3.00 g (8.00 mmol) decamethylcyclopentaphosphazene in 80 ml *THF*. After stirring for 12 h, this reaction mixture was added to a vigorously stirred solution of 8.50 g (42.0 mmol) chlorotrimethoxysilane in 100 ml *THF* at a temperature of −78°C. The mixture was warmed up to room temperature, stirred for a period of 12 h, and then filtered. The solvent and unreacted chlorotrimethoxysilane were removed *in vacuo*. The crude product was dissolved in 80 ml dichloromethane and filtered over a 2 cm layer of silica gel 60. After evaporation of the solvent, 11.5 g (72%) **6** were obtained as a colourless viscous liquid.

^{1}H NMR ($CDCl_3$, δ, 400 MHz): 0.96 (s, PCH_3, 21H), 1.27 (br, PCH_2Si, 6H), 3.38 (s, OCH_3, 18H) ppm; ^{13}C NMR ($CDCl_3$, δ, 100 MHz): 6.31 (PCH_3) 9.09 (CH_2Si), 56.2 (OCH_3) ppm; ^{31}P NMR ($CDCl_3$, δ, 162 MHz): 25.2 (PCH_3CH_2Si) ppm; IR (KBr): $\tilde{\nu} = 1187$ (P=N) cm^{-1}.

(NP[CH$_2$Si(OMe)$_3$]$_2$)$_5$ (**7**; $C_{40}H_{105}N_5O_{30}P_5Si_{10}$)

7 was prepared analogous to **6** but using twofold amounts of *n*-BuLi and chlorotrimethyoxysilane.

Yield: 72%; ^{1}H NMR ($CDCl_3$, δ, 400 MHz) 1.42 (br, PCH_2Si, 20H), 3.23 (s, OCH_3, 90H) ppm; ^{13}C NMR ($CDCl_3$, δ, 100 MHz): 9.09 (CH_2Si), 56.2 (OCH_3)ppm; ^{31}P NMR ($CDCl_3$, δ, 162 MHz): 25.2 ($P(CH_2Si)_2$) ppm; IR (KBr): $\tilde{\nu} = 1187$ (P=N) cm^{-1}.

Hydrolysis experiments for Raman investigations

General procedure

If not mentioned otherwise, 1 g of the alkoxysilyl substituted cyclophosphazene was dissolved in 1 g of solvent (ethylacetate or 2-propanol). A stoichiometric amount of water (calculated by the number of alkoxy groups) or instead a 0.1 *M* or 1 *M* aqueous solution of a catalyst was added, and the mixture was stirred in a cell inside the *Raman* spectrometer.

Hydrolysis of **5**

3.41 g (2.44 mmol) **5** were dissolved in 20 ml ethyl acetate; 0.40 g 0.1 *M* HCl were added, and the mixture was stirred for 12 h at 20°C.

Synthesis of the coating sols

Sol 1 prepared from *MEMO* and *TEOS*:

1.16 g (64.5 mmol) 0.1 *M* aqueous solution of NH_4F were added to an ice-cooled solution of 4 g (16.1 mmol) methacryloxypropyltrimethoxysilane (*MEMO*) and 0.84 g (4.03 mmol) *TEOS* in 14.4 g ethyl acetate. After 10 min the ice-bath was removed and the mixture was stirred for another 2 h.

Sol 2 prepared from MEMO and **1**:

1.16 g (64.5 mmol) 0.1 *M* aqueous solution of NH_4F were added to an ice cooled solution of 4 g (16.1 mmol) methacryloxypropyltrimethoxysilane (*MEMO*) and 1.30 g (0.89 mmol) **1** in 14.4 g ethyl acetate. After 10 min the ice-bath was removed and the mixture was stirred for another 2 h.

Sol 3 prepared from MEMO and **2**:

To an ice cooled of 4 g (16.1 mmol) methacryloxypropyltrimethoxysilane (*MEMO*) and 1.81 g (1.79 mmol) **2** in 7.2 g ethyl acetate and 7.2 g ethanol, 1.16 g (64.5 mmol) 0.1 *M* aqueous solution of NH_4F were added. After 10 min the ice-bath was removed and the mixture was stirred for another 2 h.

Finally, photoinitiator was added to the sols, and the sols were applied on the substrates as described above.

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