Tetra(amino)methanes: Implications of Their Structure and Reactivity Pattern for Hypothetical Carbon Nitride Frameworks☆

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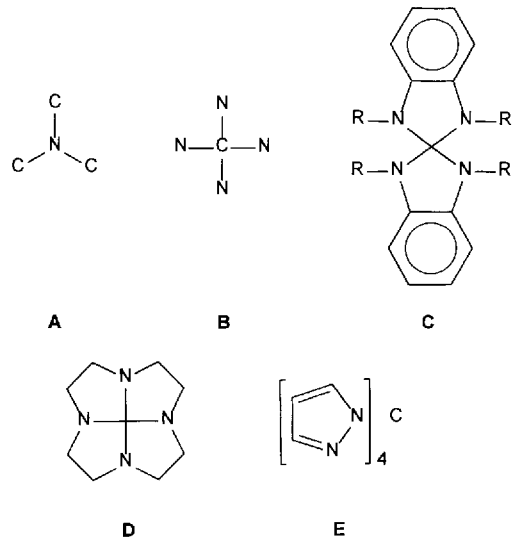
Because of their possible role as model compounds for the structural units of carbon nitride C_3N_4, the preparation, structural chemistry, and some representative reactions of tetra(amino)methanes have been (re)investigated. In the crystal, $C(NMe_2)_4$ (**1**) has a molecular geometry close to D_{2d} symmetry as proposed by theoretical calculations using state-of-the-art density functional methods. The coordination of the central carbon atom is distorted tetrahedral and the configuration of the nitrogen atoms is strongly pyramidal, as opposed to almost planar in the tetra(amino)silanes. Tetra(pyrrolidinyl)methane has a similar core structure, with all heterocyclic substituents in an envelop conformation flexible in solution. Tetra(piperidinyl)methane is more rigid in solution, owing to a more congested structure, with much higher inversion barriers for the six-membered rings. Hydrolysis of **1** leads to Me_2NH and hexamethylguanidinium hydroxide, and treatment of **1** with $HAuCl_4$(aq) affords crystalline $[C(NMe_2)_3]^+ AuCl_4^-$, the structure of which has also been determined. Compound **1** is a strong nucleophile and can be used as an aminating agent, converting e.g. halosilanes into dimethylaminosilanes, with the guanidinium cation as the leaving group. The experimental results are discussed in the light of recent predictions regarding bulk carbon nitrides.

Introduction

Recent theoretical calculations and exploratory experimental studies led to the prediction that there may be polymorphic forms of carbon nitride (C_3N_4) which are harder than diamond.[1][2] This announcement prompted extensive experimental studies in many laboratories, but to date the results are not entirely conclusive. Although it was possible e. g. to deposit thin films on a variety of substrates which are composed almost exclusively of carbon and nitrogen, no bulk material is available as yet, and there are no results of structural studies of any of the products.[3][4] It is generally assumed, however, that carbon nitride should contain nitrogen atoms connected to three carbon atoms (**A**) and carbon atoms connected to four nitrogen atoms (**B**), very much like for N and Si in silicon nitride (Si_3N_4). Structural moieties of the type **A** are very common, as represented i. a. by any tertiary amine R_3N, but the structural motif **B** is extremely rare in both organic and inorganic chemistry, including solid-state and organometallic chemistry.

The literature has less than a handful of references[5][6][7][8] on simple tetra(amino)methanes of the type $C(NR_2)_4$. There is only one preparative route to such molecules, initially developed and practiced in 1966 in an industrial laboratory,[5][6][7] and scarcely reproduced elsewhere in the following years.[8][9][10] Very few compounds were synthesized and some of their reactions investigated.[8][9][10][11][12][13] The photoelectron spectra[14] of $C(NMe_2)_4$ have been recorded and discussed regarding structure and bonding in this prototype molecule, but no definite conclusions have been reached, and molecular structures have not been determined.



Cyclic and polycyclic compounds featuring the structural unit **B** have also been obtained. These include spirocyclic species based on 1,2-diaminobenzene (**C**)[15] or a tetra-NH-crown (**D**),[16] and tetra(pyrazolyl)methanes (**E**).[17] The molecular structure of **E** has been determined by single-crystal X-ray diffraction.[17]

It should be pointed out that $C(NH_2)_4$ is not a known compound and only the existence of the ammonia-deficient decomposition products, guanidine $(H_2N)_2C{=}NH$ and carbodiimide $HN{=}C{=}NH$, has been confirmed. This situation is similar to the findings in the corresponding oxygen system, where $C(OH)_4$ is the missing link, and where even

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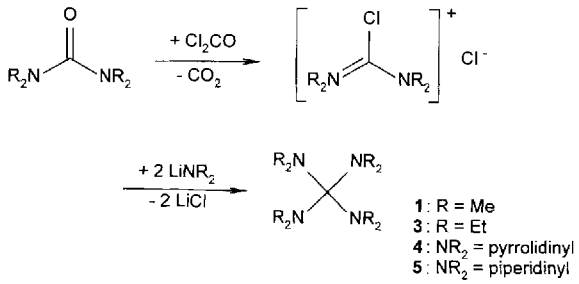
the mono-dehydration product $(HO)_2C{=}O$ is difficult to detect, and only CO_2 is indeed "readily available". On the other hand, ortho esters $C(OR)_4$ and carbonates $(RO)_2C{=}O$ have been much more thoroughly investigated than their nitrogen counterparts[18].

Scheme 1



In order to provide more information on the intrinsic properties of tetra(amino)methanes we have reinvestigated the preparation of a few representative examples of this series, studied their NMR characteristics and determined the molecular structure where single crystals could be obtained. A theoretical study using state-of-the-art density functional methods has also been initiated which was hoped to reproduce experimental findings and to allow a more general evaluation including a comparison with data for the analogous silicon–nitrogen compounds.[19] Pertinent experimental studies of tetra(amino)*silanes* have been published very recently, and the results are used in the present discussion where appropriate.[20]

It is an open question if a study of the structure and properties of tetra(amino)methanes will help to solve the problems associated with carbon nitride. Nevertheless it is presently the only way to accumulate data on molecular systems where carbon is connected to four tricoordinate nitrogen atoms.

Preparative and Spectroscopic Studies

The method of synthesis for tetra(amino)methanes introduced by Weingarten et al.[5][6][7][8] (Scheme 1) proved entirely satisfactory not only for the examples already published (**1**: R = Me; **2**: *n*-decyl), but also for other homologues (**3**: R = Et) and species derived from cyclic secondary amines [R_2N = pyrrolidinyl (**4**), piperidinyl (**5**), morpholinyl (**6**)]. The products are obtained in medium (**1**, **4**, **6**) to low yield (**3**, **5**). Except for the liquids **2** and **3**, the compounds are colorless crystalline solids, which can be purified by crystallization or sublimation (**1**). The products are readily identified through their analytical and mass spectrometric data (Experimental Section). All compounds are soluble in or miscible with non-polar solvents like pentane, hexane, benzene, or diethyl ether.

Solutions of $C(NMe_2)_4$ (**1**), in [D_6]benzene show a ^{1}H-NMR resonance at δ = 2.62 and ^{13}C-NMR resonances at δ = 40.8 (CH_3) and 102 (CN_4). This resonance of the central, quaternary carbon atom is an important reference value for the homologous series of tetra(amino)methanes. It is shifted to δ = 92.1, 97.5, and 101.7 for compounds **3**, **4**, and **5**, respectively. Although the central carbon atom is surrounded by four quadrupolar ^{14}N nuclei, the CN_4 signals show no significant line broadening owing to the low electrical field gradient at the nucleus in the center of a tetrahedron.

The ^{1}H- and ^{13}C-NMR resonances of the amino groups of **3** and **4** show no anomalies, but the spectra of the tetra(piperidinyl)methane **5** (in [D_6]benzene at room temperature) present unexpected complications: While the $\{^1H\}^{13}C$-NMR spectrum has only four singlet signals for CN_4, NCH_2, $NCCH_2$, and $NCCCH_2$, the ^{1}H-NMR spectrum features a series of multiplets which indicate a non-equivalence of each pair of hydrogen atoms at the three types of ring carbon atoms. A temperature as high as 130 °C (in [D_8]decaline) is required to induce coalescence into three resonances (for α-, β-, and γ-hydrogen atoms; relative intensity 2:2:1). These spectral data indicate that there is serious steric hindrance of the piperidinyl inversion dynamics, which equilibrate the environment of axial and equatorial hydrogen atoms at a heterocycle in a chair conformation ground state in the absence of external congestion.

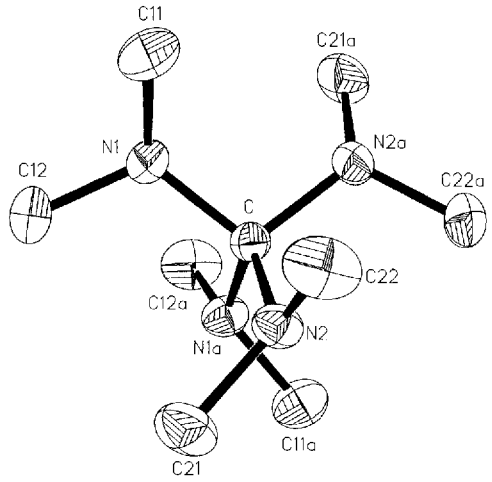
The absence of a similar phenomenon for compound **4** with four pyrrolidinyl substituents is probably due to the much lower inversion barriers of the envelop conformers of five-membered rings, but also to the reduced congestion at the $C(NC_2)_4$ core owing to smaller C–N–C angles in five-membered as compared to six-membered rings.

Structural Studies

Single crystals of *tetrakis(dimethylamino)methane* (**1**) are monoclinic (space group *C*2/*c*, *Z* = 4, from pentane at −30 °C). The molecule has a crystallographically imposed two-fold axis which relates pairs of dimethylamino groups. The overall molecular geometry closely approaches D_{2d} symmetry (Figure 1). The N–C–N angles at the central carbon atom deviate strongly from the tetrahedral standard of 109.48°. There are two large angles [N1–C–N2, N1a–C–N2a 117.02(5)°] and four smaller ones in the narrow range from 105.76(10) to 105.88(5)°. The geometry at the four nitrogen atoms is strongly pyramidal with sums of the C–N–C angles between 346.45° (N1, N1a) and 343.61° (N2, N2a). The components of these sums representing the Me–N–Me angles are regular tetrahedral angles [109.94(10)° at N1/N1a, 109.26(9)° at N2/N2a]. The core C–N bond lengths [C–N1 1.4703(11), C–N2 1.4756(11) Å] are somewhat larger than standard single bond distances as represented by the $N-CH_3$ distances in the same molecule (average 1.449 Å). The difference is probably reflecting the steric crowding at the central carbon atom.

Single crystals of *tetra(pyrrolidinyl)methane* (**4**) are orthorhombic (space group $P2_12_12_1$, *Z* = 4, from pentane at −30 °C). Although the individual molecules have no crystallographically imposed symmetry, the overall geometry is close to S_4 symmetry and differs from the structure of molecule **1** through a conrotatory twist of the $-NC_2$ groups away from the mirror planes (Figure 2). There are again two large C–N–C angles at the central carbon atom

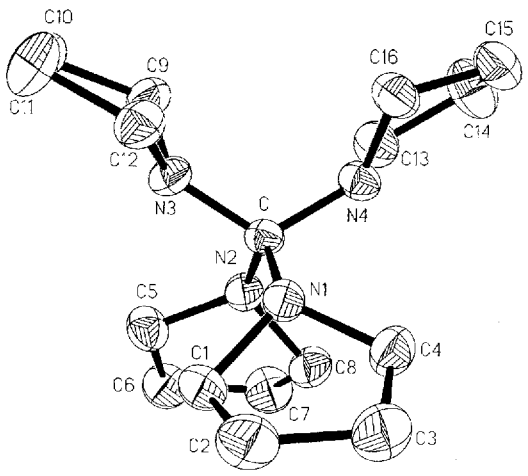
Figure 1. Molecular structure of compound **1** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: C–N1 1.4703(11), C–N2 1.4756(11), N1–C11 1.4487(14), N1–C12 1.451(2), N2–C21 1.4511(14), N2–C22 1.451(2); N1a–C–N1 105.83(11), N1a–C–N2 105.88(5), N2a–C–N2 105.76(10), N1–C–N2 117.02(5), C11–N1–C12 109.94(10), C12–N1–C 118.27(8), C11–N1–C 118.24(9), C21–N2–C22 109.26(9), C22–N2–C 116.79(8), C21–N2–C 117.56(9).

[117.57(12) and 117.74(12)°] and four small ones [105.48(14) to 105.60(14)°], the sums of the angles at the nitrogen atoms are 344.88, 345.20, 344.99, and 345.18° for N1 to N4, and the C–N distances show average values of 1.470 Å for the CN_4 core and 1.452 Å for the $-NC_2$ groups. The pyrrolidinyl groups are in envelop conformations with only minor twists which are probably due to crystal packing effects.

Figure 2. Molecular structure of compound **4** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: C–N1 1.466(2), C–N2 1.468(2), C–N3 1.466(2), C–N4 1.470(2), N1–C1 1.460(2), N1–C4 1.464(2), N2–C5 1.467(2), N2–C8 1.456(2), N3–C9 1.455(2), N3–C12 1.465(2), N4–C13 1.466(2), N4–C16 1.452(2); N1–C–N2 117.57(12), N2–C–N3 105.53(12), N3–C–N4 117.74(12), N4–C–N1 105.54(12), N1–C–N3 105.48(14), N2–C N4 105.60(14), C1–N1–C 118.79(13), C–N1–C4 120.79(13), C4–N1–C1 105.30(13), C5–N2–C 120.42(14), C–N2–C8 118.60(13), C8–N2–C5 106.18(13), C12–N3–C 121.81(13), C–N3–C9 118.29(13), C9–N3–C12 104.89(14), C13–N4–C 121.66(13), C–N4–C16 118.10(13), C16–N4–C13 105.42(14).

Crystals of the *tetra(piperidinyl)methane* (**5**) obtained by crystallization from a variety of solvents were always twinned, and therefore no satisfactory refinement of the data could be achieved.

The structures of compounds **1** and **4** are in excellent agreement with the results of theoretical calculations based on density functional methods for the $C(NH_2)_4$ molecule in the gas phase. The core distances and angles have been reproduced with only minor discrepancies, and the overall D_{2d} symmetry has also been confirmed as the conformation of minimum energy.[19]

Reactivity Studies

Tetra(amino)methanes are sensitive to *hydrolysis*.[5] It has been tacitly assumed that the reaction with water vapour or bulk water leads to hexaalkylguanidinium salts and secondary amine, but this course of the hydrolysis has actually not been proven. We therefore investigated the hydrolysis in D_2O using NMR spectroscopy as the analytical tool. It could be shown that compound **1** is indeed hydrolyzed to give dimethylamine and hexamethylguanidinium hydroxide [Eq. (1)]. The reaction mixture is strongly alkaline (pH = 13 for 10^{-3} M solutions), and it shows the ^1H- and ^{13}C-NMR resonances of Me_2NH and $[(Me_2N)_3C]^+$ cations (Experimental Section).

$$\underset{\mathbf{1}}{C(NMe_2)_4} \rightleftharpoons [C(NMe_2)_3]^+ [NMe_2]^- \xrightarrow{H_2O} [C(NMe_2)_3]^+ [OH]^- + HNMe_2$$

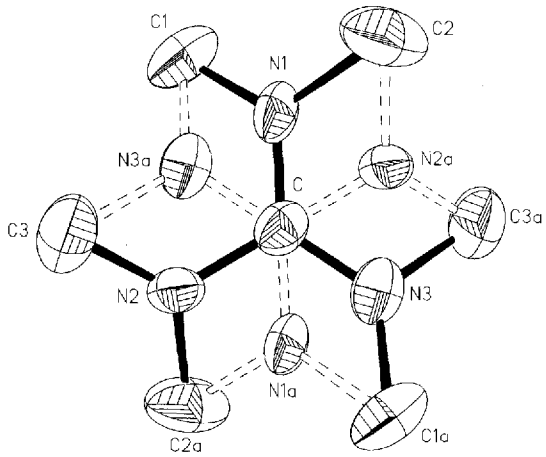
Accordingly, the reaction with acid leads to the formation of hexamethylguanidinium salts.[8] Tetrachloroauric acid was used as the reactant because it was expected that for the flat guanidinium cation there would be a preference for a flat anion to form crystals with optimum lattice energy. This assumption was confirmed and a precipitate of $[(Me_2N)_3C]^+[AuCl_4]^-$ (**7**) was readily obtained [Eq. (2)]. The product was identified by its analytical and spectroscopic data.

$$\underset{\mathbf{1}}{C(NMe_2)_4} + HAuCl_4 \cdot 3H_2O \xrightarrow[-3\,H_2O]{Et_2O} \underset{\mathbf{7}}{[C(NMe_2)_3]^+ [AuCl_4]^-} + HNMe_2$$

Crystals of compound **7** are orthorhombic (space group *Pnma*, $Z = 4$, from dichloromethane/pentane at 20 °C). In the lattice the guanidinium cations are disordered over two positions in very much the same way as in other salts containing this cation (Figure 3).[9][10][12] The cations have no crystallographically imposed symmetry, but the geometrical details approach very closely the requirements of point group C_3. The bond distances and angles are similar to those found in other salts and a discussion therefore would be redundant. The cations are separated by square planar $[AuCl_4]^-$ anions.

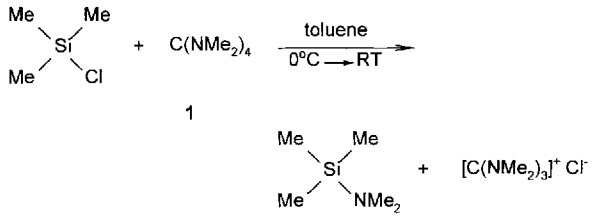
Compound **1** is a strong aminating agent. This is nicely demonstrated by the reaction with chlorotrimethylsilane, which affords virtually quantitative yields of (dimethylami-

Figure 3. Molecular structure of the disordered guanidinium cation of compound **7** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: C–N1 1.30(2), C–N2 1.38(2), C–N3 1.30(2), N1–C1 1.52(2), N1–C2 1.53(2), N2–C2a 1.56(2), N2–C3 1.44(2), N3–C1a 1.47(2), N3–C3a 1.62(2); N1–C–N2 117.0(10), N1–C–N3 125.4(11), N2–C–N3 117.2(10).

no)trimethylsilane and hexamethylguanidinium chloride [Eq. (3)]. GLC analysis of the reaction mixture shows no other volatile by-product. If compound **4** is used as the reagent for chlorotrimorpholinosilane, the sole volatile product is trimorpholino(*N*-pyrrolidinyl)silane as also demonstrated by GLC analysis.



This small number of reactions show that tetra(amino)-methanes are strong nucleophiles which transfer amino groups to standard electrophiles with formation of guanidinium salts as the by-products. Clearly, the resonance stabilisation of this unique type of cations in the by-products provides a powerful driving force for these processes, making $C(NR_2)_4$ compounds versatile amination reagents.

Conclusions

In full agreement with the theoretical studies,[19] the present experimental investigations have shown that the structural units (**A** and **B**) to be proposed for the three-dimensional lattice of carbon nitride (C_3N_4) have intrinsic differences as compared to the corresponding moieties of a silicon nitride lattice (Si_3N_4).

While the geometry of bonding at the carbon and silicon atoms appears to be angularly similar, the configuration of the nitrogen atoms is found to be strongly pyramidal in the carbon compound, but almost planar in the silicon analogue. This difference must have significant consequences for the lattice characteristics of the two materials.

Preliminary investigations by Weingarten et al. have shown already[7] that tetra(amino)methanes are readily decomposed upon heating to give olefins and imines following a radical pathway. By contrast, tetra(amino)silanes are thermally much more robust,[21] the decomposition temperatures being shifted to much higher temperatures. These differences are also reproduced very well by the theoretical data.[19]

In heterolytic reactions tetra(amino)methanes act as strong bases. Their amino groups are powerful nucleophiles, and the reactions benefit from a driving force related to the high stability of the corresponding guanidinium cations. Such a driving force is absent in the heterolysis of the tetra-(amino)silanes, where the tri(amino)siliconium cations are much higher in energy.[22]

In summary the results of our studies of simple model compounds with CN_4 and SiN_4 units suggest significant structural differences for carbon and silicon nitride and are not indicative of a particularly high thermal and chemical stability of the carbon compound. It should be noted, however, that amino- and iminoboranes are not really reflecting the properties of the modifications of boron nitride, except for the structural concepts regarding the interplay of trigonal-planar and tetrahedral units. Similar parallels should be expected for carbon/nitrogen phases.

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Experimental Section

General Methods: All experiments were routinely carried out in dry nitrogen. Solvents were dried and saturated with nitrogen; glassware was oven-dried and filled with nitrogen. Starting materials were commercially available or prepared and purified according to published procedures. – ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Jeol JNM-GX 270 spectrometer (^{1}H at 270.17 MHz, ^{13}C at 67.94 MHz) or a Jeol JNM-GX 400 spectrometer (^{1}H at 399.78 MHz, ^{13}C at 100.54 MHz). – Mass spectra were obtained with a Finnigan MAT 90 spectrometer. – Analytical GLC-MS was performed with a Hewlett-Packard 5890 Series II chromatograph (column HP1, crosslinked methylsilicon gum 12 m/0.2 mm, thickness of film 0.33 μm) with mass-selective detector HP MS 5971 A (EI-MS 70 eV). – Microanalyses were performed in-house by combustion.

1,1′-Carbonyldipyrrolidine: To freshly distilled pyrrolidine (20 ml, 0.242 mol) in toluene (20 ml) a solution of *n*-butyllithium in hexane (125 ml, 1.74 M, 0.218 mol) was added while cooling the reaction mixture with an ice bath. The resulting slurry was stirred at room temperature for several hours. Subsequently, a cooled solution of phosgene in toluene (92 ml, 1.93 M, 0.178 mol, 0 °C) was added dropwise keeping the reaction temperature below 10 °C. The resulting slurry was allowed to warm to room temperature and stirred for one night. The solvent was distilled off using a slight vacuum. The remaining yellowish brown solid was distilled at 80 °C/0.02 Torr to give 10.1 g (50% yield) of 1,1′-carbonyldipyrrolidine as a colourless liquid. – ^{1}H NMR (C_6D_6): δ = 1.71 (m, 8 H, 2-H), 3.30 (m, 8 H, 1-H). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.9 (C-2), 47.3 (C-1), 160.8 (CO). – EI-MS; *m/z*: 168 $[M]^+$, 98 $[M - \text{pyrrolidine}]^+$,

70 [pyrrolidine]$^+$. – $C_9H_{16}N_2O$ (168.24): calcd. C 64.25, H 9.59, N 16.65, O 9.51; found C 63.50, H 9.62, N 16.36, O 10.52.

Synthesis of the Tetraalkylchloroformamidinium Chlorides: Tetraalkylchloroformamidinium chlorides were obtained from the reaction of the corresponding tetraalkylurea with phosgene according to the procedure of Eilingsfeld.[23] The resulting white or slightly brown solids were washed once with tetrahydrofuran and identified by NMR spectroscopy.

Tetramethylchloroformamidinum Chloride: Yield 98%. – ^{1}H NMR ($CDCl_3$): δ = 3.54 (s, CH_3). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 45.0 (CH_3), 159.1 (C^+).

Tetraethylchloroformamidinium Chloride: Yield 82%. – ^{1}H NMR ($CDCl_3$): δ = 0.55 (t, 12 H, $^3J_{H,H}$ = 7 Hz, CH_3), 3.04 (q, 8 H, $^3J_{H,H}$ = 7 Hz, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.4 (CH_3), 48.3 (CH_2), 156.6 (C^+).

Dichlorodipyrrolidinylmethane: Yield 95%. – ^{1}H NMR ($CDCl_3$): δ = 2.02 (m, 8 H, 2-H), 3.93 (m, 8 H, 1-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 25.3 (C-2), 54.8 (C-1), 151.8 (C^+).

Dichlorodipiperidinylmethane: Yield 82%. – ^{1}H NMR ($CDCl_3$): δ = 1.75 (m, 12 H, 2-H, 3-H), 3.93 (m, 8 H, 1-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 22.6 (C-3), 25.8 (C-2), 54.6 (C-1), 155.5 (C^+).

Synthesis of the Tetrakis(dialkylamino)methanes: Tetrakis(dialkylamino)methanes were obtained from the reaction of the corresponding tetraalkylchloroformamidinium chlorides with the lithium dialkylamides according to the procedure of Weingarten.[5]

Tetrakis(dimethylamino)methane (**1**): Isolated and purified by repeated crystallisation from *n*-pentane or sublimation at 30 °C/0.02 Torr: Yield 54%; colourless hygroscopic solid; mp 120 °C. – ^{1}H NMR (C_6D_6): δ = 2.62 (s, CH_3). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 40.8 (CH_3), 102.0 (CN_4). – CI-MS; *m/z*: 144 [M – NMe_2]$^+$, 101 [M – 2 NMe_2 + H]$^+$. – $C_9H_{24}N_4$ (188.32): calcd. C 57.40, H 12.85, N 29.75; found C 56.53, H 12.82, N 29.08.

Tetrakis(diethylamino)methane (**3**): Isolated by distillation at 20 °C/0.02 Torr: Yield 25%; colourless liquid; rapid decomposition even at low temperature. – ^{1}H NMR (C_6D_6): δ = 1.02 (t, 24 H, $^3J_{H,H}$ = 7 Hz, CH_3), 2.67 (q, 16 H, $^3J_{H,H}$ = 7 Hz, CH_2). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 14.1 (CH_3), 43.1 (CH_2), 92.1 (CN_4). – $C_{17}H_{40}N_4$ (300.53): calcd. C 67.94, H 13.42, N 18.64; found C 64.89, H 12.66, N 17.42. Because of the limited stability of the compound no correct elemental analysis could be obtained.

Tetrapyrrolidinylmethane (**4**): Isolated and purified by repeated crystallisation from *n*-pentane: Yield 49%; colourless hygroscopic solid; mp 115 °C. – ^{1}H NMR (C_6D_6): δ = 1.65 (m, 16 H, 2-H), 3.13 (m, 16 H, 1-H). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 25.2 (C-2), 47.9 (C-1), 97.5 (CN_4). – CI-MS; *m/z*: 222 [M – pyrrolidine]$^+$. – $C_{17}H_{32}N_4$ (292.47): calcd. C 69.81, H 11.03, N 19.16; found C 69.23, H 10.91, N 19.06.

Tetrapiperidinylmethane (**5**): Isolated and purified by repeated crystallisation from *n*-pentane: Yield 12%; colourless solid; stable to air; decomposition above 150 °C. – ^{1}H NMR (C_6D_6, 20 °C): δ = 1.2–1.7 (m, 6 H, β-H, γ-H), 2.57 (pseudo-t, 2 H, $^2J_{H,H}$ = 12 Hz, $^3J_{H,H}$ = 12 Hz, α_{ax}-H), 3.59 (pseudo-d, 2 H, $^2J_{H,H}$ = 12 Hz, α_{eq}-H); ([D_{18}]decaline, 80 °C): δ = 1.2–1.7 (m, 6 H, β-H, γ-H), 2.56 (br. s, 2 H, α_{ax}-H), 3.54 (br. s, 2 H, α_{eq}-H); ([D_{18}]decaline, 100 °C): δ = 1.3–1.6 (br. s, β-H, γ-H), 2.60 (br. s, α_{ax}-H), 3.51 (br. s, H-α_{eq}); ([D_{18}]decaline, 130 °C): δ = 1.41 (br. s, 6 H, β-H, γ-H), 2.9–3.2 (br. s, 4 H, α-H); ([D_{18}]decaline, 150 °C): δ = 1.42 (br. s, 6 H, β-H, γ-H), 3.06 (s, 4 H, α-H). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 26.1 (C-3), 27.3 (C-2), 50.2 (C-1), 101.7 (CN_4). – CI-MS; *m/z*: 264 [M – piperidine]$^+$. – $C_{21}H_{40}N_4$ (348.57): calcd. C 72.36, H 11.57, N 16.07; found C 72.62, H 11.50, N 16.06.

Hydrolysis of Tetrakis(dimethylamino)methane (**1**): Aqueous solution of **1** (100 mg, 0.53 mmol) in D_2O (4 ml) at 20 °C. – ^{1}H NMR: δ = 2.08 [s, 6 H, $DN(CH_3)_2$], 2.72 (s, 18 H, $C[N(CH_3)_2]_3^+$). – $^{13}C\{^1H\}$ NMR: δ = 36.9 [$DN(CH_3)_2$], 39.5 ($C[N(CH_3)_2]_3^+$), 163.6 ($C[N(CH_3)_2]_3^+$).

Hexamethylguanidinium Tetrachloroaurate (**7**): To a solution of tetrakis(dimethylamino)methane (**1**) (32.0 mg, 0.17 mmol) in diethyl ether (2 ml) tetrachloroauric(III) acid trihydrate (65.4 mg, 0.17 mmol) was added at room temperature. After stirring the yellow slurry for several minutes the solvent was evaporated to give **7** as a yellow solid (78.0 mg, 95%). Single crystals were obtained by layering a solution of **7** in dichloromethane with *n*-pentane: mp 89 °C. – ^{1}H NMR ($CDCl_3$): δ = 3.03 [s, $C(CH_3)$]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 41.0 (CH_3), (CN_3^+) not detectable. – FAB-MS (NBA); *m/z*: 144 [M]$^+$, 130 [M – Me]$^+$, 100 [M – NMe_2]$^+$, 341 [M + 2]$^-$, 304 [M – Cl]$^-$, 267 [M – 2 Cl] . – $C_7H_{18}AuCl_4N_3$ (483.01): calcd. C 17.41, H 3.76, N 8.70; found C 16.49, H 4.00, N 8.12.

Table 1. Crystal data, data collection, and structure refinement for compounds **1**, **4** and **7**

	1	**4**	**7**
Crystal data			
Formula	$C_9H_{24}N_4$	$C_{17}H_{32}N_4$	$C_7H_{18}AuCl_4N_3$
M_r	188.32	292.47	483.01
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	*C2/c*	$P2_12_12_1$	*Pnma*
a [Å]	14.207(1)	7.382(1)	11.039(2)
b [Å]	7.687(1)	13.817(2)	15.750(1)
c [Å]	11.151(1)	16.161(2)	8.590(1)
α [°]	90	90	90
β [°]	109.52(1)	90	90
γ [°]	90	90	90
V [Å^3]	1147.8(2)	1648.4(4)	1493.5(3)
$\rho_{calcd.}$ [gcm^{-3}]	1.090	1.178	2.148
Z	4	4	4
F(000)	424	648	912
μ(Mo-K_α) [cm^{-1}]	0.69	0.71	105.4
Data collection			
T [°C]	−74	−68	−74
Scan mode	ω−θ	ω	ω
hkl range	−18 → 14	−9 → 9	−14 → 14
	−8 → 0	0 → 17	−20 → 20
	−14 → 14	0 → 17	−10 → 10
$\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.64	0.64	0.64
Measured reflections	2208	3376	2839
Unique reflections	1185	3181	1508
	(R_{int} = 0.0112)	(R_{int} = 0.0204)	(R_{int} = 0.0195)
Refls. used for refinement	1184	3177	1507
Absorption correction	none	none	ψ scans
T_{min}/T_{max}	–	–	0.27/0.99
Refinement			
Refined parameters	108	190	88
H atoms (found/calcd.)	24/0	0/32	0/9
Final *R* values [$I > 2\sigma(I)$]			
$R1$[a]	0.0369	0.0465	0.0489
$wR2$[b]	0.1016	0.1195	0.1316
$(\text{shift/error})_{max}$	< 0.001	< 0.001	< 0.001
ρ_{fin}(max/min) [eÅ^{-3}]	0.195/−0.185	0.169/−0.251	1.597/−2.24

[a] $= \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. – [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(ap)^2 + bp]\,p = (F_o^2 + 2F_c^2)/3$; a = 0.0671 (**1**), 0.0767 (**4**), 0.0982 (**7**); b = 0.28 (**1**), 0.13 (**4**), 2.00 (**7**).

Amination Reactions with Chorosilanes: The chlorosilane and one equivalent of tetrakis(dimethylamino)methane (**1**) or **4** were dissolved in toluene at 0 °C. The resulting slurry was allowed to warm to room temperature and stirred overnight. The hexaalkylguanidinium chloride precipitate was filtered off and the remaining solution analysed by GLC-MS.

(Dimethylamino)trimethylsilane: EI-MS; *m/z*: 117 $[M]^+$, 102 $[M - Me]^+$, 73 $[M - NMe_2]^+$.

Trimorpholino(N-pyrrolidinyl)silane: EI-MS; *m/z*: 356 $[M]^+$, 270 [M − morpholine]$^+$, 185 [M − 2 morpholine]$^+$, 116 [M − 2 morpholine − pyrrolidine]$^+$, 100 [M − 3 morpholine]$^+$, 86 [morpholine]$^+$, 70 [pyrrolidine]$^+$.

Crystal-Structure Determinations: Specimens of suitable quality and size of compounds **1**, **4**, and **7** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection with an Enraf Nonius CAD4 diffractometer [Mo-K_α radiation, λ(Mo-K_α) = 0.71073 Å] . During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for compounds **1** and **4**, whereas the data of compound **7** were corrected for decay (−23.4%). Lp correction was applied and intensity data of **7** were corrected for absorption effects. The structures were solved by direct methods (SHELXS-86) and completed by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically. The nitrogen atoms in the cation of compound **7** were disordered and refined in split positions. All hydrogen atoms of compound **1** were located and refined with isotropic contributions, whereas all H atoms of compounds **4** and **7** were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5 \times U_{eq}$ of the attached C atom). Further information on crystal data, data collection, and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding Figure captions. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting the depository numbers CSD-407215 (**1**), -407217 (**4**), and -407216 (**7**).

☆ Dedicated to Professor *George A. Olah*.

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