Selective Synthesis of *N*-Methylanilinooligosilanes

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Keywords: Amides / Silanes / Disilanes / Aminosilanes / Stereochemistry

Defined crystalline amino-substituted organosilanes were prepared by reaction of *N*-methylaniline with 1,1,2,2-tetrachloro-1,2-dimethyldisilane. It is possible to selectively prepare mono-, di-, and triaminodisilanes depending on the reactant ratio. The X-ray structure analyses of 1,2-dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (**2**), 1-chloro-1,2-dimethyl-1,2,2-tris(*N*-methylanilino)disilane (**3**), and 1,2-dimethyl-1,1,2,2-tetrakis(*N*-methylanilino)disilane (**4**) were performed. The absolute structure of **2** was determined by crystallographic methods. Compound **2** is a useful reagent for preparing a variety of other aminoorganodisilanes like $[Me(PhMeN)_2Si]_2$ (**4**), $[FMe(PhMeN)Si]_2$ (**12**), [(PhCC)-Me(PhMeN)Si]$_2$ (**13**), $[(p\text{-}MeC_6H_4)Me(PhMeN)Si]_2$ (**14**), and $[(PhCH_2)Me(PhMeN)Si]_2$ (**15**). Other chloroorganooligosilanes also react with *N*-methylaniline to give PhMeN[Si-$Me_2]_2Cl$ (**5**), PhMeN$[SiMe_2]_2$NMePh (**6**), Cl$[SiMe_2]_3$NMePh (**7**), PhMeN$[SiMe_2]_3$NMePh (**8**), Cl$[SiMe_2]_4$NMePh (**9**), MeClSi[Si(NMePh)ClMe]$_2$ (**10**), and MeSi[Si(NMePh)-ClMe]$_3$ (**11**).

Introduction

Functionally substituted di- and oligosilanes are valuable building blocks for preparing organopolysilanes and silicon-containing materials.[1] A good method for preparing such compounds is the reductive coupling of chloroorganosilanes with alkaline metals[2] and subsequent cleavage of aromatic substituents with gaseous hydrogen chloride and $AlCl_3$[3] or trifluoromethylsulfonic acid.[4] The preparation of chloro(methyl)oligosilanes by halogen/methyl exchange using Me_3SiCl and $AlCl_3$ is another frequently used method.[5]

The reductive coupling of chloro(diethylamino)organosilanes is a convenient new way to prepare functionalized oligosilanes. The diethylamino group in the resulting oligosilanes can be replaced, under very mild conditions, by various reagents such as alcohols or hydrogen chloride. A number of amino(chloro)organooligosilanes have been prepared, but these are often oils and it is very difficult to separate pure compounds from the mixture of liquid products.[6,7] Some X-ray structures of amino(organo)oligosilanes without chlorine substituents are known.[8] Until now very little structural data on amino(chloro)organooligosilanes has been available.[9]

We have developed reliable synthetic pathways to a variety of crystalline amino(chloro)methyloligosilanes. A number of different aromatic diorganoamines were tested for their reactivity with 1,1,2,2-tetrachloro-1,2-dimethyldisilane.[9] The large flat aromatic groups should help to obtain crystalline products. The products obtained with *N*-methylaniline are soluble in aprotic organic solvents and are extremely crystalline.

Results and Discussion

The reaction of *N*-methylaniline with 1,1,2,2-tetrachloro-1,2-dimethyldisilane in the presence of excess NEt_3 gives mono-, di-, and triaminodisilanes depending on the reactant ratio. 1,1,2-Trichloro-2-(*N*-methylanilino)-1,2-dimethyldisilane (**1**) was obtained as a colorless oil. According to the ^{29}Si NMR spectrum, the product contains about 20% impurities, which were identified as **2** and 1,1,2,2-tetrachloro-1,2-dimethyldisilane. Because of these impurities we did not use this compound in further reactions. 1,2-Dichloro-1,2-bis(*N*-methylanilino)-1,2-dimethyldisilane (**2**) was isolated as an ivory-colored solid. The crude product contains traces of **3** and was recrystallized from a pentane/diethyl ether mixture (5:1); **3** was synthesized by the same experimental procedure and obtained as a white crystalline solid (Scheme 1).

The ^{29}Si NMR spectra of **2**, **3**, and **4** have some interesting features. The tetraamide **4** shows one signal at $\delta = -7.53$ ppm for the spectroscopically equivalent silicon atoms; **3** has two chemically and spectroscopically different silicon atoms. The (*R*) and (*S*) isomers have identical signals in the spectrum. Thus, two signals with an intensity ratio of 1:1 are observed at $\delta = -7.94$ and 6.27 ppm. The silicon atoms in **2** are chemically equivalent, and chiral. Two signals are expected, one for the racemate [(*R*,*R*) and (*S*,*S*) isomer] and one for the *meso* form and there are indeed two such signals at $\delta = 3.66$ and 1.37 ppm. The intensity ratio

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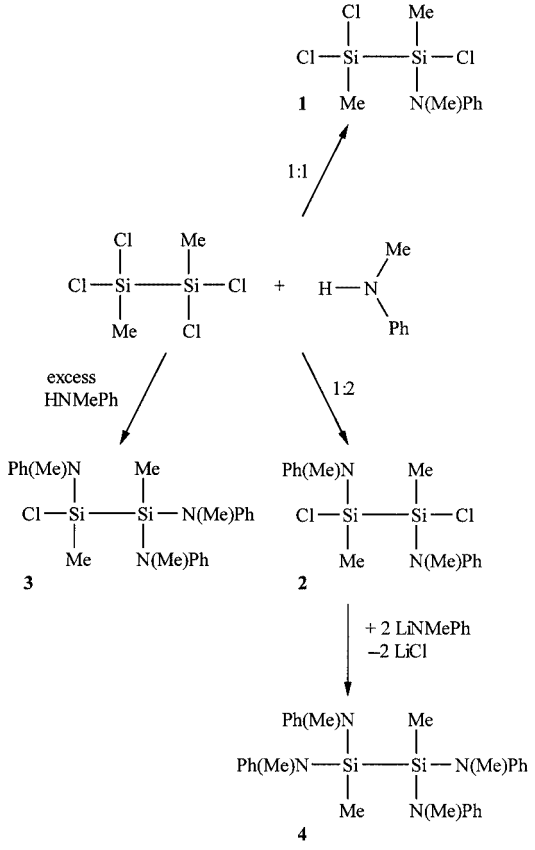


Scheme 1

of the two signals is always between 5:1 and 6:1. We assume that the main product is the racemate. It is rather unusual that one isomer is formed preferentially over another. Investigations concerning the isomerization of diastereomers of $(FArMeSi)_2$ have shown that a *rac*/*meso* mixture of 1:1 was obtained during the preparation process.[10] Detailed experiments regarding the isomerization processes of this compound have shown that the enrichment of the *meso* form proceeds by crystallization-induced asymmetric transformation (AT).[11]

We investigated the quantitative composition of the crude product of **2** by in situ NMR spectroscopy and found a relative intensity ratio of 5.5:1. In further experiments, we used NMR spectroscopy to monitor the course of the reaction for several weeks. We prepared two reaction batches, one with pentane and the other with DME as the solvent. In both experiments, we found no substantial change in the relative product composition! The relative product ratio was always between 5.5:1 and 6:1. Furthermore, samples of **2** can be dissolved and recrystallized without change in the composition of the diastereomers. In summary, we found no evidence for a crystallization-induced asymmetric transformation of **2**.

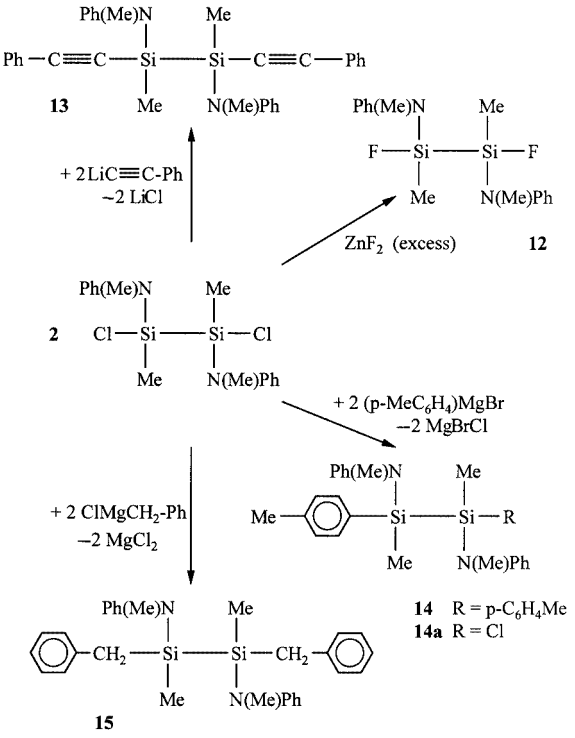
Quantum chemical calculations on the diastereomers of **2** show that the *rac* form has a substantially lower total energy. The energy difference between the (*R*,*R*) and the *meso* form is 18 kJ/mol at the B3LYP/6-31G* level of theory.[12] This suggests a preferred formation of the racemate during the synthesis of **2**.

In order to explore further the available range of *N*-methylanilinosilanes, we treated different oligomeric chloro(organo)silanes with *N*-methylaniline. It was possible to selectively obtain mono- and disubstituted aminosilanes (**5**, **7** and **6**, **8**) from $Cl[SiMe_2]_nCl$. The reactivity of the homologous α,ω-dichlorooligosilanes decreases with increasing chain length. Therefore, the tetrasilane $Cl[SiMe_2]_4Cl$ gave only the monosubstituted product $Cl[SiMe_2]_4NMePh$ (**9**). The branched chlorosilanes $MeClSi(SiCl_2Me)_2$ and $MeSi(SiCl_2Me)_3$ were prepared by disproportionation of 1,1,2,2-tetrachloro-1,2-dimethyldisilane.[13] The reaction of these compounds with *N*-methylaniline in different stoichiometric ratios gave product mixtures. We succeeded in obtaining defined reaction products only when an excess of *N*-methylaniline was used. One chlorine atom remains at each silicon atom and the products formed under these conditions were characterized as $MeClSi[Si(NMePh)ClMe]_2$ (**10**) and $MeSi[Si(NMePh)ClMe]_3$ (**11**). It was not possible to replace all the chlorine atoms in these chlorine-rich organosilanes with the *N*-methylanilido group. Although, it might be possible to replace the last chlorine atoms when using the corresponding lithium amide. The compounds **5**−**11** were characterized by NMR spectroscopy (see Exp. Sect.).

The reactivity of **2** and **3** was investigated: 1-chloro-1,2-dimethyl-1,2,2-tris(*N*-methylanilino)disilane (**3**) is rather inert with respect to nucleophilic reagents. The compound does not react with diorganoamines, such as $HNEt_2$ and Grignard reagents. The treatment of **3** with alkyllithium compounds yields mainly unchanged starting material. Aside from this, small amounts of reaction products were detected by NMR spectroscopy. It was not possible to isolate pure compounds by recrystallization of the product mixtures. ^{29}Si NMR spectroscopy identified one of the compounds in these mixtures as 1,2-dimethyl-1,1,2,2-tetrakis(*N*-methylanilino)disilane (**4**), which was also synthesized by an alternative method, see below; **4** was formed in these reactions, probably by transamination with the strong nucleophilic alkyllithium compound. The alkyllithium compound might form in situ lithium *N*-methylanilide which reacts with **3**.

In contrast to **3**, 1,2-dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (**2**) reacts with nucleophiles with the substitution of both chlorine atoms in a straightforward reaction (see Scheme 2). It was possible to prepare a variety of derivatives with different nucleophiles, such as lithium amides (**4**), zinc fluoride (**12**), alkynyllithium compounds (**13**), and Grignard reagents (**14** and **15**; see Scheme 2). Since the *N*-methylanilino group remains unaffected in these reactions, it acts as a valuable protecting group.

1,2-Difluoro-1,2-dimethyl-1,2-bis(*N*-methylanilino)-disilane (**12**) was prepared by the reaction of excess of ZnF_2 with **2**. The reaction between the dissolved amino(chloro)silane and the solid zinc fluoride took about 6 d. The progress of the reaction was monitored by NMR spectroscopy. A mixture of ClMe(PhMeN)SiSi(NMePh)MeF and



Scheme 2

$[FMe(PhMeN)Si]_2$ (**12**) was formed during the first 48 h. This mixture slowly converted to **12** in the presence of excess ZnF_2. Signals for the diastereomers of **12** (*rac* and *meso*) were observed in the reaction mixture but only one diastereomer was obtained after the workup procedure. This suggests that the solubility for both diastereomers is very different. It might also be caused by crystallization-induced asymmetric transformation.

$[(p\text{-}MeC_6H_4)Me(PhMeN)Si]_2$ (**14**) was obtained as a mixture with the monosubstituted product $(p\text{-}MeC_6H_4)$-Me(PhMeN)SiSi(NMePh)MeCl (**14a**) (ratio **14**/**14a** = 2:1). The reaction of **2** with excess *p*-tolylmagnesium bromide gave a slightly different product ratio of 2.2:1, but this synthesis did not enable pure **14** to be obtained. The compounds $[(PhCC)Me(PhMeN)Si]_2$ (**13**), $[(p\text{-}MeC_6H_4)$-$Me(PhMeN)Si]_2$ (**14**), and $[(PhCH_2)Me(PhMeN)Si]_2$ (**15**) were obtained as a mixture of diastereomers. Integration of the MeSi signals in the ^1H NMR spectra provides the relative ratio of *rac*/*meso* isomers; **13** and **15** have a ratio of about 1:1, and **14** a ratio of 1.5:1. This means that the substitution reactions with the organometallic reagents are not stereoselective.

Crystal and Molecular Structures

The solid-state structures of **2**−**4** were determined from the data obtained by X-ray diffraction. Details of the structure determinations and refinement are summarized in Table 3. The X-ray structure analyses confirm the structures of the compounds **2**−**4** as proposed in Scheme 1; **3** crystallizes in the space group $P2_1/n$ as a racemate and **4** crystallizes in the space group $P2_1/a$; **2** was obtained as separated pure enantiomorphic crystals that crystallize in the noncentrosymmetric space group $C222_1$. The structure of one crystalline modification was determined. Only the half-molecule, ClSi(NMePh)Me, is found in the asymmetric unit, so the unit cell only contains four molecules. The second part of the molecule is generated by symmetry elements. Three times more reflections were collected than normally necessary for an orthorhombic space group, in order to determine the absolute configuration through the anomalous scattering effect. Refinement of the Flack enantiopole parameter led to a value of ca. 0, thus confirming the absolute structure of the crystal.[14] The molecular structure of **2** is shown in Figure 1. The silicon atom has an (*R*) configuration. The fact that both silicon atoms have the same configuration means that, in the crystal under examination, the molecules have an (*R*,*R*) configuration. There are a number of chiral silicon compounds reported in the literature.[15,16] Diastereomers have mainly been prepared with one chiral silicon atom and one chiral organic group such as the (−)-menthoxy group. Only one diastereomeric dichlorodisilane with two chiral silicon atoms was found in the Cambridge Crystallographic Database.[17] The value of optical rotation was estimated to be $\alpha = 377°$ (20 °C, 302 nm, *n*-pentane) from a randomly chosen crystal of **2**.

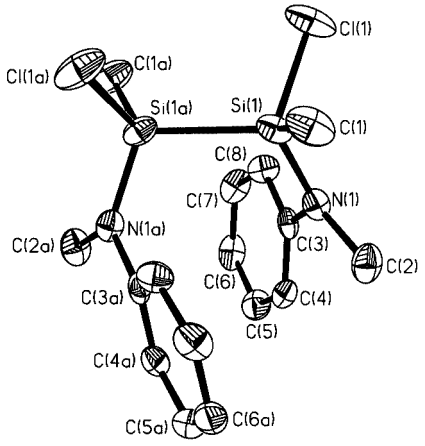


Figure 1. Molecular structure of 1,2-dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (**2**) with 50% thermal ellipsoids; hydrogen atoms are omitted for clarity

The compounds **2** (Figure 1), **3** (Figure 2), and **4** (Figure 3) are homologous amino(methyl)disilanes with an increasing number of *N*-methylanilino groups bonded to the silicon atoms. The increasing degree of substitution with *N*-methylanilino groups causes some changes in the molecular structure of these three compounds. The silicon−silicon bond length is 2.375 Å in **4**, which is an increase in length from that seen in **2**. The Si−N bonds in **4** (1.754 Å, average value) are also longer than those in **2** (1.718 Å) and **3** (1.740 Å). The Si−C bond is slightly shorter in **2** than it is in **3** and **4**. The torsion angle C−Si−Si−C has similar values for **2** (141.9°) and **3** (−130.4°);[18] **4** has a *transoid* conformation around this torsion angle which is 173.6°. All bond lengths are in the normal range for covalent bonds, the silicon

Table 1. Selected bond lengths [Å] and bond angles [°]

1,2-Dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (**2**)			
Si(1)−Si(1a)	2.341(1)	N(1)−Si(1)−Cl(1)	111.88(8)
Si(1)−Cl(1)	2.097(1)	N(1)−Si(1)−Si(1a)	109.34(6)
Si(1)−N(1)	1.718(2)	Cl(1)−Si(1)−Si(1a)	104.41(4)
Si(1)−C(1)	1.845(3)	C(1a)−Si(1a)−Si1−C1	141.9(1)
1-Chloro-1,2-dimethyl-1,2,2-tris(*N*-methylanilino)disilane (**3**)			
Si(1)−Si(2)	2.3726(6)	N(1)−Si(1)−Si(2)	109.04(6)
Si(1)−N(1)	1.751(2)	N(2)−Si(1)−Si(2)	109.26(6)
Si(1)−N(2)	1.736(2)	N(3)−Si(2)−Si(1)	114.42(6)
Si(2)−N(3)	1.732(2)	Cl(1)−Si(2)−Si(1)	104.84(3)
Si(2)−Cl(1)	2.1068(7)	C(1)−Si(1)−Si(2)−C(2)	−130.4(1)
Si(1)−C(1)	1.894(2)		
Si(2)−C(2)	1.859(2)		
1,2-Dimethyl-1,1,2,2-tetrakis(*N*-methylanilino)disilane (**4**)			
Si(1)−Si(2)	2.375(1)	N(1)−Si(1)−Si(2)	115.80(9)
Si(1)−N(1)	1.755(2)	N(2)−Si(1)−Si(2)	102.92(8)
Si(1)−N(2)	1.761(3)	N(3)−Si(2)−Si(1)	113.22(8)
Si(2)−N(3)	1.749(2)	N(4)−Si(2)−Si(1)	101.98(9)
Si(2)−N(4)	1.752(2)	C(1)−Si(1)−Si(2)	111.2(1)
Si(1)−C(1)	1.868(3)	C(2)−Si(2)−Si(1)	114.2(1)
Si(2)−C(2)	1.864(3)	C(1)−Si(1)−Si(2)−C(2)	173.6(2)

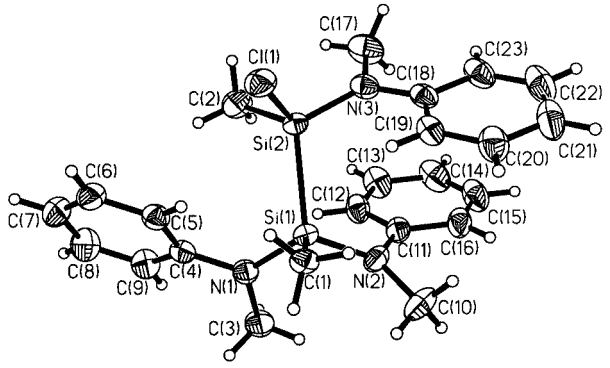


Figure 2. Molecular structure of 1-chloro-1,2-dimethyl-1,2,2-tris(*N*-methylanilino)disilane (**3**) with 50% thermal ellipsoids

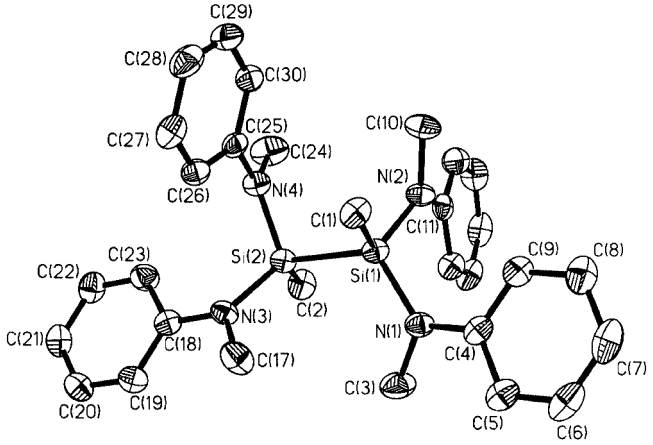


Figure 3. Molecular structure of 1,2-dimethyl-1,1,2,2-tetrakis(*N*-methylanilino)disilane (**4**) with 50% thermal ellipsoids; hydrogen atoms are omitted for clarity

atoms are tetrahedrally coordinated and no significant intermolecular interactions are observed.

Conclusions

The ease of preparing a variety of structurally different linear and branched chloro(methyl)(*N*-methylanilino)oligosilanes was demonstrated throughout this work. We were able to show that the *N*-methylanilino group is a highly useful substituent for chloro(organo)silanes in two respects. First, it is possible to obtain crystalline amino(organo)disilanes with this substituent. Second, the *N*-methylanilino group acts as a protecting group in further substitution reactions. With this strategy we were able to prepare a variety of amino(organo)disilanes starting from 1,2-dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (**2**).

Experimental Section

General: All preparative work and handling of the samples was carried out under Ar using dry glassware and dry solvents. Pentane was freshly distilled from $LiAlH_4$. Triethylamine was refluxed over sodium/benzophenone until the color of the solution was violet, then freshly distilled prior to use. Zinc fluoride was dried 6 h in vacuo to remove all traces of moisture. Commercially available *N*-methylaniline was distilled prior to use from KOH pellets. 1,1,2,2-Tetrachloro-1,2-dimethyldisilane was prepared according to a well-known procedure.[19] Melting points were recorded in capillary tubes and are uncorrected. NMR spectra were recorded with a Bruker DPX 400 with $SiMe_4$ (TMS) as internal standard at 25 °C with 400.13 MHz for ^{1}H NMR, 100.62 MHz for ^{13}C NMR, and 79.49 MHz for ^{29}Si NMR spectroscopy. Signals are noted as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and dd (doublet, doublet). The Si-Si coupling constants have been calculated from the shift differences of the Si satellites in the ^{29}Si NMR spectrum. Elemental analyses were performed with a CHN-O-RAPID (Hanau). The carbon content values were lower than expected due to the formation of silicon carbide. GC-MS spectra were obtained with a 70 eV Hewlett Packard 5890 Series II/5971 Series GC/MS system.

1,1,2-Trichloro-1,2-dimethyl-2-(*N*-methylanilino)disilane (1): *N*-methylaniline (2.4 g, 23 mmol) was added to a solution of 1,1,2,2-tetrachloro-1,2-dimethyldisilane (5.2 g, 23 mmol) and triethylamine (4.7 g, 46 mmol) in pentane (200 mL). The mixture was stirred for 140 h at room temperature. A white precipitate formed after a few hours. The resulting suspension was filtered to remove the resulting Et_3NHCl. The solvent was removed in vacuo and the resulting oily product was dried in vacuo. The purity of the product was 80%, estimated by ^{29}Si NMR spectroscopy. About 15% 1,2-dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (**2**) and 5% 1,1,2,2-tetrachloro-1,2-dimethyldisilane were detected as impurities. NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.65 ppm (s, 3 H, MeSiClN), 0.77 (s, 3 H, $MeSiCl_2$), 3.07 (s, 3 H, MeN), 6.4−7.48 (m, 5 H, Ph). ^{13}C: δ = 1.29 ppm ($MeSiCl_2$), 6.61 (MeSiClN), 37.84 (MeN), 123.40, 123.85, 129.30 (*o*-, *m*-, *p*-Ph), 148.52 (*i*-Ph). ^{29}Si: δ = −0.6 ppm (MeSiClN), 21.4 ($MeSiCl_2$).

1,2-Dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (2): Triethylamine (14 mL, 10.1 g, 100 mmol) was added to a solution of 1,1,2,2-tetrachloro-1,2-dimethyldisilane (6.0 g, 26 mmol) in pentane (150 mL). *N*-Methylaniline (5.7 mL, 5.6 g, 52 mmol) was mixed

with pentane (60 mL) and added dropwise over a period of 1 h to the reaction mixture. The reaction mixture became warm, and a voluminous white precipitate formed. The suspension was stirred at room temperature for 10 h, and then the precipitate consisting of Et_3NHCl was removed by filtration. The volume of the filtrate was reduced in vacuo to ca. 100 mL and left overnight at 5 °C. A white precipitate formed that consisted mainly of Et_3NHCl. The precipitate was removed by filtration and the filtrate was concentrated to give **2** (6.4 g , 67% yield) as a crystalline product. The crude product contained traces of **3** and was recrystallized from a pentane/diethyl ether (5:1) mixture. Ivory-colored crystals (5.9 g, 61.5%) resulted with m.p. 38 °C. $[\alpha]_\lambda$ = 377° (0.165 g/100 mL *n*-pentane, 20 °C, 302 nm). NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.51 ppm (s, SiMe, *meso*), 0.77 (s, SiMe, *rac*), 2.67 (s, NMe, *rac*), 3.0 (s, NMe, *meso*), 6.83−7.23 (m, Ph). ^{13}C: δ = 3.08 ppm (SiMe, *meso*), 3.57 (SiMe, *rac*), 36.43 (NMe, *rac*), 37.86 (NMe, *meso*), 120.95, 122.19, 123.01, 123.10, 128.83, 129.0, 148.99, 149.18 (Ph). ^{29}Si: δ = 3.66 ppm (*rac*), 1.37 (*meso*). MS: *m*/*z* = 368 [M^+], 262 [M^+ − NMePh], 184 (98) [M^+ − NMePh − HCl], 149 (100%) [Si(NMePh)Me^+]. $C_{16}H_{22}Cl_2N_2Si_2$ (369.45): calcd. C 52.02, H 6.00, N 7.58; found calcd. C 51.89, H 6.08, N 7.54.

1-Chloro-1,2-dimethyl-1,2,2-tris(*N*-methylanilino)disilane (3): To synthesize compound **3**, the same approach was applied as described for **2** using 1,1,2,2-tetrachloro-1,2-dimethyldisilane (5.47 g, 24 mmol), triethylamine (16.7 mL, 12.1 g, 120 mmol) and *N*-methylaniline (13 mL, 12.8 g, 120 mmol). White crystals (7.6 g, 72% yield), m.p. 76 °C. NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.33 ppm (s, 3 H, SiMe), 0.72 (s, 3 H, SiMe), 2.52 (s, 3 H, NMe), 2.57 (s, 3 H, NMe), 2.91 (s, 3 H, NMe), 6.72−7.27 (m, 18 H, Ph). ^{13}C: δ = 1.47, 4.71 ppm (SiMe); 30.72, 34.50, 36.50 (NMe); 112.41, 117.09, 117.25, 118.67, 119.51, 120.06, 120.87, 121.07, 121.54, 128.57, 128.64, 128.83, 149.57, 149.66, 149.79 (Ph). ^{29}Si: δ = −7.94 ppm [SiMe(NMePh)$_2$], 6.27 [SiMe(NMePh)Cl], $^1J_{Si\text{-}Si}$ = 152 Hz. MS: *m*/*z* = 439 [M^+], 255 (100%) [Si(NMePh)$_2$$Me^+$], 226 [PhSi(NMePh)$Me^+$], 184 [ClSi(NMePh)$Me^+$]. $C_{23}H_{30}ClN_3Si_2$ (440.14): calcd. C 62.76, H 6.87, N 9.55; found calcd. C 62.24, H 7.53, N 9.24.

1,2-Dimethyl-1,1,2,2-tetrakis(*N*-methylanilino)disilane (4): A solution of lithium *N*-methylanilide (1.2 g, 10.3 mmol) in diethyl ether (20 mL) was added to a solution of 1,2-dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (1.4 g, 3.7 mmol) at 0 °C. A white precipitate was formed after 4 h. The solution was stirred for an additional 24 h at room temperature. Afterwards, the solvent was removed completely in vacuo. The remaining oily residue was extracted with diethyl ether and the resulting suspension was filtered. The solvent was partially removed in vacuo and the remaining solution was cooled to 5 °C to yield the product as a white crystalline solid. The product contained crystals that were suitable for X-ray structure analysis. Yield: 1.08 g (57.2%), m.p. 116−118 °C NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.48 ppm (s, 6 H), 2.74 (s, 12 H), 7.11−7.16 (m, 20 H). ^{13}C: δ = 2.31 ppm (MeSi), 36.09 (MeN), 119.18, 120.30, 129.19 (*o*-, *m*-, *p*-Ph), 150.4 (*i*-Ph). ^{29}Si: δ = −7.53 ppm. $C_{30}H_{38}N_4Si_2$ (510.54): calcd. C 70.52, H 7.50, N 10.98; found calcd. C 70.15, H 7.38, N 9.95.

1-Chloro-1,1,2,2-tetramethyl-2-(*N*-methylanilino)disilane (5) and 1,1,2,2-Tetramethyl-1,2-bis(*N*-methylanilino)disilane (6): A solution of *N*-methylaniline (15.0 g, 140 mmol) in pentane (50 mL) was added dropwise to a solution of 1,2-dichloro-1,1,2,2-tetramethyldisilane (8.5 g, 45 mmol) and triethylamine (14.2 g, 140 mmol) in pentane (100 mL). A voluminous white precipitate formed during this procedure. The suspension was stirred at reflux temperature for 28 h and for a further 60 h at room temperature. The suspension was then filtered, the solvent was removed in vacuo and the remaining residue was distilled under high vacuum to give **5** and **6** in separated fractions. 1st fraction, b.p. (0.025 Torr) 56−59 °C, 1-chloro-1,1,2,2-tetramethyl-2-(*N*-methylanilino)disilane (**5**); 2nd fraction, b.p. (0.025 Torr) 66−70 °C, 1-chloro-1,1,2,2-tetramethyl-2-(*N*-methylanilino)disilane (**5**); 3rd fraction, b.p. (0.025 Torr) 129−137 °C, 1,1,2,2-tetramethyl-1,2-bis(*N*-methylanilino)disilane (**6**). Compound **5**: Colorless oil, fractions 1 and 2 together are 3.6 g (31.1% yield, 98% purity). NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.40 ppm (s, 6 H, MeSiN), 0.46 (s, 6 H, MeSiCl), 2.93 (s, 3 H, MeN), 6.81−7.21 (m, 5 H, Ph). ^{13}C: δ = −0.30 ppm (MeSiCl), 2.95 (MeSiN), 35.81 (MeN), 117.85, 119.24, 128.86 (*o*-, *p*-, *m*-Ph), 150.98 (*i*-Ph). ^{29}Si: δ = −1.9 ppm (SiN), 20.9 (SiCl); $^1J_{Si\text{-}Si}$ = 106 Hz. Compound **6**: Pale yellow oil, yield: 3.8 g (25.7% yield, 87% purity). The product contains 13% of **5**. NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.34 ppm (s, 12 H, MeSi), 2.72 (s, 6 H, MeN), 6.71−7.16 (m, 10 H, Ph). ^{13}C: δ = 1.07 ppm (MeSi), 34.99 (MeN), 116.65, 117.99, 128.59 (*o*-, *p*-, *m*-Ph), 151.09 (*i*-Ph). ^{29}Si: δ = −1.9 ppm. MS: 164 (100%) [$Me_2SiNMePh^+$], 59 [Me_2SiH^+], 222 [$Me_4Si_2NMePh^+$], 328 [M^+].

General Procedure for Preparing the Chloro(methyl)oligosilanes 7−11: An excess of triethylamine (1.5 mol per mol of reactive chlorine) was added to a solution of the chloro(methyl)oligosilane (5 mmol) in 100 mL of pentane. The stoichiometric amount of *N*-methylaniline (see Table 2) was mixed with pentane and added dropwise to the reaction mixture. A voluminous white precipitate of triethylammonium chloride was formed. The suspension was stirred at room temperature for at least 10 h. The solvent and the excess triethylamine was distilled off at reduced pressure. The remaining solid was extracted with pentane and filtered. The solvent

Table 2. Reaction products of oligomeric chloro(methyl)oligosilanes with *N*-methylaniline in the presence of excess triethylamine

Chlorosilane	Ratio chlorosilane/HNMePh	Product
$Cl_2Si(Me)SiMeCl_2$	1:1	$Cl_2MeSiSi(NMePh)ClMe$ (**1**)
$Cl_2Si(M)eSiMeCl_2$	1:2	$[ClMe(PhMeN)Si]_2$ (**2**)
$Cl_2Si(Me)SiMeCl_2$	1:5−6	$ClMe(PhMeN)SiSi(NMePh)_2Me$ (**3**)
$Cl[SiMe_2]_2Cl$	1:1	$PhMeN[SiMe_2]_2Cl$ (**5**)
$Cl[SiMe_2]_2Cl$	1:2	$PhMeN[SiMe_2]_2NMePh$ (**6**)
$Cl[SiMe_2]_3Cl$	1:1	$Cl[SiMe_2]_3NMePh$ (**7**)
$Cl[SiMe_2]_3Cl$	1:2	$PhMeN[SiMe_2]_3NMePh$ (**8**)
$Cl[SiMe_2]_4Cl$	1:2	$Cl[SiMe_2]_4NMePh$ (**9**)
$MeClSi(SiCl_2Me)_2$	excess HNMePh	$MeClSi[Si(NMePh)ClMe]_2$ (**10**)
$MeSi(SiCl_2Me)_3$	excess HNMePh	$MeSi[Si(NMePh)ClMe]_3$ (**11**)

was partially removed from the filtrate in a vacuum and the concentrated solution was left for several days at 5 °C; **9**, **10**, and **11** formed a white precipitate which was isolated by filtration and dried in vacuo; **7** and **8** did not crystallize and were therefore purified by vacuum distillation.

Cl[SiMe$_2$]$_3$NMePh (7): Colorless oil, yield: 340 mg (22%), b.p.$_{0.01Torr}$ 97 °C. NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.16 ppm (s, 6 H, (PhMeNSiMe$_2$Si*Me*$_2$), 0.28 (s, 6 H, (PhMeNSi*Me*$_2$SiMe$_2$), 0.59 (s, 6 H,ClSi*Me*$_2$), 2.79 (s, 6 H, Ph*Me*N), 6.83−7.24 (m, 5 H, Ph). ^{13}C: δ = −1.6 ppm (PhMeNSiMe$_2$Si*Me*$_2$), 0.8 (PhMeNSi*Me*$_2$-SiMe$_2$), 5.2 (ClSi*Me*$_2$), 37.3 (Ph*Me*N), 119.2.120.1.127.9, 149.8 (Ph). ^{29}Si: δ = 25.9 ppm, 2.4, −45.2.

PhMeN[SiMe$_2$]$_3$NMePh (8): Yellow oil, yield: 600 mg (31%), b.p.$_{0.01Torr}$ 128 °C. NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.16 ppm [s, 6 H, (PhMeNSiMe$_2$)$_2$Si*Me*$_2$], 0.28 [s, 12 H, (PhMeNSi*Me*$_2$)$_2$-SiMe$_2$], 2.82 (s, 6 H, Ph*Me*N), 6.76−7.19 (m, 10 H, Ph). ^{13}C: δ = −3.8 ppm [(PhMeNSiMe$_2$)$_2$Si*Me*$_2$], 0.7 [(PhMeNSi*Me*$_2$)$_2$SiMe$_2$], 35.6 (Ph*Me*N), 117.1, 118.1.128.6, 151.3 (Ph). ^{29}Si: δ = 3.0 ppm, −47.6; $^1J_{Si\text{-}Si}$ = 80 Hz.

Cl[SiMe$_2$]$_4$NMePh (9): Pale yellow oil, yield: 880 mg (47%). NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.23 ppm (s, 6 H, Si*Me*$_2$SiMe$_2$N-MePh), 0.34 (s, 6 H, ClSiMe$_2$Si*Me*$_2$), 0.42 (s, 6 H, Si*Me*$_2$NMePh), 0.61 (s, 6 H, ClSi*Me*$_2$), 2.92 (s, 3 H, N*Me*Ph), 6.96−7.31 (m, 5 H, Ph). ^{13}C: δ = 2.3 ppm (Si*Me*$_2$SiMe$_2$NMePh), 3.4 (ClSiMe$_2$Si*Me*$_2$), 3.9 (Si*Me*$_2$NMePh), 6.1 (ClSi*Me*$_2$), 36.3 (N*Me*Ph), 118.3, 122.4, 123.3, 148.7 (Ph). ^{29}Si: δ = 26.4, 3.3, −41.3, −43.9 ppm.

MeClSi[Si(NMePh)ClMe]$_2$ (10): Yellow oil, yield: 510 mg (23%). NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.37 ppm {s, 6 H, MeClSi[Si-(NMePh)Cl*Me*]$_2$}, 0.58 {s, 3 H, *Me*ClSi[Si(NMePh)ClMe]$_2$}, 2.73, 2.74, 2.82, 2.86, {s, 6 H, MeClSi[Si(N*Me*Ph)ClMe]$_2$}, 6.54−7.09 (m, 10 H, Ph). ^{13}C: δ = −0.8 ppm {*Me*ClSi[Si(NMePh)ClMe]$_2$}, 6.3 {MeClSi[Si(NMePh)Cl*Me*]$_2$}, 36.9, 37.1, 37.7, 37.9 {MeClSi[Si(N*Me*Ph)ClMe]$_2$, diastereomers}, 122.9, 123.6, 128.6, 128.7, 129.1, 129.3, 149.2 (Ph, diastereomers). ^{29}Si: δ = −4.3 ppm, 3.0; $^1J_{Si\text{-}Si}$ = 58 Hz.

MeSi[Si(NMePh)ClMe]$_3$ (11): Yellow oil, yield: 2.17 g (73%). NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.64 ppm, 0.5 {s, 9 H, MeSi-[Si(NMePh)Cl*Me*]$_3$, diastereomers}, 0.50 {s, 3 H, *Me*Si[Si-(NMePh)ClMe]$_3$, diastereomers}, 2.93, 2.96.2.97.3.01 {s, 9 H, MeSi[Si(N*Me*Ph)ClMe]$_3$, diastereomers} 6.99-7.26 (m, 15 H, Ph). ^{13}C: δ = −7.6 ppm, −7.4 {*Me*Si[Si(NMePh)ClMe]$_3$, diastereomers}, 5.2, 5.5 {MeSi[Si(NMePh)Cl*Me*]$_3$, diastereomers}, 38.1, 38.4, 38.7, 38.8 {MeSi[Si(N*Me*Ph)ClMe]$_3$, diastereomers}, 122.2, 122.5, 122.8.122.9, 123.0, 123.4, 128.9, 129.0, 148.8, 148.9, (Ph, diastereomers). ^{29}Si: δ = −73.3 ppm, −72.9, 12.45, 12.62, 12.76, 12.80 ($^1J_{Si\text{-}Si}$ = 88 Hz, diastereomers).

1,2-Difluoro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (12): A suspension of 1,2-dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)-disilane (**2**) (3.9 g, 10.6 mmol) and zinc fluoride (11.4 g, 110 mmol) in DME (50 mL) was stirred for 150 h at room temperature. Afterwards, the solvent was removed under reduced pressure. The remaining oily residue was extracted with pentane, filtered, and cooled to 5 °C. A white crystalline solid was formed. The product was isolated by filtration, washed with pentane, and dried in vacuo to yield 2.55 g (71.5%) white crystalline powder with m.p. 89−90 °C. NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.48 ppm (dd, 6 H, MeSi, $^3J_{H\text{-}F}$ = 3 Hz), 2.44 (d, 6 H, MeN), 6.72−7.23 (10 H, Ph). ^{13}C: δ = 0.43 ppm (MeSi), 43.13 (MeN), 118.16, 20.88, 128.88 (*o*-, *m*-, *p*-Ph), 149.41 (*i*-Ph). ^{29}Si: δ = 2.45 ppm (dd, $^1J_{Si\text{-}F}$ = 326, $^2J_{Si\text{-}F}$ = 63 Hz). $C_{16}H_{22}F_2N_2Si_2$ (336.54): calcd. C 57.10, H 6.59, N 8.32; found C 57.71, H 6.98, N 7.96.

1,2-Dimethyl-1,2-bis(*N*-methylanilino)-1,2-bis(phenylethynyl)-disilane (13): A solution of lithium phenylacetylide (0.17 g, 17.0 mmol) in diethyl ether (30 mL) was added dropwise to a solution of 1,2-dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (**2**) (3.15 g, 8.5 mmol) in DME (80 mL) at 0 °C. A white precipitate formed immediately. The suspension was stirred for an additional 24 h. The solvent was then removed under reduced pressure. The remaining oily residue was extracted with pentane, filtered and the clear filtrate was stored in the refrigerator. The cooling of the solution led to a phase separation. The solvent was removed completely in vacuo and the product was isolated as a pale yellow oil, yield: 2.72 g (64%). NMR ($CDCl_3$, 395 K, TMS) ^{1}H: δ = 0.65 ppm, 0.72 (6 H, MeSi, *rac*/*meso* = 1:1), 2.73, 2.90 (6 H, MeN, *rac*, *meso*); 6.76−7.47 (m, 10 H, Ph). ^{13}C: δ = 0.43 ppm (MeSi), 35.2, 35.7 (MeN, *rac*, *meso*), 91.3, 91.6 (SiC*C*Ph, *rac*, *meso*), 109.2 (Si*C*CPh), 116.7, 117.0, 128.1, 128.2, 128.48, 128.53, 128.6, 128.7, 131.8 (*o*-, *m*-, *p*-Ph, *rac*, *meso*), 122.2 (*i*-CC*Ph*), 150.0 (*i*-PhN). ^{29}Si: δ = −25.78, −25.82 ppm (*rac*, *meso*).

1,2-Dimethyl-1,2-bis(*N*-methylanilino)-1,2-bis(*p*-tolyl)disilane (14) and 1-Chloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)-2-(*p*-tolyl)disilane (14a): A solution of *p*-tolylmagnesium bromide (3.6 g, 18.6 mmol) in THF (20 mL) was added slowly to a solution of 1,2-dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (**2**) (3.4 g, 9.3 mmol) in DME (60 mL) at 0 °C. The resulting mixture was stirred for 24 h at room temperature. The solvent was removed completely in vacuo. The residue was extracted with a pentane/DME mixture (3:1). The resulting suspension was filtered and the solvent was partially removed in vacuo. The addition of a small amount diethyl ether and cooling to −16 °C gave a white precipitate, which was isolated by filtration and dried in vacuo. The product consisted of a mixture of **14** and **14a** in a product ratio of 2:1. It was not possible to separate both products by fractional crystallization. 1,2-Dimethyl-1,2-bis(*N*-methylanilino)-1,2-bis(*p*-tolyl)disilane (**14**): ^{29}Si NMR ($CDCl_3$, 25 °C, TMS): δ = −7.7 ppm, −7.5 (*rac*/*meso* = 1.5:1). 1-Chloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)-2-(*p*-tolyl)disilane (**14a**): ^{29}Si NMR ($CDCl_3$, 25 °C, TMS): δ = −9.6 ppm (MeSiTolN), 8.5 (MeSiClN); $^1J_{Si\text{-}Si}$ = 20 Hz (only one diastereomer was detected).

1,2-Dibenzyl-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (15): A solution of benzylmagnesium chloride (3.2 g, 21.2 mmol) in diethyl ether (17 mL) was added dropwise to a solution of 1,2-dichloro-1,2-dimethyl-1,2-bis(*N*-methylanilino)disilane (**2**) (3.9 g, 10.6 mmol) in DME (80 mL) at 0 °C. The solution was stirred for an additional 24 h. Afterwards, the solvent was removed under reduced pressure. The remaining residue was extracted with pentane, filtered and the solvent was partially removed in vacuo. Storage of the concentrated solution at −16 °C yielded a white precipitate which was separated by filtration, washed with cold pentane and dried in vacuo; yield: 1.8 g (35.4%), m.p. 98−100 °C. NMR ($CDCl_3$, 25 °C, TMS): ^{1}H: δ = 0.17 ppm, 0.25 (6 H, MeSi, *rac*/*meso* = 1:1), 2.10, 2.13, 2.64, 2.67 (4 H, CH_2Ph, *rac*, *meso*), 2.45, 2.54 (6 H, MeN, *rac*, *meso*), 6.68−7.21 (m, 10 H, Ph). ^{13}C: δ = −1.8 ppm, −1.4 (MeSi, *rac*, *meso*), 27.1, 27.5 (CH_2, *rac*, *meso*), 35.6 (MeN), 117.3, 117.5, 128.07, 128.12, 128.52, 128.58 (*o*-, *m*-, *p*-CH_2*Ph*, *rac*, *meso*), 118.6, 124.3, 128.8 (*o*-, *m*-, *p*-*Ph*N), 138.6 (*i*-CH_2*Ph*), 151.0 (*i*-PhN). ^{29}Si: δ = −3.4 ppm, −4.3 (*rac*, *meso*). $C_{30}H_{36}N_2Si_2$ (480.80): calcd. C 74.94, H 7.55, N 5.83; found C 74.35, H 7.48, N 5.46.

X-ray Crystal Structure Determinations: Suitable single crystals were mounted on glass fibers under paraffin oil and transferred to the diffractometer. Diffraction measurements were made with an Enraf−Nonius CAD-4 diffractometer. Further details on crystal data and structure determination are summarized in Table 3.

Table 3. Crystal data and structure refinement for compounds **2**, **3**, and **4**

	2	**3**	**4**
Empirical formula	$C_{16}H_{22}Cl_2N_2Si_2$	$C_{23}H_{30}ClN_3Si_2$	$C_{30}H_{38}N_4Si_2$
Formula mass	369.44	440.13	510.82
Temperature [K]	172(2)	208(2)	193(2)
Wavelength [Å]	0.71073	1.54178	1.54178
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$C222_1$	$P21/n$	$P21/a$
Unit cell dimensions			
a [Å]	9.273(2)	12.597(1)	12.222(2)
b [Å]	15.090(3)	13.863(1)	13.641(2)
c [Å]	13.322(3)	13.394(1)	17.588(3)
β [°]	90	90.05(1)	109.32(1)
Volume [Å^3]	1864.1(7)	2339.0(3)	2767.1(8)
Z	4	4	4
Calculated density [mg·m^{-3}]	1.316	1.250	1.226
Absorption coefficient [mm^{-1}]	0.475	2.529	1.352
F(000)	776	936	1096
Crystal size [mm]	0.7 × 0.3 × 0.3	0.6 × 0.5 × 0.3	0.6 × 0.5 × 0.5 mm
θ range for data collection [°]	2.58−27.98	4.59−74.88	2.66−75.49
Limiting indices	$-12 \le h \le 12$, $-19 \le k \le 19$, $-17 \le l \le 9$	$-15 \le h \le 15$, $-17 \le k \le 0$, $-16 \le l \le 0$	$-15 \le h \le 14$, $-17 \le k \le 6$, $0 \le l \le 22$
Reflections collected/unique	6984/2256 [R(int) = 0.0535]	5015/4809 [R(int) = 0.0179]	8632/5665 [R(int) = 0.0715]
Completeness to θ [°]	27.98/100.0%	74.88/100.0%	75.49/98.9%
Absorption correction	none	empirical	none
Max./min. transmission	−	0.999/0.647	−
Refinement method		Full-matrix least-squares on F^2	
Data/restraints/parameters	2256/0/102	4809/0/267	5665/0/331
Goodness-of-fit on F^2	1.006	1.056	1.062
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0376, $wR2$ = 0.0656	$R1$ = 0.0431, $wR2$ = 0.1214	$R1$ = 0.0572, $wR2$ = 0.1324
R indices (all data)	$R1$ = 0.0648, $wR2$ = 0.0723	$R1$ = 0.0454, $wR2$ = 0.1235	$R1$ = 0.0888, $wR2$ = 0.1481
Absolute structure parameter	−0.08(9)	−	−
Largest diff. peak/hole [e·Å^3]	0.245/−0.206	0.369/−0.496	0.532/−0.322

CCDC-116146 (**2**), -111583 (**3**), and -144275 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Financial support for this work from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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Received July 3, 2002
[I02362]