

Poly(propylenimine) dendrimers: large-scale synthesis via heterogeneously catalyzed hydrogenation

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GPC analyses, coupling reactions can be excluded. Interestingly, the solution behavior of poly(ethylene oxide), a typical random-coil polymer, is quite different from that of the two types of highly functional poly(trimethylene imine) cascade molecules prepared by us. As apparent from Figure 5, the polyamine-functional cascade molecules require higher elution volumes, which increase with increasing number of generations. In agreement with earlier observations,^[1, 16] it ap-

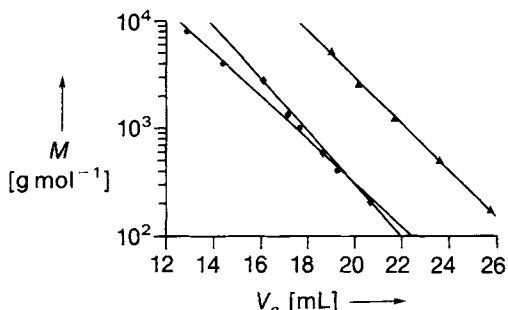


Fig. 5. Correlation of molecular weight M and elution volume V_e in GPC analyses of poly(ethylene oxide) (●), polynitrile- (▲) and polyamine-functional poly(trimethylene imines) (◆).

pears likely that cascade molecules when compared with conventional random-coil polymers exhibit higher densities, which increase with increasing molecular weight. The very high elution volumes found for the polynitrile-functional cascade molecules may result from adsorption phenomena, which do not interfere with the GPC analysis of the molecular weight distributions. In all three polymers there exists a linear correlation between molecular weight, determined by vapor pressure osmometry, and elution volume.

In conclusion, the divergent synthesis involving cyanoethylation and catalytic hydrogenation efficiently doubles the amino groups. With this reaction sequence poly(trimethylene imine) cascade molecules can be prepared in high yields and purity without requiring extensive purifications and excess reagent.

Experimental Procedure

Typical syntheses for the higher generations G4N, G4A, and G5N; the yields are summarized in Table 1.

G4N: To a cold solution of G3A (2.56 g, 2.10 mmol) in methanol (20 mL) were added acrylonitrile (20.0 mL, 305 mmol) (distilled over CaH_2 and stabilized with 0.05 wt % hydroquinonemonomethyl ether) within 90 minutes at 5–10 °C. After stirring 1 h at 10 °C and 4 days at 60 °C, the quantitative bis(cyanoethylation) was obtained. For separation of the stabilizer, the reaction mixture was passed through a neutral Al_2O_3 column and eluted with methanol/ethyl acetate (7:3), and the methanol content was increased slowly to 100%. The solvent was evaporated in vacuo to obtain 5.02 g (96%) of the highly viscous G4N. Correct elemental analysis for $\text{C}_{135}\text{H}_{222}\text{N}_{46}$ (2489.55 g mol^{-1}): $^1\text{H NMR}$ (400 MHz, CD_2Cl_2): $\delta = 1.62$ (q, $J = 7$ Hz, 42H; $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.56 (m, 132H; CH_2N), 2.83 (t, $J = 7$ Hz, 48H; CH_2CN); $^{13}\text{C NMR}$ (100 MHz, CD_2Cl_2): $\delta = 17.3$ (CH_2CN), 23.9, 25.1 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 49.9 ($\text{CH}_2\text{CH}_2\text{CN}$), 51.7, 51.9, 52.2, 52.4 (CH_2N), 119.5 (CN); IR (neat): $\tilde{\nu}[\text{cm}^{-1}] = 2920, 2800, 2220, 1450, 1410, 1350, 1250, 1160, 1120, 1050$.

G4A: The hydrogenation was carried out in a 2 L stainless steel autoclave (Büchi AG, Uster/Switzerland). To 100 mL of a 1.4 M solution of NaOH in $\text{EtOH}/\text{H}_2\text{O}$ (95:5), G4N (4.20 g, 1.69 mmol) was added. Under nitrogen the mixture was treated with Raney-nickel (2.5 g) (slurry in water, Aldrich), and the mixture was hydrogenated at 1000 rpm at 8 bar H_2 pressure for 4 days at 25 °C. The catalyst was filtered and washed with $\text{EtOH}/\text{H}_2\text{O}$ (95:5). After diluting the filtrate with H_2O (100 mL), EtOH was evaporated and the residue extracted several times with CH_2Cl_2 . Thereby, the NaOH concentration in the aqueous phase was increased in every extraction step. The organic layers were dried with Na_2SO_4 and the solvent evaporated in vacuo to give 3.01 g (69%) G4A. Correct elemental analysis for $\text{C}_{135}\text{H}_{318}\text{N}_{46}$ (2586.31 g mol^{-1}): $^1\text{H NMR}$ (250 MHz, CDCl_3): $\delta = 1.54$ (m, 138H; $\text{CH}_2\text{CH}_2\text{CH}_2$, NH_2), 2.36 (m, 84H; CH_2N), 2.42 (t, $J = 7$ Hz, 48H; $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 2.67 (t, $J = 7$ Hz, 48H; CH_2NH_2); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 24.6$ ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 30.9 ($\text{CH}_2\text{CH}_2\text{NH}_2$),

40.7 (CH_2NH_2), 51.9, 52.3, 52.4, 52.6 (CH_2N); IR (neat): $\tilde{\nu}[\text{cm}^{-1}] = 3300, 3260, 2910, 2780, 1570, 1450, 1360, 1170, 1070, 960-770$.

G5N: The procedure was equivalent to that reported for the synthesis of G4N. From G4A (600 mg, 0.232 mmol) was obtained 1.11 g (93%) of the highly viscous substance G5N. Correct elemental analysis for $\text{C}_{279}\text{H}_{462}\text{N}_{94}$ (5133.35 g mol^{-1}): $^1\text{H NMR}$ (400 MHz, CD_2Cl_2): $\delta = 1.62$ (m, 90H; $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.52 (m, 276H; CH_2N), 2.82 (t, $J = 7$ Hz, 96H; CH_2CN); $^{13}\text{C NMR}$ (100 MHz, CD_2Cl_2): $\delta = 17.2$ (CH_2CN), 23.8, 25.1 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 49.8 ($\text{CH}_2\text{CH}_2\text{CN}$), 51.6, 51.8, 52.1, 52.3 (CH_2N), 119.5 (CN); IR (neat): $\tilde{\nu}[\text{cm}^{-1}] = 2920, 2790, 2220, 1450, 1410, 1350, 1230, 1160, 1120, 1060$.

The $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra were measured with a Bruker AC 400 spectrometer with tetramethylsilane as internal standard; CD_2Cl_2 was used for the nitrile-functional and CDCl_3 for the amine-functional generations. End group titration was performed in a solution of $\text{H}_2\text{O}/\text{Et}_2\text{O}$ (1:1) with 0.1 N HCl with a Mettler DC 25 titrator. Vapor pressure osmometry was carried out with a Perkin-Elmer Molecular Weight Apparatus Type 115 at 30 °C with CHCl_3 as solvent. The GPC analysis was performed on a Shimadzu LC-4A at 60 °C with a 0.05 M K_2HPO_4 buffer $\text{MeOH}/\text{H}_2\text{O}$ (70:30) at pH = 11 (HEMA 40 and HEMA 100 column (MZ Analysentechnik), flow rate 0.5 mL min^{-1} , UV detector 228 nm, RI detector, calibrated with the values obtained from vapour pressure osmometry).

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Poly(propylene imine) Dendrimers: Large-Scale Synthesis by Heterogeneously Catalyzed Hydrogenations**

By Ellen M. M. de Brabander-van den Berg* and E. W. Meijer

Dendritic macromolecules are hyperbranched polymers that emanate from a central core, have a defined number of generations and functional end groups, and are synthesized in a stepwise way by a repetitive reaction sequence.^[1] The syntheses described so far are either convergent, this is discrete

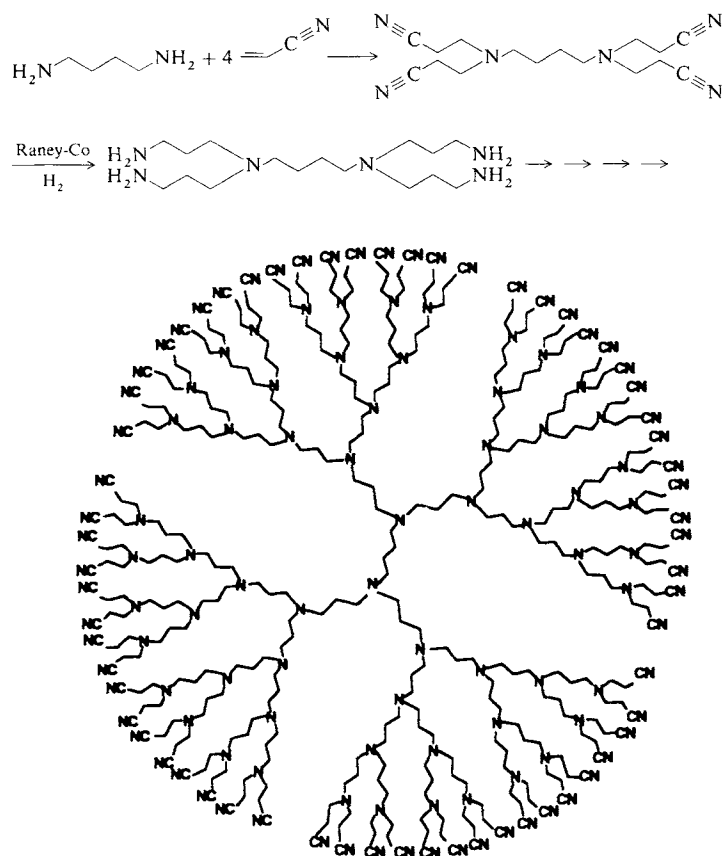
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organic compounds are synthesized, or divergent, that is the construction of dendrimers can be regarded as a step polymerization with polydispersities of almost 1.^[2-4] Detailed studies show that only a limited number of reaction schemes can be used for the synthesis of these dendrimers;^[1, 5-7] all known methods to date do not deliver pure dendrimers in large quantities, which is due to the use of sophisticated building blocks and/or (large excesses of) expensive reagents and/or complicated purifications.^[6] In this paper we present a very convenient reaction sequence for the large-scale production of pure poly(propylene imine) dendrimers.

The reaction sequence presented here (Scheme 1) is based on the first approaches to dendrimeric structures by Vögtle et al. in which the low yields in the reduction hampered the synthesis of higher generations.^[8] Our sequence is a repeti-



Scheme 1. Synthetic scheme for poly(propylene imine) dendrimers with diaminobutane as core.

tion of a double Michael addition of acrylonitrile to primary amines, followed by the heterogeneously catalyzed hydrogenation of the nitriles, resulting in a doubling of the number of primary amines. In this sequence 1,4-diaminobutane has been used as the dendrimer core; but a variety of molecules with primary or secondary amine groups can also be used. We have optimized conditions for both reaction steps in the sequence so that this occurs almost quantitatively and with optimal selectivity.^[9]

All Michael reactions were performed similarly; 2.5–4 equivalents of acrylonitrile per primary amine are used at a concentration of 0.1 M in water; the first equivalent of acrylonitrile is added at room temperature and the second equivalent at 80 °C. The reaction time for complete conversion increases with every generation: 1 h for generation 0.5 (DAB-dendr-(CN)₄), 3 h for generation 4.5 (DAB-dendr-

(CN)₆₄).^[10] The excess of acrylonitrile is distilled off as a water azeotrope, leaving a clear two-phase system, from which the pure dendrimers with nitrile end groups can be isolated by pouring off the water layer. If necessary the water-soluble side products for example HOCH₂CH₂CN (the Michael addition adduct of H₂O to acrylonitrile) or incompletely cyanoethylated products can be separated by washing the residue with water.

The hydrogenations of the cyanoethylated structures with H₂ (30–70 bar) and Raney/Cobalt as catalyst are also performed preferably in water. The reaction time required for complete hydrogenation increases at higher generations, but even at the higher generations this heterogeneous hydrogenation is quantitative and selective. Dendrimers with NH₂ end groups are isolated by evaporating the water from the filtered reaction mixture. The process window for a quantitative hydrogenation is small and side reactions easily occur. Three major side reactions which lead to dendrimers with structural defects have been observed, and the corresponding side products have been characterized: a) the occurrence of the retro-Michael addition during the hydrogenation, yielding secondary amines,^[11] b) incomplete cyanoethylation in the Michael addition, resulting in dendrimers missing one ethyl cyanide side chain, and c) the formation of cyclic diamines and NH₃ by intramolecular addition of amines to the intermediate imines during the hydrogenation reactions. Under the optimized conditions these side products are not detectable and poly(propylene imine) dendrimers can be synthesized up to generation 4.5 with 64 terminal nitrile groups, a molecular weight of 6912 g mol⁻¹ and in quantities of several grams up to several kilograms. Apart from the first generation (0.5) which is a white crystalline solid, all other generations are colourless oils, which are readily soluble: the DAB-dendr-(NH₂)_x in H₂O and methanol, the DAB-dendr-(CN)_x in common organic solvents.

All products were characterized by ¹H, ¹³C NMR and IR spectroscopy, mass spectrometry, HPLC, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and intrinsic viscosity. All data are consistent with the proposed dendrimer structures. NMR spectroscopy appears to be a very suitable technique to detect and assign structural failures in the outermost dendrimer generation. In the ¹H NMR spectra of the dendrimers with CN end groups the shape and intensity of the most downfield triplet of the NCH₂CH₂CN group at δ = 2.85 is characteristic for defects in the outer generation, whilst the growth of the dendrimers is clearly indicated by the ratio of the integrals of the signal at δ = 1.40 (NCH₂CH₂CH₂CH₂N protons of the dendrimer core) to the integral of the signal at δ = 1.58 (NCH₂CH₂CH₂N branch protons). Incompletely cyanoethylated dendrimers are most readily concluded from additional signals in the ¹³C NMR spectra at δ = 45.1 (NHCH₂CH₂CN) and 18.7 (NHCH₂CH₂CN) as well as the products of retro-Michael additions of dendrimers with NH₂ end groups with signals at δ = 47.7, 46.7, 39.1, 32.0, and 25.6.

Dendrimers with CN end groups can be separated and analyzed with HPLC. In Figure 1 a typical chromatogram of DAB-dendr-(CN)₈ from a kg-scale run is shown. From mass spectrometric experiments it has been concluded that the small peak corresponds with the fully cyanoethylated product of DAB-dendr-(NH₂)₃. If equal absorption coefficients are assumed for both compounds, the average selectivity per conversion in the first three steps is 99.8%.

Figure 2 shows a typical gel permeation chromatogram of various dendrimers with NH₂ end groups taken from a large-scale synthesis. The absence of detectable impurities is evi-

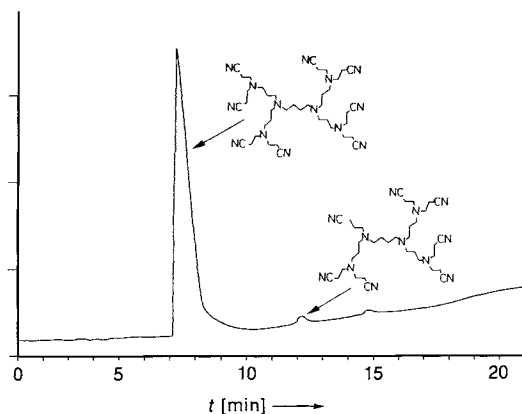


Fig. 1. Typical HPLC chromatograph of DAB-dendr-(CN)₈.

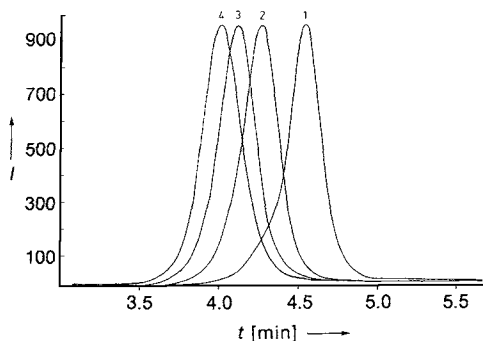


Fig. 2. Typical GPC trace of DAB-dendr-(NH₂)₁ (1), DAB-dendr-(NH₂)₂ (2), DAB-dendr-(NH₂)₃ (3), and DAB-dendr-(NH₂)₄ (4).

dent from the chromatograms. Furthermore, the characteristic relation between the molecular weight M_n and the intrinsic viscosity η is presented in Figure 3. As reported for two other classes of dendrimers, the intrinsic viscosity of the poly(propylene imine) dendrimers with CN end groups decreases with increasing molecular weight at a certain generation;^[1, 12] in this case after the fourth generation.

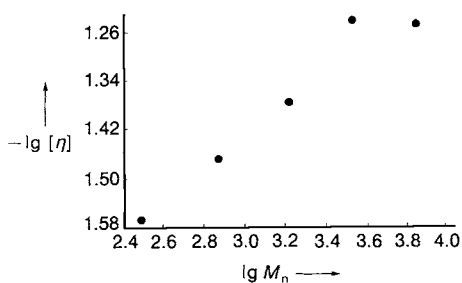


Fig. 3. Plot of $-\lg \eta$ vs. $\lg M_n$ of the various poly(propylene imine) dendrimers with CN end groups.

Thermal analysis of the dendrimers synthesized shows a number of interesting features. The glass transition temperature T_g has been recorded with DSC (Fig. 4); in both series of dendrimers with NH₂ and CN end groups the T_g 's observed are low and an increase in T_g is observed by increasing molecular weight. In all cases the CN dendrimers possess the highest T_g , which is expected on basis of the dipole-dipole interaction of the CN groups. The thermal stability of the dendrimers with NH₂ end groups is unexpectedly high

and again increases with increasing molecular weight as determined by TGA (For DAB-dendr-(NH₂)₄, DAB-dendr-(NH₂)₈, DAB-dendr-(NH₂)₁₆, DAB-dendr-(NH₂)₃₂, TGA_{max} are 330, 378, 424, and 470 °C, respectively. For the DAB-dendr-(NH₂)₈ less than 1.0% weight loss is observed at $T = 310$ °C and scan speed 20 °C min⁻¹.) Dendrimers with CN end groups are less stable, although also in this case the stability increases at higher generations. With TGA-MS, a thermally induced retro-Michael addition is observed for DAB-dendr-(CN)₆₄, followed by a degradation similar to DAB-dendr-(NH₂)₃₂. A molecular interpretation of the latter is not possible with the data available.

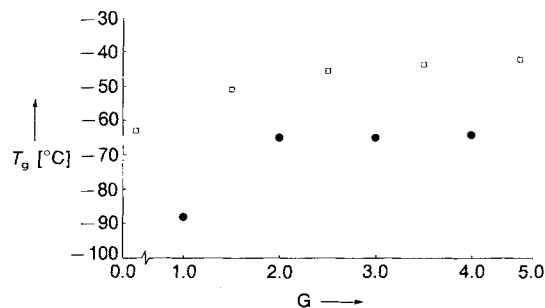


Fig. 4. Plot of the glass transition temperatures (T_g) of the poly(propylene imine) dendrimers with nitrile (□) and amino groups (●). G = generation.

As a consequence of the extensive purifications and low yields in the first approaches,^[8] it was assumed until recently that this acrylonitrile-hydrogenation sequence is not suitable for dendrimer synthesis. However, by the correct choice of reagents and reaction conditions we have shown that this reaction sequence is very efficient. The main advantages of our synthetic procedures are 1) the simple reaction and isolation procedures which can readily be scaled up; 2) the use of one solvent for all reaction steps, so that the intermediates must not be isolated; 3) the use of readily available reagents which do not have to be protected; 4) the high yields and selectivities obtained; 5) a simple purification method which can easily be applied to large-scale quantities; 6) the versatility of the reaction sequence which allows for the introduction of a variety of end and core groups.

The dendrimers with NH₂ end groups offer remarkable thermal and good hydrolytic stability, and have a low T_g . The drop in intrinsic viscosity after the fourth generation indicates that a spherical shape with a sterically hindered shell is formed at the fifth generation. The low T_g indicates that the dendrimers possess a large degree of conformational freedom, despite their hyperbranching and well-defined chemical and geometrical structure. Research into the synthesis of higher generations and the functionalization of the dendrimers is in progress.

Experimental Procedure

DAB-dendr-(CN)₄: Acrylonitrile (8.35 mol, 443 g) was added to a solution of diaminobutane (1.67 mol, 147 g) in 1.176 kg water. The exothermic reaction caused the temperature to rise to 38 °C. After this exothermic effect the reaction mixture was heated at 80 °C for 1 h to complete the addition. Then the excess of acrylonitrile was removed as a water azeotrope by vacuum distillation (16 mbar, bottom temperature 40 °C). Phase separation of the reaction mixture afforded 499 g (99%) HPLC-pure DAB-dendr-(CN)₄, which was recrystallized from methanol.

¹³C NMR (50 MHz, CDCl₃): $\delta = 119$ (CN), 53.1 (NCH₂CH₂CH₂CH₂N), 49.4 (NCH₂CH₂-CN), 24.9 (NCH₂CH₂CH₂CH₂N), 16.9 (CH₂CN); ¹H NMR (200 MHz, CDCl₃): $\delta = 2.85$ (t, 8H, NCH₂CH₂CN), 2.55 (m, 4H, NCH₂CH₂CH₂CH₂N), 2.48 (t, 8H, CH₂CN), 1.55 (m, 4H, NCH₂CH₂CH₂CH₂N); IR (KBr): $\tilde{\nu} = 2245$ cm⁻¹ (CN).

DAB-dendr-(NH₂)₄: To a hydrogenation vessel, filled with Raney Cobalt catalyst (Cr promoted, Grace 2724, pretreated with hydroxide, 900 g) and water (22.5 L) was added DAB-dendr-(CN)₄ (450 g) dissolved in methanol. Subsequently the mixture was hydrogenated at 40 atm hydrogen pressure at 70 °C for 1 h. The cooled reaction mixture was then filtered and the solvents were evaporated at reduced pressure. The residue contained 450 g (95%) NMR spectroscopically pure DAB-dendr-(NH₂)₄ as a colorless oil.

¹³C NMR (50 MHz, D₂O): δ = 53.4 (NCH₂CH₂CH₂CH₂N), 51.1 (NCH₂CH₂CH₂NH₂), 39.5 (CH₂NH₂), 28.8 (CH₂CH₂NH₂), 23.9 (NCH₂CH₂CH₂CH₂N); ¹H NMR (200 MHz, CDCl₃): δ = 2.70 (t, 8H, CH₂NH₂), 2.44 (t, 8H, NCH₂CH₂CH₂NH₂), 2.40 (m, 4H, NCH₂CH₂CH₂CH₂N), 1.58 (quin, 8H, CH₂CH₂NH₂), 1.42 (m, 12H, NCH₂CH₂CH₂CH₂N, NH₂); IR (film): ν̄ = 3284, 3355 cm⁻¹ (NH₂).

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[10] DAB-dendr-(CN)_x means a dendrimer with DAB (DiAminoButane) as core and x nitrile end groups; DAB-dendr-(NH₂)_x one with x primary amine end groups. A proposal for the systematic naming of dendrimers is given by G. R. Newkome, G. R. Baker, J. K. Young, J. G. Traynham, *J. Polym. Sci. Part A* **1993**, *31*, 641–651.
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Intramolecular Base Stabilization of Silicenium Ions: A New Route to Siliconium Ions

By Claude Chuit, Robert J. P. Corriu,* Ahmad Mehdi, and Catherine Reyé

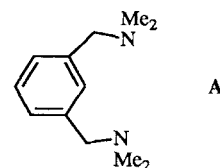
The possible existence of trisubstituted silylium "silicenium" ions (R₃Si⁺) has intrigued chemists for a long time.^[1, 2] Nevertheless claims to have generated such species in solution^[3] have been disputed,^[4] and the question whether triorganosilyl perchlorates undergo ionization in solvents has been reviewed by Eaborn^[5] and Lickiss.^[6] Recently silyl cations have been prepared in nonnucleophilic solvents with weakly coordinating anions.^[7–8] However, the structural analysis of one of these derivatives showed a strong interaction between anion and cation.^[8]

Some silyl cations that can be prepared are stabilized by the π-pentamethylcyclopentadienyl ligand,^[9] intermolecular coordination,^[8, 10–13] or intramolecular coordination.^[14–15]

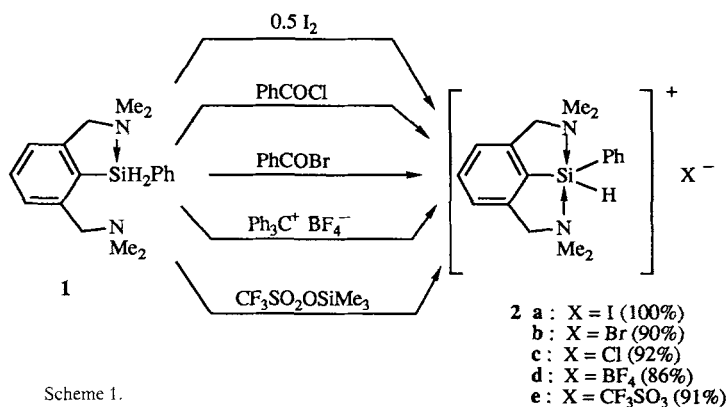
However, these examples do not constitute a general route to cationic silicon species with a functional group at silicon that enables reactivity studies.

Some years ago, we showed that pentacoordinate neutral and anionic silicon species have unusual, often unexpected reactivity.^[16] That led us to prepare cations containing pentacoordinate silicon centers (silicenium ions) in order to study their reactivity.

Since intramolecular coordination of the amino group stabilizes silanethione,^[17] silaphosphene,^[18] silanimine,^[18] and transition metal silanediyl complexes very efficiently,^[18, 19] we decided to extend this intramolecular stabilization to the silylium ions. We report here a novel and general route to functional and nonfunctional silenium ions using the potentially bichelating ligand **A**.^[20]



The reaction of the silane **1** with half an equivalent of iodine in ether at room temperature results in the formation of a precipitate and loss of half an equivalent of H₂ in a redox reaction. The precipitate was identified as the ionic species **2a** (Scheme 1).



Scheme 1.

The ¹H NMR spectrum of **2a** shows a singlet at δ = 5.3, shifted to low field with respect to the resonance signal of the SiH₂ protons of **1** and assigned to the SiH proton. The signal of the methylene protons in **2a** has an AB pattern. The two NMe₂ groups are magnetically equivalent as a result of the coordination of both nitrogen atoms to the silicon center and give rise to two singlets of equal intensity. In the coupled ¹H ²⁹Si NMR spectrum of **2a**, a doublet is observed at δ = –29.7 (¹J_{Si,H} = 280 Hz), whereas the ²⁹Si resonance of the pentacoordinate silane **1**^[21] appears as a triplet at δ = –51.5 (¹J_{Si,H} = 200 Hz). Interestingly, the ²⁹Si NMR spectrum of **2a** in the solid state shows a sharp signal with the same chemical shift (δ = –28.8) as in solution, which indicates that **2a** remains ionic even in the solid state.

The IR spectrum of **2a** in CHCl₃ shows a Si–H stretch at ν̄ = 2202 cm⁻¹, substantially higher than for **1** (2111 cm⁻¹). Moreover this frequency is very close to that observed by Jutzi et al.^[9] for the silyl cation [(π-Me₅C₅)₂SiH]⁺.

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