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The reduction of Ag(I) by α-silylamines $R_2NCH_2SiX_3$

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The introduction of the organosilicon substituent into the α-position of an amino group results in cardinal change of the amine reactivity irrespective of the coordination state of silicon. Amines $R_2NCH_2SiX_3$ [R = Me, Et, $PhCH_2$, CH_2SiX_3; SiX_3 = $SiMe_3$, $Si(OEt)_3$, $Si(OCH_2CH_2)_3N$] easily react with $AgNO_3$, to give the corresponding ammonium salts (R_2NH^+ CH_2SiX_3)·NO_3^-. At the same time, Ag(I) is reduced to Ag(0). The interaction of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine with $AgNO_3$ has been investigated by EPR spectroscopy. It was proven that the reaction involved a single electron transfer stage with the formation of cation radical of this amine. A mechanism of the reaction is proposed. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: α-silylamine; *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine; reduction; cation radical

INTRODUCTION

The compounds containing carbofunctional groups[1–7] are of the greatest interest among the variety of organosilicon compounds forming complexes with salts of metals.[8–11] The amino group in compounds of various structures is a typical donor center in the formation of complexes with salts of Ag(I), Cu(II), Ni(II) and other metals.[12–27] In addition, an increase in the number of alkyl groups of the nitrogen atom leads to increasing complex stability.[28] The nature, basicity and spatial structure of the amine determine the catalytic properties of Cu(II) complexes.[29–31] Silver nitrate catalyzes the classical reaction of triethylamine alkylation due to the formation of an $Et_3N{-}AgNO_3$ complex.[32,33] Within the group of metals complexes with ligands containing cage structures, the silatranyl group can lead to the development of new highly efficient catalysts. Previously we have synthesized the first complexes of this type by the reaction of *N*-(silatranylalkyl)ethylenediamines $H_2N(CH_2)_2NH(CH_2)_nSi(OCH_2CH_2)_3N$ ($n = 1$, 3) with $CuCl_2$.[3]

RESULTS AND DISCUSSION

In continuation of our investigations of amines[34–36] containing tetra- or pentacoordinated group $R_nN(CH_2SiX_3)_{3-n}$ in an α-position, we tried to synthesize their complexes with $AgNO_3$. However, mixing equimolar solutions of silver nitrate and *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine **1** in acetonitrile resulted in an almost instantaneous precipitation of silver metal in the form of a silver mirror. The reaction was completed within 1 h. We isolated the nitrate salt of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine, **11,** from the reaction mixture after decantation of the solution and removal of the solvent (Scheme 1).

IR and NMR spectroscopy confirmed the structure of the reaction product. In the IR spectra of the product intensive bands were observed in the 1320–1450 cm^{-1} region, which can be assigned to the NO_3^- anion.[37] As compared with the starting compound the product **11** shows significant low-field shift of the $N{-}CH_3$ and $N{-}CH_2{-}Si$ signals in the NMR spectra (Table 1). It is indicative of the exocyclic nitrogen atom quaternization.[38] The protonation of the nitrogen atom in *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine **1** (i.e. the formation of a tetrahedral environment of this atom) results in prochirality of the $CH_2Si(OCH_2CH_2)_3N$ groups (Scheme 2). NMR spectra show that the $N{-}CH_2{-}Si$- and $N{-}CH_2{-}C$ protons of each silatranylmethyl group become anisochronic. The proton resonance of the $N{-}CH_2{-}Si$-group represents an AB quartet ($J_{AB} = 14.0$ Hz), and the proton resonance of the $N{-}CH_2{-}C$

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†Professor Vadim Aleksandrovich Pestunovich, our chief, teacher and friend died on 4 July 2004..

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Table 1. Parameters of ^1H NMR of organosilicon amines $R_2NCH_2SiX_3$ and their ammonium salts $[R_2NH^+CH_2SiX_3]Y^-$ (solvent CD_3CN)

	$R_2NCH_2SiX_3$				$[R_2NH^+CH_2SiX_3]Y^-$		
	δ, ppm				δ, ppm		
Number	R–N	N–CH_2–Si	SiX_3	Number	R–N	N–CH_2–Si	SiX_3
1	2.17 s	1.89 s	2.83 t	**11**	2.83 s;	2.17 ($J_{AB} = 14.0$ Hz);	3.03 ($J_{AB} = 12.5$ Hz, $^3J = 6.2$ Hz);
			3.79 t		6.33 (NH^+)	2.39	3.82 t
				21	2.82 s;	2.15 ($J_{AB} = 14.0$ Hz); 2.37	3.04 ($J_{AB} = 12.5$ Hz, $^3J = 6.2$ Hz);
					6. 28 (NH^+)		3.81 t
				22	2.83 s;	2.17 ($J_{AB} = 14.0$ Hz); 2.39	3.03 ($J_{AB} = 12.5$ Hz, $^3J = 6.2$ Hz);
					6.33 (NH^+)		3.82 t
				23	2.82 s;	2.15 ($J_{AB} = 14.0$ Hz); 2.37	3.04 ($J_{AB} = 12.5$ Hz, $^3J = 6.2$ Hz);
					6. 28 (NH^+)		3.81 t
2[a]	2.22 s	1.65 s	3.77 t 2.82 t	**12**[a]	2.86 s 9.02 (NH^+)	2.26 s	2.96 t; 3.82 t
3	0.91 t 2.49 q	1.63 s	2.78 t 3.74 t	**13**	1.20 s 3.74 q 2.39 s (NH^+)	2.13 s	2.95 t 3.80 t
4[a]	1.59 m; 2.41 m	1.80 s	3.77 t 2.80 t	**14**[a]	1.57 m; 3.05 m	2.17 s	3.83 t 2.91 t
5	3.52 s 7.15 m	1.94 s	2.77 t 3.79 t	**15**	4.18 d ($^3J = 5.38$ Hz 7.44 m 6.62 (NH^+)	2.16 ($J_{AB} = 14.43$ Hz); 2.36	3.74 t 2.95 t
6	2.26	1.97 s	1.16 t 3.80 q	**16**	2.56 s	2.34 s	1.18 t 3.79 q
7	2.39 s	2.01 s	0.03 s	**17**	2.73 s	2.62 s	0,17 s
8	2.22 s	1.85 s	0.06 s	**18**	2.60 s	2.31 s	0.19 s
9	0.98 t 2.46 q	1.92 s	0.04 s	**19**	1.33 t 3.18 q	2.61s	0.24 s
10	1.18 (NH) 3.71 s (CH_2) 7.29 m (Ph)	1.97 s	−0.01 s	**20**	3.86 s (CH_2) 4.97 8 (NH^+) 7.38 m (Ph)	2.31 s	0.04 s

[a] Solvent $CDCl_3$.

(a skeleton of silatranes) is an AB-quartet, where each component is split into a triplet with a vicinal coupling constant ($J_{AB} = 12.5$ Hz, $^3J = 6.2$ Hz). The spectrum of the compound **11** is completely identical to the spectrum of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine nitrate **22,** which was synthesized by an exchange reaction of hydrochloride *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine **21** with $AgNO_3$ (Scheme 3).

The amines **2–4,** containing one silatranylmethyl group, interact more slowly with $AgNO_3$; the reaction is completed within some hours with the formation of the corresponding salts **12–14**. The substitution of the pentacoordinated silatranyl group by the tetracoordinated silyl group $SiMe_n(OEt)_{3-n}$ does not significantly change the process. Compounds **6–10** reduce silver nitrate within several hours, giving rise to the corresponding nitrates of the amines **16–20**. The constitution of the products was confirmed by NMR (Tables 1–3) and IR spectroscopy (the IR spectra of **10–20** contained intensive bands in the 1320–1450 cm^{-1} region, which can be assigned to the NO_3^- anion).[37] Under the same conditions, Et_2NH, Et_3N and Ph_2NH do not react with silver nitrate, even over several weeks. Earlier we postulated that the reactivity of amines containing a silyl group in α-position is determined by the high basicity of their nitrogen atom.[34–36] However, the reaction of such strong base such as DABCO with $AgNO_3$ leads to immediate formation of a white crystalline precipitate (complex salt having 1 : 1 composition) without any signs of reduction. Besides, DBU (the strongest organic base of amidines series) does not interact with $AgNO_3$ even over several days.

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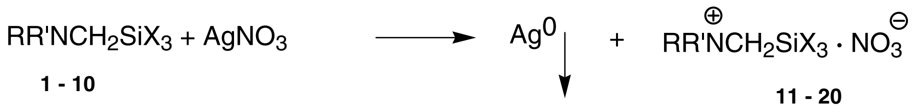
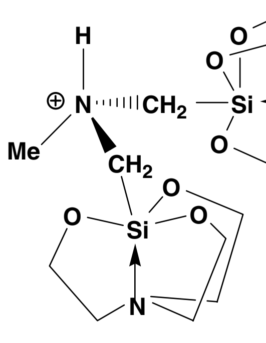


$$\underset{\mathbf{1-10}}{RR'NCH_2SiX_3} + AgNO_3 \longrightarrow Ag^0\downarrow + \underset{\mathbf{11-20}}{\overset{\oplus}{RR'NCH_2SiX_3}\cdot NO_3^{\ominus}}$$

R = Me, R' = CH_2SiX_3, SiX_3 = $Si(OCH_2CH_2)_3N$ (**1, 11**);
R = R' = Me, SiX_3 = $Si(OCH_2CH_2)_3N$ (**2, 12);**
R = R' = Et, SiX_3 = $Si(OCH_2CH_2)_3N$ (**3, 13**);
RR' = $(CH_2)_5$, SiX_3 = $Si(OCH_2CH_2)_3N$ (**4, 14**);
R = $PhCH_2$, R' = CH_2SiX_3, SiX_3 = $Si(OCH_2CH_2)_3N$ (**5, 15);**
R = Me, R' = CH_2SiX_3, SiX_3 = $Si(OEt)_3$ (**6, 16**);
R = Me, R' = H; SiX_3 = $SiMe_3$ (**7, 17**);
R = R' = Me; SiX_3 = $SiMe_3$ (**8, 18**);
R = R' = Et; SiX_3 = $SiMe_3$ (**9, 19**);
R = $PhCH_2$, R' = H; SiX_3 = $SiMe_3$ (**10, 20**);

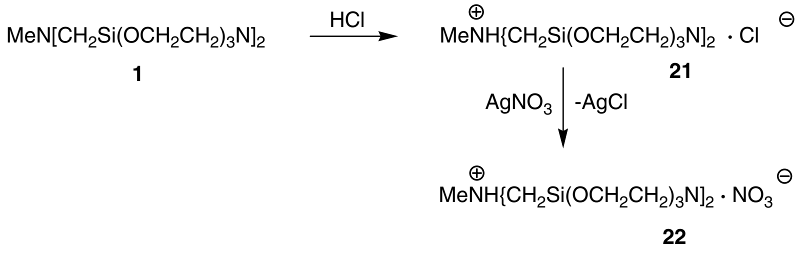
Scheme 1. Reaction of α-silylamines **1–10** with $AgNO_3$.



Scheme 2. The protonation of the nitrogen atom in *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine **1** results in prochirality of the $CH_2Si(OCH_2CH_2)_3N$ groups.

The data on oxidation of amines by silver salts are extremely poor, even though the AgX salts are applied in the synthesis as oxidants (the value of the Ag^+—Ag pair redox potential −0.799 V[39]). The investigations on the oxidation potential of $AgBF_4$ in CH_2Cl_2, PhMe, CH_3CN and THF have shown that $N(C_6H_4Br\text{-}n)_3$ and NPh_3 amines were oxidized only by a suspension of $AgBF_4$ in CH_2Cl_2 to give the corresponding cation, but the experimental part had no description of these reactions.[40] The reaction of vinylidenbis-dialkylamines $R_2C{=}C(NMe_2)_2$ with silver nitrate in acetonitrile leads to oxidative dimerization with the formation of amidines salts $(R_2N)_2C^+CH{=}CHC^+(NR_2){\cdot}2NO_3^-$ and silver metal.[41] The complexes of macrocyclic amines [5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L) and related compounds] with Ag(I) are stable in dry acetonitrile, but in aqueous-methanol solution they disproportionated under formation of Ag(II)L complexes and silver metal.[42,43]

The compounds X–CH_2–M with heteroatoms X = O, S or N in geminal position relative to a group 14 element (M = Si, Ge, Sn) often show unusual reactivity and exhibit unexpected spectroscopic properties.[44–49] The nature of this α-effect has been described with various models of orbital interaction.[50–54] The influence of the silyl group on lone pair ionization energies of the heteroatom is substantial and compounds of this type are electron donor and easily generate radical cation.[55–62] The amines, containing $R_2NCH_2SiX_3$ silyl fragment in α-position, have the value of oxidation potential lower than of trialkylamines.[63–65] These compounds can be involved in the single electron transfer reactions with the formation of the corresponding cation radicals.[66] All above-mentioned allows us to suggest that the reaction of $AgNO_3$ with $R_2NCH_2SiX_3$ amines begins with electron transfer from the amine to a silver cation and at this stage the radical cation of the corresponding amine and silver metal are formed. The interaction of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine **1** with $AgNO_3$ has been investigated by EPR spectroscopy to verify the proposed mechanism. EPR spectra in polar solvating solvents (CH_3CN, HMPTA) show well-resolved multicomponent signals. In DMFA the intensity of the signal observed is much lower and does not allow a



Scheme 3. Synthesis of hydrochloride and nitrate of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine.

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Table 2. Parameters of ^{13}C NMR of organosilicon amines $R_2NCH_2SiX_3$ and their ammonium salts $[R_2NH^+CH_2SiX_3]Y^-$ (solvent CD_3CN)

	$R_2NCH_2SiX_3$				$[R_2NH^+CH_2SiX_3]Y^-$		
	δ, ppm				δ, ppm		
Number	R–N	N–CH_2–Si	SiX_3	Number	R–N	N–CH_2–Si	SiX_3
1	54.51	47.46	50.96	**11**	53.52	46.69	50.07
			57.26				57.02
2	50.21	49.31	50.66	**12**	48.14	47.97	50.29
			58.29				57.19
3	14.73	50.37	51.74	**13**	12.26	48.62	50.31
	54.68		58.33		53.59		57.25
4	24.76	51.42	51.92	**14**	22.18	49.86	50.12
	26.77		58.43		25.27		57.27
	59.01				58.87		
5	62.16	57.34	50.91	**15**	60.49	49.95	50.25
	129.39		58.26		129.87		57.91
	129.49				131.23		
	128.41				133.46		
	139.74						
6	49.95	43.83	18.17	**16**	49.07	42.58	18.00
			57.93				56.79
8	49.74	43.40	−1.49	**18**	48.69	40.98	0.63
9	12.34	43.93	−1.59	**19**	9.55	50.83	0.69
	51.03				52.17		
10	58.0	39.51	−2.6	**20**	51.2	36.93	−0.59
	126.6				127.34		
	128.1				128.96		
	128.3				129.07		
	140.4				133.12		

Table 3. Parameters of ^{29}Si NMR of organosilicon amines $R_2NCH_2SiX_3$ and their ammonium salts $[R_2NH^+CH_2SiX_3]Y^-$ (solvent CD_3CN)

Number	$R_2NCH_2SiX_3$	Number	$[R_2NH^+CH_2SiX_3]Y^-$
1	−81.56	**11**	−84.96
2	−74.39	**12**	−79.51
3	−75.12	**13**	−81.97
4	−73.48	**14**	−82.87
5	−80.96	**15**	−85.26
6	−47.48	**16**	−54.18
8	−1.55	**18**	−1.78
9	−1.63	**19**	−1.89

high-quality spectrum to be obtained. The strong signal (10 components, *g*-factor 2.0049) is registered in the EPR spectrum in acetonitrile just after thawing. The intensity of the signal decreases by two orders within several minutes and at the same time the bands narrow, and an additional superfine structure becomes clearly visible (Fig. 1). The signal is registered within 45 min. The superfine structure corresponds to the interaction of non-paired electrons with one nitrogen nucleus, two groups of two equivalent protons and one group of three equivalent protons.

In HMPTA the clear signal is registered about 15 min after mixing of the reagents. The intensity of the EPR signal increases within approximately 15 min, and then decreases quickly. The superfine structure and the value of the STS constant indicates partial redistribution of spin density due to the solvent effect (hyperfine coupling constants, mT: $a_{H(2)} = 2.100$; $a_{N(1)} = 1.900$; $a_{H(2)} = 1.700$; $a_{H(3)} = 1.600$). The solvatation of silver ions by nitriles[67] promotes the mild proceeding of this reaction in CH_3CN. The superfine structure and the values of hyperfine coupling constants allows assignation of the EPR signals to a radical cation of the $RN^{+\bullet}(CH_2SiX_3)_2$ type, which correlates well with the available data for the radical cation of tris(trimethylsilylmethyl)amine.[68] We failed to observe the EPR signal in the course of the reaction of 1-piperidinomethylsilatrane **4** with $AgNO_3$. Apparently, a limiting stage of this process is the initial electron transfer from the amine to the silver ion, which is rate determined by the nature of the amine, its basicity and stereo-electronic

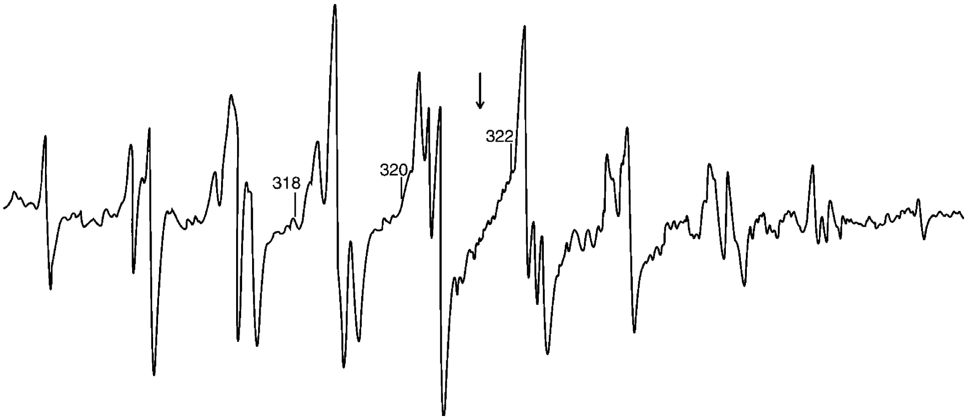
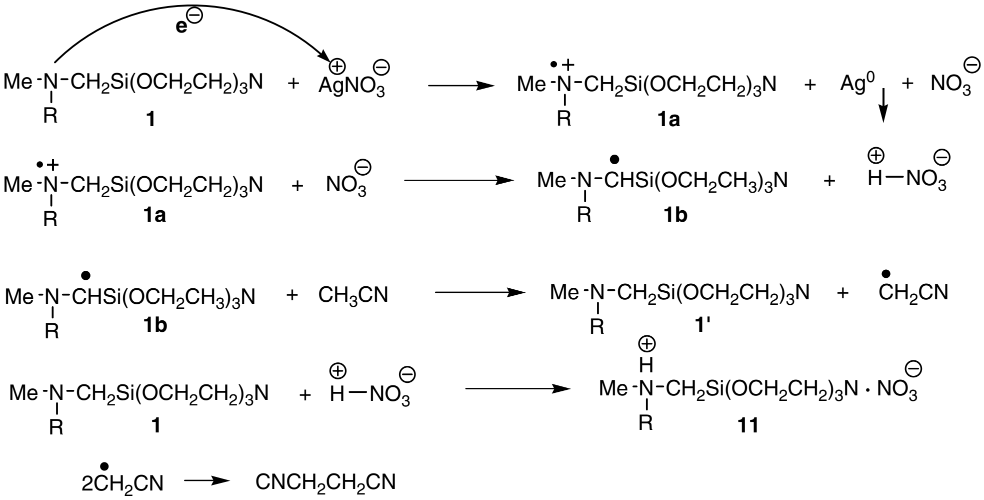


Figure 1. EPR spectrum of the reaction of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine with $AgNO_3$ was recorded in acetonitrile (modulation 0.125 mT; the arrow indicates the center of the spectrum; hyperfine coupling constants, mT: $a_{H(3)} = 2.050$; $a_{H(2)} = 1.912$; $a_{N(1)} = 1.822$; $a_{H(2)} = 1.556$).



Scheme 4. The possible version of the mechanism for the reaction between $AgNO_3$ and organosilicon amines.

structure as well as by the solvation ability of the solvent. The absence of an EPR signal during the oxidation of **4** can be caused just as low concentrations of the radical cation are formed, and so a lower rate of the electron transfer or its significantly lower stability. On the basis of these results we postulate the mechanism for the reaction between $AgNO_3$ and organosilicon amines shown in Scheme 4.

The electron transfer reaction from the amine **1** produces a formation of the amine radical cation **1a** and metal silver. The available literature data allow us to state that α-deprotonation of an amine radical cation is the most probable path for its decomposition.[69–72] The deprotonation of **1a** can lead to the production of the amine radical **1b**. Unfortunately, we did not manage to register the amine radical **1b**. It is known that CH_3CN is a donor of the hydrogen atom.[73–75] For example, it has been proved that the methyl group of acetonitrile is a more effective donor of hydrogen atom than the propyl group in butyronitrile and intermolecular hydrogen transfer from acetonitrile to the nitrogen atom of CN groups takes place.[75] If the amino radical **1b** reacts with CH_3CN, then the formation of amine **1** and the radical $^{\bullet}CH_2CN$ can be observed. The radical $^{\bullet}CH_2CN$ undergoes dimerization. This transfer leads to production of $CNCH_2CH_2CN$. The formation of the succinonitrile is confirmed by the data from NMR and IR spectroscopy, which were obtained from the study of the mixture of the products of the reaction [^1H, 2.78 ppm (CH_2–CN); ^{13}C, 14.9 (CH_2) and 119.2 (CN) ppm; the IR spectrum has ν_{CN} 2250 cm^{-1}]. We synthesized succinonitrile, which had data for the spectra as follows: ^1H, 2.77 ppm (CH_2–CN); ^{13}C, 14.8 (CH_2) and 118.9 (CN) ppm; IR spectrum has ν_{CN} at 2251 cm^{-1}. These data confirm the proposed mechanism of the reaction of $AgNO_3$ with **1**. The succinonitrile is not formed in the presence of traces of water, which can be proton donors.

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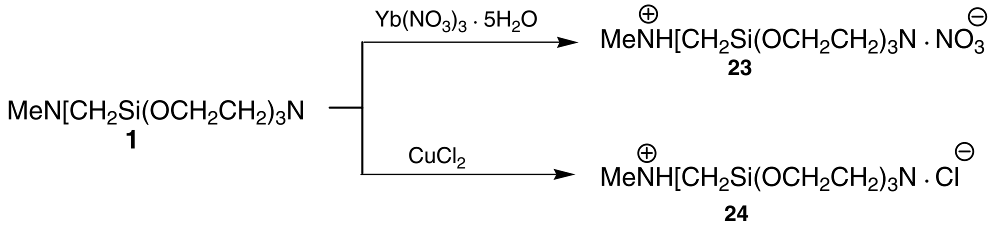

Scheme 5. Interaction of α-silylamines **1** with $CuCl_2$ and $Yb(NO_3)_3{\cdot}5H_2O$.

As mentioned above, this reaction resembles the 'silver mirror' reaction. The reaction vessel is covered with thinnest, bright and strong (not destroyed even after 1 year) layer of silver metal. Aminoalkylsilanes are used in compositions for increased adhesion of glass.[76] Probably, this is one of the causes of hardness of the formed silver mirror. It is likely to be caused by the stabilization of silver particles by the organosilicon amine. The addition of an organylsilanes stabilizes nanoparticles of silver.[77] The authors of this article have used γ-aminopropyltriethoxysilane as anticoagulant, but they do not give any data on its chemical function.

The reduction of silver nitrate by organosilicon amines is a remarkable chemical process, but it is not unique. *N*-Methyl-*N*,*N*-bis(silatranylmethyl)amine interacts with $CuCl_2$ and $Yb(NO_3)_3{\cdot}5H_2O$ under the same conditions, in acetonitrile solution at room temperature (Scheme 5).

The organosilicon amine is transformed into the corresponding ammonium salt over several hours. The NMR and IR spectra of **23** coincide with spectra of products **11** and **22**. The molecules of H_2O contained in $Yb(NO_3)_3{\cdot}5H_2O$ produced the partial hydrolysis of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine. The bands 3350 and 3680 cm^{-1} appeared in the IR spectrum of the solid residue received on the evaporation of a reaction mixture. Therefore the yield of **23** is decreased considerably in comparison with **11**. The spectra of compound **24** are the same as the spectra of compound **21** synthesized by the interaction of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine **1** with equimolar amounts of the dry hydrogen chloride dissolved in carefully dried benzene. Most likely the amine **1** reduces the ions Cu(II) and Yb(III) with the formation accordingly of Cu(I) and Yb(II). However, we have only determined a structure of salts of the ammonium formed at oxidation of the amine **1**. $CuCl_2$ is reduced to CuCl. It is confirmed by the data of the element analysis and the definition of melting point of the solid precipitate which has formed as a result of this reaction. However, any data on $Yb(NO_3)_2$ are absent in the literature. We could also not define a structure of a formed inorganic product in the reaction of **1** with $Yb(NO_3)_3{\cdot}5H_2O$. It is possibly a mix of the salts Yb(II) and Yb(III). Notice that the ability of organosilicon amines to reduces metal ions can find applications both in the reception of thin films, and in making new catalysts. It is not improbable that the ions of Au(I) and the ions of some other metals can be reduced by α-silylmethylamines.

CONCLUSION

The results obtained show that the introduction of the organosilicon substituent into the α-position of an amino group causes a cardinal change in the amine reactivity irrespective of silicon coordination state. The $R_2NCH_2SiX_3$ amines possess high basicity and low ionization potential. The latter promotes to the electron transfer on the first stage of the described reaction, and the high basicity of amine allows efficient binding of an acid formed *in situ* and formation of a stable ammonium salt. Diphenylamine has a low ionization potential (7.25 eV) and very low basicity (p*K* 0.79)[37] does not react under these conditions with $AgNO_3$. Recently we found that the $P(NMe_2)_3$ (the compound belongs to a different class) reduces silver nitrate. This can be explained by the fact that it has a low ionization potential[78] and, simultaneously, easily forms phosphonium salts.[79]

N-Silatranylmethylethylenediamine $H_2NCH_2CH_2NHCH_2SiX_3$ forms complexes with $CuCl_2^3$ and $AgNO_3$ without any signs of reduction. The reactivity of the nitrogen atom of the $N{-}CH_2{-}Si$ ethylenediamine fragment depends not only on the effect of the SiX_3 group, but also on the existence of intramolecular interactions between two nitrogen atoms.[80,81] Probably, the same reasons hinder the redox reaction between DABCO and $AgNO_3$, despite its high basicity and low ionization potential.

EXPERIMENTAL

NMR spectra of the compounds (20% solutions in $CDCl_3$) were recorded on a Bruker instrument (400 MHz, TMS or cyclohexane, internal standards). IR spectra were run on a Specord IR-75 spectrometer (KBr pellets). EPR spectra of the reaction mixtures were recorded in vacuum cells at room temperature on an SE/X-2547 spectrometer (Radiopan, Poland) equipped with a magnetometer and a high-frequency instrument. The solvents were purified and dried according to standard procedures.[37] Salts of silver and copper were dried in a vacuum dessicator. *N*-methyl- and *N*-benzyl-*N*,*N*-bis(silatranylmethyl)amines (**1** and **5**) were synthesized by the method given in Lazareve *et al.*[82] 1-Dimethylamino-, 1-diethylamino- and 1-piperidinomethylsilatranes **2–4** were synthesized using the method in Lukevics *et al.*[83] The alkylaminomethyltrimethylsilanes were synthesized by the

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method in Noll *et al.*[84] All experiments were performed under protection by inert dry gas (argon).

Reaction 1 with $AgNO_3$

Compound **1** (0.0608 g, 0.15 mmol) was dissolved in CH_3CN (1.5 ml) and mixed with the solution of $AgNO_3$ (0.0254 g, 0.15 mmol) in CH_3CN (1.5 ml). The generation of the metal silver was observed immediately after the mixing of the solutions. The reaction mixture was kept for 1 h at room temperature, decanted and evaporated in vacuum. Recrystallization from chloroform–hexane (3 : 1) yielded **11** as a colorless solid (0.0623 g, 0.13 mmol, 89%); elemental analysis (%) calculated for $C_{15}H_{32}N_4O_9Si_2$: C 38.45, H 6.88, N 11.96, Si 11.99; found: C 38.05, H 6.56, N 11.82, Si 12.54; IR (KBr): $\nu = 580$ w, 650 m, 790 s, 810 s, 905 s, 935 m, 1010 vs, 1085 vs, 1105 vs, 1275 vs, 1320 vs, 1450 s, 2430 w, 2520 w, 2890 m, 2940 m cm^{-1} (abbreviations: s, strong; m, medium; w, weak; v, very).

Reaction 2 with $AgNO_3$

Compound **2** (0.0348 g, 0.15 mmol) was dissolved in CH_3CN (1.5 ml) and mixed with the solution of $AgNO_3$ (0.0254 g, 0.15 mmol) in CH_3CN (1.5 ml). The formation of metal silver in the reactionary mix was observed 15 min after mixing solutions. The reaction mixture was allowed to proceed for 6 h at room temperature, decanted and evaporated in a vacuum. Recrystallization from chloroform–hexane (3 : 1) yielded **12** as a colorless solid (0.0412 g, 0.14 mmol, 93%); elemental analysis (%) calculated for $C_9H_{21}N_3O_6Si$: C 36.60, H 7.17, N 14.23; found: C 36.82, H 7.47, N 14.34; IR (KBr): $\nu = 582$ w, 625 w, 690 m, 795 s, 805 s, 900 m, 925 m, 1005 vs, 1080 vs, 1105 vs, 1275 vs, 1350 vs, 1450 s, 2350 w, 2520 m, 2880 m, 2940 m cm^{-1}.

Reaction 3 with $AgNO_3$

Compound **3** (0.0391 g, 0.15 mmol) was dissolved in CH_3CN (1.5 ml) and mixed with a solution of $AgNO_3$ (0.0254 g, 0.15 mmol) in CH_3CN (1.5 ml). The formation of metal silver in the reactionary mix was observed 20 min after mixing the solutions. The reaction mixture was allowed to proceed for 6 h at room temperature, decanted and evaporated in vacuum. Recrystallization from chloroform–hexane (3 : 1) yielded **13** as a colorless solid (0.0451g, 0.14 mmol, 93%); elemental analysis (%) calculated for $C_{11}H_{25}N_3O_6Si$: C 40.85, H 7.79, N 12.99; found: C 41.12, H 7.91, N 12.84; IR (KBr): $\nu = 584$ w, 635 w, 690 m, 798 s, 810 s, 900 m, 930 m, 1010 vs, 1080 vs, 1105 vs, 1275 vs, 1350 vs, 1450 s, 2380 w, 2530 m, 2880 m, 2940 m cm^{-1}.

Reaction 4 with $AgNO_3$

Compound **4** (0.0409 g, 0.15 mmol) was dissolved in CH_3CN (1.5 ml) and mixed with a solution of $AgNO_3$ (0.0254 g, 0.15 mmol) in CH_3CN (1.5 ml). The formation of metal silver in the reactionary mix was observed 20 min after mixing the solutions. The reaction mixture was allowed to proceed for 6 h at room temperature, decanted and evaporated in a vacuum. Recrystallization from chloroform–hexane (3 : 1) or toluene yielded **14** as a colorless solid (0.0408g, 0.12 mmol, 81%); elemental analysis (%) calculated for $C_{12}H_{25}N_3O_6Si$: C 42.97, H 7.51, N 12.53; found: C 42.64, H 7.21, N 12.43; IR (KBr): $\nu = 570$ w, 650 w, 770 s, 800 s, 815 s, 900 s, 915 m, 945 m, 1050 vs, 1085 vs, 1115 vs, 1270 vs, 1350 vs, 1450 s, 2430 w, 2520 m, 2630 m, 2870 m, 2940 m cm^{-1}.

Reaction 5 with $AgNO_3$

Compound **5** (0.0723 g, 0.15 mmol) was dissolved in CH_3CN (1.5 ml) and mixed with the solution of $AgNO_3$ (0.0254 g, 0.15 mmol) in CH_3CN (1.5 ml). The formation of the metal silver was observed immediately after the mixing of the solutions. The reaction mixture was allowed to proceed for 1 h at room temperature, decanted and evaporated in a vacuum. Recrystallization from chloroform–hexane (3 : 1) or chloroform–benzene (1 : 1) yielded **15** as a yellowish solid (0.0686 g, 0.13 mmol, 84%); elemental analysis (%) calculated for $C_{21}H_{36}N_4O_9Si_2$: C 46.31, H 6.66, N 10.29; found: C 46.03, H 6.57, N 10.34; IR (KBr): $\nu = 584$ w, 652 w, 695 w, 775 s, 795 s, 810 s, 915 s, 939 m, 1010 vs, 1080 vs, 1110 vs, 1275 vs, 1320 vs, 1450 s, 1482 m, 1590 w, 2475 w, 2545 w, 2890 m, 2940 m, 3055 m cm^{-1}.

Reaction 6 with $AgNO_3$

Compound **6** (0.0576 g, 0.15 mmol) was dissolved in CH_3CN (1.5 ml) and mixed with the solution of $AgNO_3$ (0.0254 g, 0.15 mmol) in CH_3CN (1.5 ml). The formation of the metal silver was observed 30 min after the mixing the solutions. The reaction mixture was allowed to proceed for 24 h at room temperature, decanted and evaporated in a vacuum. Recrystallization from chloroform–hexane (3 : 1) yielded **16** as a colorless oil (0.0616 g, 0.14 mmol, 92%); elemental analysis (%) calculated for $C_{15}H_{38}N_2O_9Si_2$: C 40.34, H 8.58, N 6.27; found: C 40.59, H 8.75, N 6.19; IR (KBr): $\nu = 752$ m, 765 s, 915 w, 955 m, 1100 vs, 1120 vs, 1265 vs, 1340 vs, 1420 s, 1475 m, 2545 w, 2580 w, 2642 w, 2675 w, 2850 m, 2950 m cm^{-1}.

Reaction 7 with $AgNO_3$

Compound **7** (0.0174 g, 0.15 mmol) was dissolved in CH_3CN (1.5 ml) and mixed with the solution of $AgNO_3$ (0.0254 g, 0.15 mmol) in CH_3CN (1.5 ml). The formation of the metal silver was observed 1 h after the mixing of the solutions. The reaction mixture was allowed to proceed for 24 h at room temperature, decanted and evaporated in a vacuum. Recrystallization from chloroform–hexane (3 : 1) or CH_2Cl_2–Et_2O (4 : 1) yielded **17** as a colorless oil (0.021 g, 0.12 mmol, 78%); elemental analysis (%) calculated for $C_5H_{15}N_2O_3Si$: C 33.50, H 8.43, N 15.63; found: C 33.11, H 8.23, N 15.72; IR (KBr): $\nu = 525$ w, 750 m, 820 m, 840 m, 1250 vs, 1310 vs, 1380 s, 1450 w, 2595 w, 2850 w, 2940 m cm^{-1}.

Reaction 8 with $AgNO_3$

Compound **8** (0.02 g, 0.15 mmol) was dissolved in CH_3CN (1.5 ml) and mixed with the solution of $AgNO_3$ (0.0254 g, 0.15 mmol) in CH_3CN (1.5 ml). The formation of the metal silver was observed 1 h after the mixing of the solutions. The reaction mixture was allowed to proceed for 24 h at room temperature, decanted and evaporated in vacuum. Recrystallization from chloroform–hexane (3 : 1) or CH_2Cl_2–Et_2O (3 : 1) yielded **18** as a colorless solid (0.0256 g, 0.13 mmol, 88%); elemental analysis (%) calculated for $C_6H_{18}N_2O_3Si$: C 37.09, H 9.34, N 14.42; found: C 36.87, H 9.18, N 14.34; IR (KBr): $\nu = 530$ w, 740 w, 790 w, 815 w, 920 m, 1260 vs, 1380 vs, 1445 vs, 2620 w, 2875 m, 2960 m cm^{-1}.

Reaction 9 with $AgNO_3$

Compound **9** (0.0239 g, 0.15 mmol) was dissolved in CH_3CN (1.5 ml) and mixed with the solution of $AgNO_3$ (0.0254 g, 0.15 mmol) in CH_3CN (1.5 ml). The formation of the metal silver was observed 1 h after the mixing of the solutions. The reaction mixture was allowed to proceed for 24 h at room temperature, decanted and evaporated in a vacuum. Recrystallization from chloroform–hexane (3 : 1) or CH_2Cl_2–pentane (4 : 1) yielded **19** as a colorless solid (0.027 g, 0.12 mmol, 81%); elemental analysis (%) calcd for $C_8H_{22}N_2O_3Si$: C 43.21, H 9.97, N 12.60; found: C 43.47, H 10.12, N 12.67; IR (KBr): $\nu = 528$ w, 740 w, 795 w, 810 w, 924 m, 1265 vs, 1380 vs, 1445 vs, 2635 w, 2870 m, 2950 m cm^{-1}.

Reaction 10 with $AgNO_3$

Compound **10** (0.0289 g, 0.15 mmol) was dissolved in CH_3CN (1.5 ml) and mixed with the solution of $AgNO_3$ (0.0254 g, 0.15 mmol) in CH_3CN (1.5 ml). The formation of the metal silver was observed 40 min after the mixing of the solutions. The reaction mixture was allowed to proceed for 24 h at room temperature, decanted and evaporated in a vacuum. Recrystallization from chloroform–hexane (3 : 1) or xylene yielded **20** as a yellow solid (0.0334 g, 0.13 mmol, 87%); elemental analysis (%) calculated for $C_{11}H_{19}N_2O_3Si$: C 51.74, H 7.50, N 10.97; found: C 52.01, H 7.83, N 11.07; IR (KBr): $\nu = 688$ w, 760 s, 795 s, 810 s, 924 m, 1260 vs, 1385 vs, 1450 s, 1590 m, 2665 w, 2875 m, 2950 m, 3040 m cm^{-1}.

It is necessary to note that the reaction $AgNO_3$ with compounds **6–10** is extremely sensitive to the presence of a trace of H_2O at a reaction mixture. If this reaction is carried out in the wet CH_3CN the preferential formation of the products of the cleavage Si–C bond is observed.

Reaction of 1 with $Yb(NO_3)_3 \cdot 5H_2O$

The compound **1** (0.0608 g, 0.15 mmol) in CH_3CN (1.5 ml) was added dropwise to a solution of $Yb(NO_3)_3 \cdot 5H_2O$ (0.0674 g, 0.15 mmol) in CH_3CN (1.5 ml). The formation of a white precipitate has been registered immediately after the mix of the solutions. The reaction mixture was kept for 24 h at room temperature, was filtered and filtrate was evaporated in vacuum. The residue was crystallized from chloroform–hexane (3 : 1), yield **23** (0.04g, 0.09 mmol, 57%). Elemental analysis (%) calculated for $C_{15}H_{32}N_4O_9Si_2$: C 38.45, H 6.88, N 11.96; found: C 38.69, H 6.81, N 12, 04; IR (KBr) for residue after removal of CH_3CN: $\nu = 585$ m, 650 m, 790 s, 810 s, 850 w, 905 s, 935s, 1012 s, 1085 vs, 1105 vs, 1270 vs, 1325 vs, 1450 s, 2430 w, 2520 w, 2890 m, 2940 m, 3350 w, 3680 w cm^{-1}.

Reaction of 1 with $CuCl_2$

Compound **1** (0.0608 g, 0.15 mmol) was dissolved in CH_3CN (1.5 ml) and mixed with the solution of $CuCl_2$ (0.0202 g, 15 mmol) in CH_3CN (1.5 ml). The brown color of the anhydrous $CuCl_2$ sluggishly disappeared and the formation of a white precipitate was observed simultaneously. The reaction mixture was kept for 24 h at room temperature, filtered and the filtrate evaporated in a vacuum. Recrystallization from chloroform–hexane (1 : 1) yielded **24** as a colorless solid (0.0497 g, 0.11 mmol, 75%); elemental analysis (%) calculated for $C_{15}H_{32}ClN_3O_6Si_2$: C 40.76, H 7.30, N 9.51; found: C 40.39, H 7.18, N 9.57; IR (KBr): $\nu = 580$ w, 610 w, 740 w, 780 m, 880 m, 900 m, 935 w, 1010 vs, 1055 vs, 1100 vs, 1265 w, 2430 w, 2520 w, 2880 m, 2940 m cm^{-1}.

For analysis, the white precipitate of salts CuCl was washed with ethanol, then pentane, and was dried in vacuum at heating. Yield 0.0143 g, 96%; m.p. 425 °C (for comparison m.p. 430 °C[85]). Anal. calculated (%) for CuCl: Cl 35.81; found: 35.52.

Synthesis of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine hydrochloride 21

An 0.0365 g (1 mmol) of HCl dissolved in carefully dried benzene was slow added to 0.4056 g (1 mmol) **1** in acetonitrile solution at 10 °C. After 10 min the reaction mixture was evaporated to remove the solvent. Recrystallized from chloroform–hexane (1 : 1) to give a colorless solid of the compound **21.** Yield 0.2564 g, 0.58 mmol, 58%. Elemental analysis (%) calculated for $C_{15}H_{32}ClN_3O_6Si_2$: C 40.76, H 7.30, N 9.51; found: C 40.69, H 7.12, N 9.64; IR (KBr): $\nu = 580$ w, 615 w, 740 w, 780 m, 880 m, 910 m, 935 w, 1010 vs, 1060 vs, 1100 vs, 1265 w, 2430 w, 2530 w, 2880 m, 2940 m cm^{-1}.

Synthesis of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine nitrate 22

A 0.0849 g (0.5 mmol) aliquot of $AgNO_3$ dissolved in CH_3CN was added to 0.2210 g (0.5 mmol) **21** in solution of acetonitrile and had mixed within 15 min. The precipitate was filtered. The filtrate was evaporated in vacuum. The crystallization from chloroform–hexane (3 : 1) gave compound **22**. Yield 0.2202 g, 0.47 mmol, 94%. Elemental analysis (%) calculated for $C_{15}H_{32}N_4O_9Si_2$: C 38.45, H 6.88, N 11.96; found: C 38.17, H 6.63, N 11.91; IR (KBr): $\nu = 580$ w, 655 m, 790 s, 810 s, 905 s, 940 m, 1015 vs, 1085 vs, 1105 vs, 1275 vs, 1320 vs, 1450 s, 2430 w, 2520 w, 2880 m, 2940 m cm^{-1}.

The experimental technique in ampoule EPR

A solution of **1** (**1** = 2.4 mmol/l) was placed in an EPR ampoule, frozen (liquid N_2), and an equimolar amount of $AgNO_3$ in the same solvent was added. The ampoules were carefully degassed (not allowing the reaction to begin) and sealed in a vacuum. The ampoules were frozen. The ampoules were thawed and the solutions were mixed just before their submission in the resonator of an EPR spectrometer.

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