Synthesis and properties of novel dialkylaminocarbenium salts

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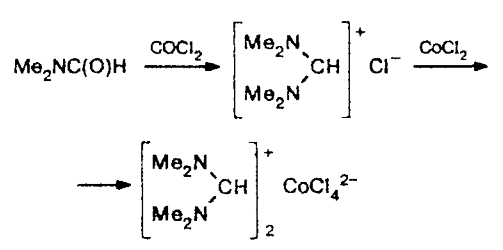
Novel dialkylaminocarbenium salts with metallocomplex counter ions were prepared by the reaction of phosgene with either DMF or tetramethylurea in the presence of metal chlorides. Reactions of organosilicon amides with phosgene gave corresponding carbenium salts, while organosilicon ureas yielded aminoiminocarbenium salts. Dialkylaminochlorocarbenium salts were reduced with hydrosilanes to give dialkylaminocarbenium salts and can be easily hydrolyzed to afford either amides or ureas. Pathways of the reaction with water and alcohols depend on the nature of reagent and the reaction conditions.

Key words: dialkylaminocarbenium salts; aminoiminocarbenium salts; phosgene, dimethylformamide, tetramethylurea, reaction; dialkylaminochlorocarbenium salts, reduction, hydrolysis, alcoholysis.

The interest in dialkylaminocarbenium salts with complex metal-containing counter ions arises from their ability to catalyze hydrosilylation of unsaturated compounds.[1–3]

To extend the number of metal-containing dialkylaminocarbenium salts and to study their chemical and physicochemical properties and catalytic activity, in this work we carried out the following syntheses of salts **1**—**5** (which proved to be preparative):

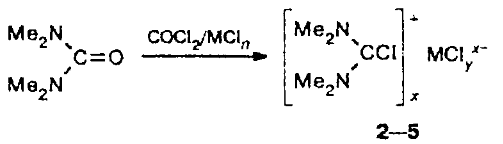
— interaction of phosgene with DMF in the presence of metal chlorides, for example $CoCl_2$:



(1)

1

— phosgenation of tetramethylurea in the presence of metal chlorides:

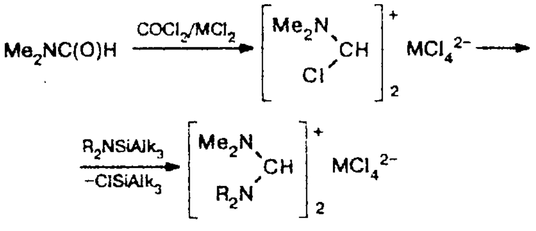


(2)

2—5

Salt	M	*n*	*x*	*y*
2	Ca	2	2	4
3	Cu	2	2	4
4	Mo	5	3	8
5	Y	3	1	4

If the first step of reaction (1) is carried out at DMF deficiency, and dialkylaminosilane is added at the second step, the salts **6**—**8** can be obtained, which contain carbocations with various substituents. Apparently the reaction occurs *via* intermediate formation of chloro(dimethylamino)carbenium salt.



(3)

6—8

6: M = Co, R = All
7: M = Mn, R = All
8: M = Co, R = Et

Yields and main characteristics of the obtained compounds are presented in Table 1.

If the reaction between aminosilane (for instance, $Me_3SiNAll_2$) and the product obtained in the reaction of phosgene with DMF is carried out in the absence of metal chloride, diallylamino(dimethylamino)carbenium chloride $Me_2N(All_2N)C^+HCl^-$ (**9**) itself can be isolated.

We made an attempt to synthesize silicon-containing dialkylaminocarbenium salts from the corresponding amides and dichlorodiphenylsilane. However, we found only cyclic siloxanes and ammonium salt among the products of the reaction of carbofunctional organosilicon amides with dichlorodiphenylsilanes. In one of our publications,[3] we conceived the formation of carbenium ion

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Table 1. Physicochemical characteristics of diaminocarbenium salts

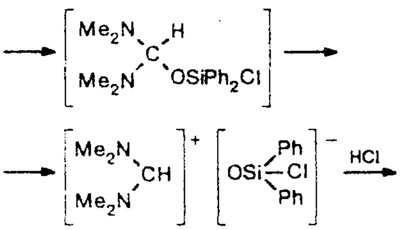
Compound	Yield (%)	M.p. /°C	Found/Calculated (%) C	H	Cl	N	Molecular formula	IR, ν(C≡N) /cm^{-1}
1	74	163	29.81 29.79	6.54 6.51	35.16 35.17	13.32 13.90	$C_{10}H_{26}Cl_4CoN_4$	1700
2	86	142	26.48 26.51	5.39 5.34	49.89 49.95	12.41 12.36	$C_{10}H_{24}CaCl_6N_4$	1650
3	89	128	25.18 25.20	5.11 5.07	44.58 44.63	11.80 11.75	$C_{10}H_{24}Cl_6CuN_4$	1650
4	87	164	22.73 22.91	4.81 4.61	48.41 49.60	10.51 10.69	$C_{15}H_{36}Cl_{11}MoN_6$	1650
5	92	215	16.34 16.39	3.35 3.30	48.28 48.39	7.69 7.65	$C_5H_{12}Cl_5N_2Y$	1650
6	78	[a]	42.64 42.61	6.77 6.77	27.32 27.95	11.08 11.05	$C_{18}H_{34}Cl_4CoN_4$	1680
7	75	[a]	42.94 42.95	6.86 6.82	28.21 28.17	11.13 11.13	$C_{18}H_{34}Cl_4MnN_4$	1680
8	61	119	38.92 39.00	7.99 7.95	32.84 32.89	6.47 6.49	$C_{14}H_{34}Cl_4CoN_2$	1700
9	86	129	57.26 57.29	9.09 9.02	18.84 18.83	14.81 14.85	$C_9H_{17}ClN_2$	1680
10	78	197	59.91 59.84	11.68 11.61	11.00 11.04	8.61 8.76	$C_{16}H_{37}ClN_2Si$	1690
11	81	[a]	62.68 62.66	10.85 10.81	10.22 10.27	8.11 8.12	$C_{18}H_{37}ClN_2Si$	1670
15	78	85	56.4 56.4	10.5 10.5	—	—	$C_{13}H_{29}ClN_2Si$	
18c	89	[a]	31.10 31.11	6.58 6.57	30.62 30.61	12.10 12.10	$C_{12}H_{30}Cl_6CoN_4O_2$	1655
19	63	80[b]	35.09 35.37	7.01 6.54	22.41 22.37	5.89 5.89	$C_{28}H_{62}Cl_6N_4O_2PtSi_2$	
21	81	195[c]						

[a] An oily product. [b] With decomposition. [c] See Ref. 4: m.p. 195 °C.

as a successive chain of transformations (reactions (4) and (5)).

$$Me_2NC(O)H + Ph_2SiCl_2 \longrightarrow Me_2NSiPh_2Cl + HCl + CO, \quad (4)$$

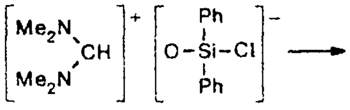
$$Me_2NC(O)H + Me_2NSiPh_2Cl \longrightarrow$$



$$\longrightarrow [(Me_2N)_2CH]^+Cl^- + Ph_2Si(Cl)OH. \quad (5)$$

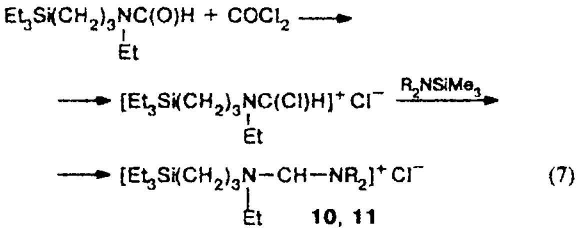
Upon heating chlorodiphenylsilanol was converted naturally to cyclosiloxane, and bis(dimethylamino)carbenium chloride was recorded in the form of salts with corresponding anions.

An alternative scheme of conversion of bis(dimethylamino)carbenium chlorodiphenylsilanolate to the corresponding chloride involves the intermediate formation of diphenylsilanone by β-elimination of chloride followed by its transformation to tetramer; however, the essence of the scheme remains unchanged.



$$\longrightarrow [(Me_2N)_2CH]^+Cl^- + 1/4\ [Ph_2SiO]_4 \quad (6)$$

We succeeded in synthesizing silicon-containing diaminocarbenium salts **10** and **11** from the corresponding amide by the reaction (7).

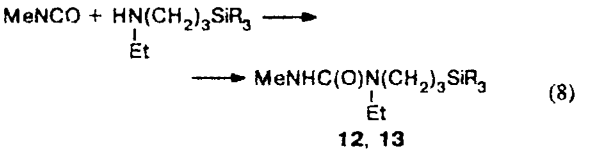


$$\mathrm{Et_3Si(CH_2)_3\underset{Et}{N}C(O)H + COCl_2 \longrightarrow [Et_3Si(CH_2)_3\underset{Et}{N}C(Cl)H]^+Cl^- \xrightarrow{R_2NSiMe_3} [Et_3Si(CH_2)_3\underset{Et}{N}-CH-NR_2]^+Cl^-} \quad (7)$$

10, 11

R = Et (**10**), All (**11**)

An alternative pattern for obtaining organosilicon diaminocarbenium salts may be the reaction of phosgene with organosilicon ureas **12** and **13**, which were synthesized by amination of methyl isocyanate.

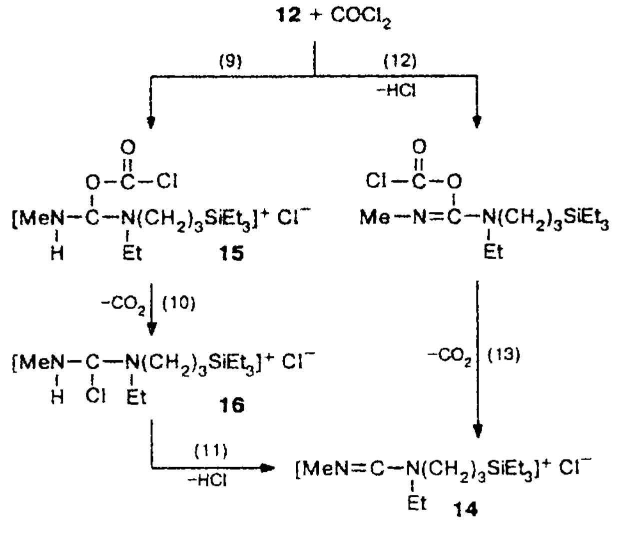


$$\mathrm{MeNCO + H\underset{Et}{N}(CH_2)_3SiR_3 \longrightarrow MeNHC(O)\underset{Et}{N}(CH_2)_3SiR_3} \quad (8)$$

12, 13

R = Et (**12**), OEt (**13**)

Using urea **12** as an example, we demonstrated that *N*-ethyl-*N*-triethylsilylpropylamino-*N*′-methyliminocarbenium chloride (**14**) was the end product of the reaction. We may assume two alternative pathways for formation of this compound: phosgenation by carbonyl group (reactions (9)—(11)) and phosgenation at the N—H bond (reactions (12) and (13)).



In the case of the first pathway, not only chlorocarbonyloxysubstituted salt **15**, but also aminochlorocarbenium salt **16** apparently proved to be not very stable, and the latter is stabilized due to spontaneous dehydrochlorination to give the end product.

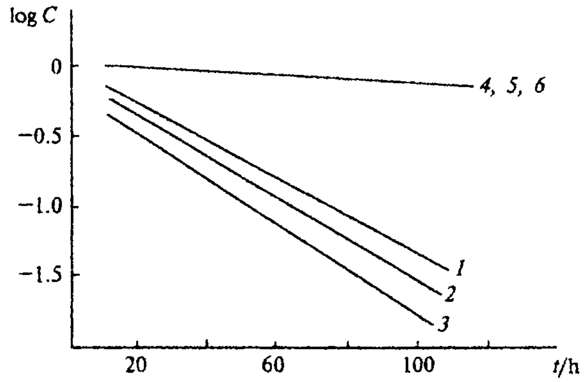


Fig. 1. Kinetic curves of hydrolysis of diaminocarbenium salts at 25 °C:
1 — $\{[(\mathrm{Me_2N})_2\mathrm{CCl}]\}^+\}_2\mathrm{CoCl_4}^{2-}$ (**22**);
2 — $\{[(\mathrm{Me_2N})_2\mathrm{CCl})]_2\}^+\mathrm{PtCl_6}^{2-}$ (**17**);
3 — $[(\mathrm{Me_2N})_2\mathrm{CCl}]^+\mathrm{Cl}^-$ (**24**);
4 — $\{[(\mathrm{Me_2N})_2\mathrm{CO}]^+\}_2\mathrm{SnCl_4}^{2-}$ (**23**);
5 — $\{[(\mathrm{Me_2N})_2\mathrm{COMe}]^+\}_2\mathrm{PtCl_6}^{2-}$ (**18d**);
6 — $\{[(\mathrm{Me_2N})_2\mathrm{CH}]^+\}_2[\mathrm{PtCl_6}]^{2-}$ (**21**).

The dialkylaminocarbenium salts we obtained possess strong electrophilic properties and behave similarly to acyl halides in the reactions with nucleophilic agents..

Hydrolysis of dialkylaminochlorocarbenium salts results in the corresponding ureas. For example, deuterolysis of chlorobis(dimethylamino)carbenium hexachloroplatinate (**17**) leads to tetramethylurea.

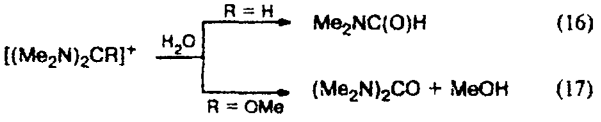
$$\underset{\mathbf{17}}{\{[(\mathrm{Me_2N})_2\mathrm{CCl}]^+\}_2\mathrm{PtCl_6}^{2-}} \xrightarrow[-\mathrm{D_2O}]{\mathrm{D_2O},\ 25\ ^\circ\mathrm{C}} (\mathrm{Me_2N})_2\mathrm{CO} + \mathrm{PtO_2} \quad (14)$$

Kinetic parameters of the hydrolysis (Fig. 1) found by ^{1}H NMR spectroscopy indicate that the hydrolysis is a first-order reaction. There are signals of the methyl groups of the chlorobis(dimethylamino)carbenium ion and tetramethylurea in the ^{1}H NMR spectra, and there is no corresponding signal of the deuteroxybis(dimethylamino)carbenium ion.

We may suggest that the step of nucleophilic substitution is limiting for the whole process of hydrolysis, because heterolysis of the O—D bond proceeds rapidly within the NMR time scale, *i.e.*, $K_2 \gg K_1$.

$$[(\mathrm{Me_2N})_2\mathrm{CCl}]^+ \xrightarrow[-\mathrm{Cl}^-]{\mathrm{DO}^-\ (K_1)} [\mathrm{DOC(NMe_2)_2}]^+ \xrightarrow[-\mathrm{D}^+]{(K_2)} (\mathrm{Me_2N})_2\mathrm{CO} \quad (15)$$

Metal-containing salts of dimethylaminocarbenium $\{[(\mathrm{Me_2N})_2\mathrm{CR}]^+\}_2\mathrm{MCl}_n^{2-}$ (R = H, OMe; M = Sn$^{\mathrm{II}}$, Pt$^{\mathrm{II}}$; n = 4, 6) were stable when they underwent the action of cold water; however, they can react with water when they are heated to give a secondary amide and urea, respectively.



$$[(Me_2N)_2CR]^+ \xrightarrow{H_2O} \begin{cases} \xrightarrow{R = H} Me_2NC(O)H & (16) \\ \xrightarrow[R = OMe]{} (Me_2N)_2CO + MeOH & (17) \end{cases}$$

Hexachloroplatinate **17** reacts with methanol to form the corresponding (dimethylamino)methoxycarbenium salt **18c**. Compounds **18a,b,d** were earlier synthesized by a similar procedure.[4]

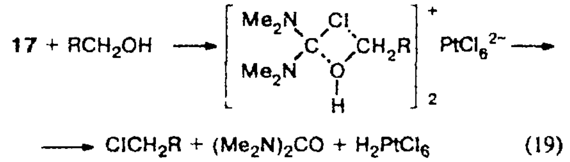
$$\{[(Me_2N)_2CCl]^+\}_2MCl_n{}^{2-} \xrightarrow[(88-97\%)]{MeOH} \{[Me_2N)_2COMe]^+\}_2MCl_n{}^{2-} \quad (18)$$

18a—d

a: M = Sn^{II}, n = 4 **c**: M = Co^{II}, n = 6

b: M = Mn^{II}, n = 4 **d**: M = Pt^{IV}, n = 6

The reactions with phenol and allyl alcohol proceed differently to give an organyl chloride and urea.



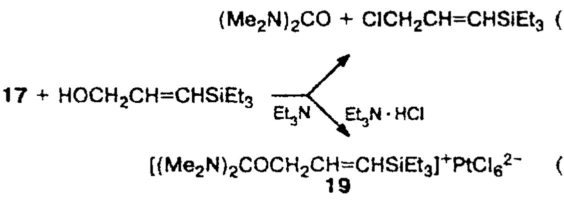
(19)

R = Ph, Vin

The Vilsmeier reagent is known to react with propargyl alcohol according to a similar scheme.[5]

$$[Me_2NC(H)Cl]^+Cl^- + HC{\equiv}CCH_2OH \xrightarrow[-HCl]{} HC{\equiv}CCH_2Cl + Me_2NCHO \quad (20)$$

It should be noted that the reaction of hexachloroplatinate **17** with triethylsilyl-1-propen-3-ol yields tetramethylurea and organyl chloride (reaction (21)), whereas in the presence of triethylamine, bis(dimethylamino)(3-triethylsilyl-2-propenyloxy)carbenium hexachloroplatinate (**19**) is formed (reaction (22)).



$$\mathbf{17} + HOCH_2CH{=}CHSiEt_3 \begin{cases} \xrightarrow{} (Me_2N)_2CO + ClCH_2CH{=}CHSiEt_3 & (21) \\ \xrightarrow[Et_3N]{Et_3N\cdot HCl} [(Me_2N)_2COCH_2CH{=}CHSiEt_3]^+PtCl_6{}^{2-} & (22) \end{cases}$$

19

The ability of chlorodialkylaminocarbenium salts to be reduced with hydrosilanes is another of their characteristic features.

$$\mathbf{17} + MePh_2SiH \longrightarrow [(Me_2N)_2CH]^+Cl^- + \{[R_3Si]^+\}_2PtCl_6{}^{2-} \longrightarrow \{[(Me_2N)_2CH]^+\}_2PtCl_6{}^{2-} + MePh_2SiCl \quad (23)$$

20, **21**

$$[(Me_2N)_2Cl]^+Cl^- + HSiR_3 \longrightarrow \mathbf{20} + ClSiR_3 \quad (24)$$

R_3 = $MeCl_2$, $MePh_2$, Me_2Ph, $(EtO)_3$, Et_3

Chlorosilane, which was liberated in the reaction, was recorded by GLC.

Formally, we can assume that reaction (23) proceeds *via* formation of the intermediate silenium ion, which is similar to the triethylsilenium ion in $(Et_3Si)^+ClO_4{}^-$ salt, derived from $(Ph_3C)^+ClO_4{}^-$ and Et_3SiH.[6] The presence of substituents capable of delocalizing the positive charge must stabilize the $(R_3Si)^+$ ion and favor the reaction. Actually, hydrosilanes can be arranged in the following order of increasing reactivity: $Ph_2MeSiH > PhMe_2SiH \gg (EtO)_3SiH > Et_3SiH > MeCl_2SiH$. However, hydrosilanes reduce not only dialkylaminocarbenium salts, but the metal itself: $Pt^{IV} \rightarrow Pt^{II} \rightarrow Pt^0$. The yield of salt **21** was 76.5% in reaction (23). Because of this a two-step procedure was proposed (reaction (25)).

$$[(Me_2N)_2CCl]^+Cl^- + MePh_2SiH \xrightarrow[-MePh_2SiCl]{MeCN} [(Me_2N)_2CH]^+Cl^- \xrightarrow[-HCl]{H_2PtCl_6} \mathbf{21} \quad (25)$$

The yield of platinum salt **21** is 93%. As would be expected the rate of the reaction increases in a polar aprotic solvent; this fact confirms the ionic character of this reaction.

Experimental

All syntheses were carried out under dry nitrogen.

GLC analysis was carried out on a Tsvet-100 chromatograph with a katharometer as detector (a 1500×1 mm column, 15% E-301 on Chromaton, evaporator temperature 400 °C, column temperature 50 to 300 °C, rate of temperature programming 20 deg per min, helium as gas-carrier (60 mL min^{-1})).

^{1}H NMR spectra were recorded on a Varian T-60a (60MHz) with $SiMe_4$ used as the internal standard.*

Bis(dimethylamino)carbenium tetrachlorocobaltate(II) (1). DMF (0.58 g, 8 mmol) and toluene (5 mL) were placed in a four-necked flask fitted with a thermometer, a dropping funnel, a reflux condenser, and a stirrer. At 0 °C 30% toluene solution of phosgene (0.4 g, 4 mmol) was added with stirring. When liberation of CO_2 was stopped, the mixture was allowed to stand at –20 °C for 7 days. The precipitated bis(dimethylamino)carbenium chloride was filtered off, dissolved in 5 mL

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* The authors thank A. V. Kisin for recording ^{1}H NMR spectra.

of dichloromethane, and cobalt chloride (0.26 g, 2 mmol) was added to the resulting solution; 2 h later the formed crystalline precipitate of salt **1** was washed with chloroform (2×3 mL) and diethyl ether (2×3 mL) and dried *in vacuo* until the weight became constant.

Synthesis of salts 2—5 (general procedure). A metal chloride (10 mmol), tetramethylurea (2.32 g, 20 mmol), and toluene (10 mL) were introduced into a flask. A 30% toluene solution of phosgene (0.3 g, 30 mmol) was then added dropwise to the resulting mixture at 0°C with stirring. After completion of liberation of gases, the reaction mixture was allowed to stand, and a salt was precipitated, which was filtered off, washed with chloroform (2×3 mL) and diethyl ether (2×3 mL), and dried *in vacuo* until the weight became constant.

***N,N*-Diallylamino-*N'*,*N'*-dimethylaminocarbenium tetrachlorocobaltate(II) and tetrachloromanganate(II) (6, 7).** A 30% toluene solution of phosgene (0.4 g, 4 mmol) was added dropwise to a solution of DMF (0.3 g, 4 mmol) and a metal chloride (2 mmol) in dichloromethane (10 mL) with stirring at 0 °C. After completion of gas liberation, the reaction mixture was kept for 2 h. Diallylamino(trimethyl)silane (0.68 g, 4 mmol) in dichloromethane (5 mL) was then added with stirring at 0 °C, and the resulting mixture was allowed to stand overnight at ~20 °C. After removal of the solvents by evaporation, the corresponding salt was obtained.

***N,N*-Diethylamino-*N'*,*N'*-dimethylaminocarbenium tetrachlorocobaltate(II) (8).** Dichlorodiphenylsilane (25.3 g, 0.1 mol), triethylamine (10.1 g, 0.1 mol), and hexane (300 mL) were placed into a flask fitted with a reflux condenser, a stirrer, a thermometer, and a dropping funnel. Diethylamine (7.3 g, 0.1 mol) was added dropwise at 0 °C with continuous stirring. The reaction mixture was controlled thermostatically for 1 h at 0 °C and for 1 h at 40 °C. After evaporation of the solvents, chloro(diethylamino)diphenylsilane (18.5 g, 64%) was isolated by fractionation, b.p. 160 °C (0.1 Torr), n_D^{20} 1.5591.

In the apparatus described above, DMF (29.2 g, 40 mmol) and $CoCl_2$ (1.3 g, 10 mmol) were placed , and the mixture was heated to 90 °C with stirring. After the salt was completely dissolved, chloro(diethylamino)diphenylsilane (5.8 g, 20 mmol) was added dropwise. The temperature of the reaction mixture was gradually increased to 150 °C, the mixture was kept for 7 h and cooled to 50 °C; toluene (30 mL) was then added. The precipitated salt **8** was filtered, washed with chloroform (2×10 mL) and dried.

***N,N*-Diallylamino-*N'*,*N'*-dimethylaminocarbenium chloride (9).** A 30% toluene solution of phosgene (0.4 g, 4 mmol) and diallylamino(trimethyl)silane (0.68 g, 4 mmol) were added to DMF (0.3 g, 4 mmol). After evaporation of the solvents, salt **9** was washed with diethyl ether and recrystallized from ether. ^1H NMR (CD_2Cl_2), δ: 3.28, 3.41 (both s, 3 H, CH_3N); 9.48 (s, HC^+); signals of allylic protons.

Salt **9** (yield 33%) and diallylamine hydrochloride were obtained similarly from DMF (0.3 g, 4 mmol), phosgene (0.4 g, 4 mmol), and diallylamine (0.39 g, 4 mmol) in dichloromethane (5 mL) after evaporation of solvents and fractional crystallization from a $CHCl_3$—CCl_4 mixture.

***N,N*-Diethylamino-*N'*-ethyl-*N'*-(3-triethylsilylpropyl)-aminocarbenium chloride (10).** A 30% toluene solution of phosgene (1 g, 10 mmol) and diethylamino(trimethyl)silane (1.5 g, 10 mmol) in dichloromethane (5 mL) were added to *N*-ethyl-*N*-triethylsilylpropylformamide (2.3 g, 10 mmol) in dichloromethane (10 mL). After evaporation of the solvents, salt **10** was washed with diethyl ether and recrystallized from ether.

***N,N*-Diallylamino-*N'*-(3-triethoxysilylpropyl)-*N'*-ethylaminocarbenium chloride (11)** was obtained similarly to salt **10**, but diallylamino(trimethyl)silane was used instead of diethylamino(trimethyl)silane.

***N*-Ethyl-*N*-(3-triethylsilylpropyl)-*N'*-methylurea (12).** *N*-Ethyl-*N*-(3-ethylsilylpropyl)amine (10 g, 50 mmol) was added dropwise to methyl isocyanate (3 g, 50 mmol) in toluene (100 mL) at 0 °C with stirring. The solvent was evaporated to afford compound **12** (12.8 g, 99%), m.p. 50 °C. ^1H NMR (CD_2Cl_2), δ: 0.3—1.2 (m, 22 H, Et_3Si, CH_2CH_2Si, $\underline{CH}_3CH_2N$); 2.6 (s, 3 H, CH_3N); 3.1 (m, 4 H, CH_2N); 4.9 (s, 1 H, HN). Found (%): C, 60.0; H, 11.8; Si, 10.4. $C_{13}H_{30}N_2OSi$. Calculated (%): C, 60.5; H, 11.6; Si, 10.8.

***N*-(3-Triethoxysilylpropyl)-*N*-ethyl-*N'*-methylurea (13)** was obtained similarly to the previously reported compound as an oily product (yield 98%). Found (%): C, 50.8; H, 10.0; Si, 9.0. $C_{13}H_{30}N_2O_4Si$. Calculated (%): C, 51.0; H, 9.8; Si, 9.1.

***N*-Ethyl-*N*-(3-triethylsilylpropyl)amino-*N'*-methyliminocarbenium chloride (14).** A 30% toluene solution of phosgene (10 mmol) was added to *N*-ethyl-*N*-triethylsilyl-*N'*-methylurea (2.6 g, 10 mmol) at 0 °C. After liberation of gases from the reaction mixture ceased, a crystalline solid was precipitated from the reaction mixture, which was washed with diethyl ether (2×3 mL), and dried *in vacuo*. Salt **14** (2.5 g) was obtained. ^1H NMR (CD_2Cl_2), δ: 0.4—1.1 (m, 19 H, EtSi, CH_2CH_2Si); 1.3 (t, CH_3C); 3.1 (s, 3 H, CH_3N); 3.6—3.9 (m, NCH_2).

Interaction of organosilicon formamides with diphenyldichlorosilane. ***A.*** *N*-Ethyl-*N*-(3-triethylsilylpropyl)formamide (11.5 g, 50 mmol), dichlorodiphenylsilane (6.3 g, 0.25 mmol), and $CoCl_2$ (0.03 g, 0.25 mmol) were placed in a flask fitted with a reflux condenser and heated at 130—150 °C for 4 h. A viscous oily product was obtained. When toluene (10 mL) was added to this product, a crystalline solid, *N*-ethyl-*N*-(3-triethylsilylpropyl)ammonium chloride, was precipitated (yield 43.6%), m.p. 220 °C (subl.). Found (%): C, 55.4; H, 12.0. $C_{11}H_{28}ClNSi$. Calculated (%): C, 55.5; H, 11.8. Hexane (5 mL) was added to the filtrate to precipitate octaphenylcyclotetrasiloxane, m.p. 200 °C (lit. data[7]: m.p. 203.4 °C).

B. An equimolar mixture of *N*-ethyl-*N*-(triethoxysilylpropyl)formamide and dichlorodiphenylsilane was heated at 130 °C for 1 h. In this case liberation of ethyl chloride was observed. As a result a viscous organosilicon material was obtained, which was not identified.

Bis(dimethylamino)methoxycarbenium tetrachlorocobaltate (18c). A mixture of chlorobis(dimethylamino)carbenium tetrachlorocobaltate (0.1 g, 0.2 mmol) and methanol (5 mL) was refluxed at 65 °C for 3 h. An excess of methanol was evaporated, and the salt (**18c**) formed was dried *in vacuo* to constant weight.

Hydrolysis of metal-containing dialkylaminocarbenium salts. ***A.*** Compounds $\{[(Me_2N)_2CCl)]^+\}_2PtCl_6^{2-}$ (**17**), $\{[(Me_2N)_2COMe]^+\}_2PtCl_6^{2-}$ (**18d**), $\{[(Me_2N)_2CH]^+\}_2PtCl_6^{2-}$ (**21**), as well as $\{[(Me_2N)_2CCl]^+\}_2CoCl_4^{2-}$ (**22**), $\{[(Me_2N)_2CO]^+\}_2SnCl_4^{2-}$ (**23**), $\{[(Me_2N)_2CCl]^+\}Cl^-$ (**24**) (salts **22—24** were obtained earlier[4]) in the form of 10% solutions in D_2O were sealed in glass tubes and analyzed using ^1H NMR spectroscopy at regular intervals by measuring intensities of singlets from corresponding protons of methyl groups (20 °C). 2,2-Dimethyl-2-sila-5-pentenesulfonic acid was used as the internal standard.

B. Salt **23** (1 g) was dissolved in water (2 mL) and heated at 70 °C. Tetramethylurea was identified in the solution by GLC.

C. DMF was obtained similarly from salt **21** and identified.

Interaction of chlorobis(dimethylamino)carbenium hexachloroplatinate (17) with allyl and benzyl alcohols. A mixture of equimolar amounts of salt and alcohol (0.8 mole each) in

5 mL of dichloroethane were refluxed for 10 h 84 °C. Tetramethylurea and the corresponding alkyl halide were found in the reaction mixture by GLC. Hydrogen hexachloroplatinate was precipitated with hexane, b.p. 56—58 °C (lit. data[8]: b.p. 60 °C).

Interaction of hexachloroplatinate 17 with 1-(triethylsilyl)-1-propen-3-ol. Salt **17** (0.54 g, 0.8 mmol), 1-(triethylsilyl)-1-propen-3-ol (0.14 g, 0.8 mmol), triethylamine (0.1 g, 0.9 mmol), and dichloromethane (5 mL) were placed in a flask equipped with a reflux condenser and a thermometer. The reaction mixture was boiled for 10 h at 40 °C. CCl_4 (5 mL) was added to the resulting reddish brown solution, and 7 days later a precipitate was formed. The precipitate was filtered off, washed with diethyl ether (2×3 mL), and dried *in vacuo*. Bis(dimethylamino)(3-triethylsilyl-2-propenyloxy)-carbenium hexachloroplatinate (0.41 g, 63%) was obtained as a rose-colored crystalline solid, m.p. 80 °C. ^{1}H NMR (CD_2Cl_2), δ: 0.4—1.2 (m, 15 H, Et_3Si); 3.1 (s, 12 H, Me_2N); 4.5 (d, 2 H, CH_2); 5.30—5.85 (m, 2 H, CHCH).

Tetramethylurea and 3-chloro-1-triethylsilyl-1-propene were obtained when the reaction was carried out similarly, but in the absence of triethylamine.

Interaction of carbenium salts with hydrosilanes. *A.* A mixture of equimolar amounts of chlorobis(dimethylamino)-carbenium chloride and methyldiphenylsilane (20 mole each) in 10 mL of acetonitrile were controlled thermostatically at 62 °C for 4 h. Bis(dimethylamino)carbenium chloride (2.5 g, 91%) and chloro(methyl)diphenylsilane (4.5 g) were obtained.

B. An acetonitrile solution of chlorobis(dimethylamino)-carbenium chloride with equimolar amounts of hydrosilanes was controlled thermostatically similarly. Four hours later conversion of hydrosilanes was determined by GLC. Found (%): $MePh_2SiH$, 96.7; Me_2PhSiH, 64.3; $(EtO)_3SiH$, 12.5; Et_3SiH, 7.4.

C. A mixture of chlorobis(dimethylamino)carbenium chloride (3.4 g, 20 mmol) and methyldiphenylsilane (3.9 g, 20 mmol) in 10 mL of chloroform was heated with a reflux condenser at 62 °C for 8 h. After cooling diethyl ether (5 mL) was added and crystalline bis(dimethylamino)carbenium chloride (2.2 g, 81%) was filtered off. Chloromethyldiphenylsilane (4.5 g) was isolated from the concentrated filtrate. Hydrogen hexachloroplatinate (1 g) was added to the obtained chloride (0.3 g), and the resulting mixture was allowed to stand. A rose solid was precipitated, it was filtered off, washed with diethyl ether (2×3 mL), and dried *in vacuo* to a constant weight (1.1 g). Yield of hexachloroplatinate **21** was 93%.

D. Methyldiphenylsilane (0.3 g, 1.5 mmol) was added to a solution of salt **17** (1 g, 1.5 mmol) in acetonitrile (5 mL) and heated in a flask fitted with a reflux condenser for 4 h at 60 °C. Formation of colloid platinum was observed in the course of the reaction. The reaction mixture was filtered, diethyl ether (3 mL) was added to the filtrate, and salt **21** was obtained, which was washed with diethyl ether (2×3 mL) and dried to the fixed weight (0.7 g). Yield 76.5%.

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