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Syntheses of Functionalized Oligosilanes[#]

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Summary. A number of differently substituted isotetra- and isoheptasilanes were synthesized.

Keywords. Silicon; Isotetrasilanes; Crystal Structure.

Introduction

The chemistry of exactly defined molecular structures with oligosilane backbones has experienced an enormous development within the last few years. This is in part a result of the development of methods facilitating the introduction of multiple functional groups under conditions preserving silicon–silicon bonds. In the current account we would like to disclose the syntheses of a number of key intermediates for the building of extended structures like cage molecules and polysilane dendrimers [1]. These can be obtained starting from isotetra- and/or isoheptasilanes, which bear functional groups either in a reactive form like halides or masked like phenyl groups, which allow the easy conversion into leaving groups. Recent studies from our laboratory showed that even the trimethylsilyl group can be considered as a masked functional group which can be easily substituted by potassium with potassium *tert*-butoxide [2].

The reactions which can be used for synthesis and manipulation of these molecules can be categorised into Si–Si bond forming reactions and functional group generating or manipulating reactions. The most frequently used method to obtain polysilanes is the *Wurtz* type coupling. Disadvantages of this reaction are the relatively harsh reaction conditions (alkali metals) and an intrinsic restriction to symmetric products. However, for the synthesis of larger quantities of starting materials this is often the method of choice. An attractive alternative is the salt elimination reaction between a silylanion and a silyl electrophile (usually either

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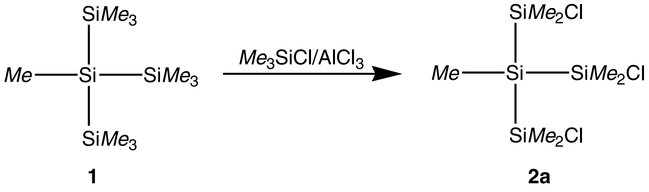
[#] Dedicated to Prof. *Ulrich Schubert* (TU Wien) on the occasion of his 60th birthday

halide or triflate). The additional flexibility provided by this reaction is gained at the expense of the separate generation of nucleophiles and electrophiles. A few other synthetic methods for the formation of polysilanes comprise transition metal catalysis of hydrosilanes [3] and coupling of silyl radicals [4].

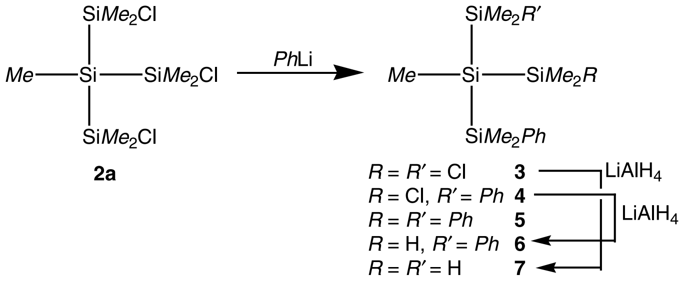
The second important class of reactions deals with the conversion of the products of the just mentioned building reactions. Introduction of halides or triflates can be accomplished most easily either *via* protodesilylation reaction of a phenylsilane or by halogenation of a hydrosilane with CX_4, CX_3H, or phosphorus pentahalides. For the generation of silylanions also a number of different methods are known, the most convenient, however, is still cleavage of disilanes with lithium.

Results and Discussion

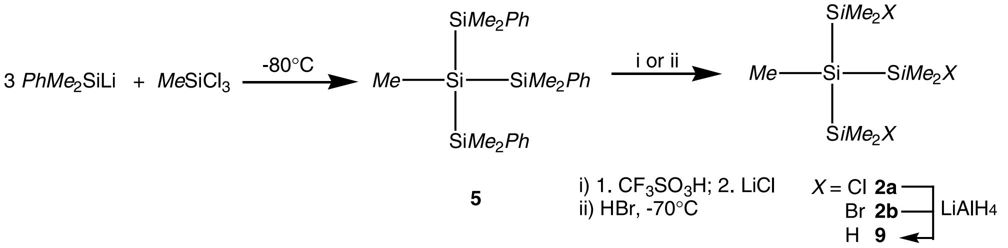
For our purposes we frequently use methylated isotetrasilanes as starting materials. Tris(trimethylsilyl)methylsilane (**1**), which is the parent compound of this structural type, can easily be obtained for example by *Wurtz* type reaction of trichloromethylsilane with three equivalents of chlorotrimethylsilane in the presence of alkali metals [5]. In order to functionalize the trimethylsilyl groups $AlCl_3$ catalyzed reaction with hydrogen chloride, acetyl chloride, or trimethylchlorosilane is required (**2a**) [6]. However, this can be a very capricious reaction, which frequently requires long reaction times.



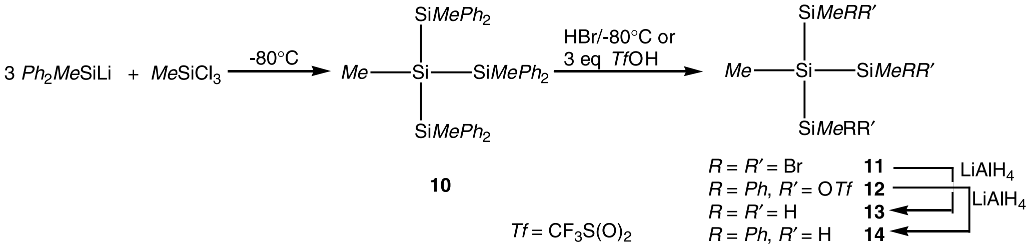
Phenylation of **2a** with phenyllithium gives a mixture of the mono-, double-, and triple phenylated products **3**, **4**, and **5**. As they can not be separated easily by crystallisation or distillation, the reaction mixture was subjected to reduction with lithium aluminum hydride which results in a mixture of **5** and hydrosilanes **6** and **7** which can be separated by distillation. Pure **3** and **4** then can be obtained by reaction of **7** and **6** with PCl_5.



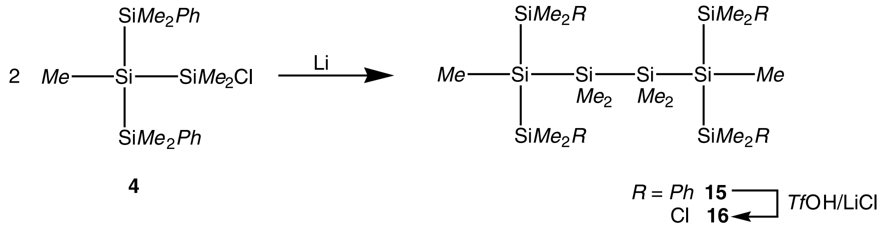
Because of the above mentioned difficulties, the introduction of phenyl groups into the isotetrasilane early on is an attractive strategy. The *Wurtz* type reaction to the corresponding isotetrasilane **5** with three dimethylphenylsilyl groups, however, often does not give clean reactions as frequently partial silylation of phenyl groups [7] occurs. Sometimes it is even accompanied by the formation of neopentasilane **8** [8]. Whereas these problems can be avoided for the preparation of **5** by a salt elimination reaction between three equivalents of dimethylphenylsilyllithium and trichloromethylsilane the analogous reaction of tetrachlorosilane with four equivalents of dimethylphenylsilyllithium gives **8** only in poor yield [8]. The obtained isotetrasilane **5** can be converted easily into the respective trichloride **2a** by reaction with trifluoromethanesulphonic acid [9] and subsequent treatment with LiCl. Alternatively, reaction of **5** in neat HBr at −70°C leads to the respective tribromide **2b** [11]. Both trihalides can be reduced to the corresponding trihydrosilane **9** [8, 11] using lithium aluminum hydride.



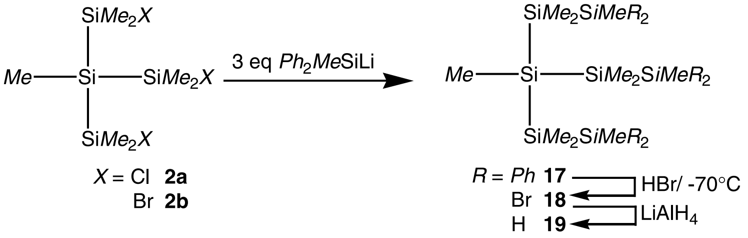
The just outlined procedure can also be applied for the introduction of difunctional silyl groups. Reaction between three equivalents of methyldiphenylsilyllithium and trichloromethylsilane in this case leads to the formation of tris(methyldiphenylsilyl)methylsilane (**10**) [10]. This compound can be converted either to the hexabromide **11** [11] employing reaction with HBr or to the half-functionalised **12** by addition of three equivalents of trifluoromethanesulfonic acid. Compound **12** is obtained as a mixture of two diastereomers [12]. Compounds **11** and **12** again can be converted to the respective hydroisotetrasilanes **13** and **14** by reaction with lithium aluminum hydride.



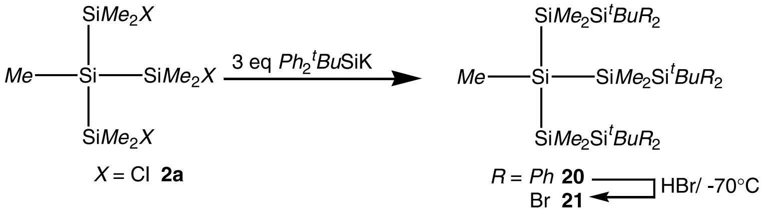
The so far described chemistry provides access to isotetrasilane units with either one or two reactive residues on the terminal silyl groups as well as the possibility to activate only one or two silyl groups. In the following section it will be shown that these compounds can be used to produce more extended polysilanes in a selective way. For example, reaction of two equivalents **4** with Li leads to the formation of tetraphenyloctasilane **15** [13]. The respective tetrachlorooctasilane **16** can be obtained by the above mentioned treatment with trifluoromethanesulfonic acid and LiCl.



Reaction of the trihalides **2a** or **2b** with three equivalents of methyldiphenylsilyllithium leads to the formation of isoheptasilane **17**. Again this very stable compound can be activated by treatment at low temperature with neat HBr to give the hexabromide **18**, which subsequently can be reduced to the hexahydrosilane **19**.



The same reaction sequence starting from trichloride **2a** can also be carried out using *tert*-butyldiphenylsilylpotassium as the silylation reagent in the first step leading to structurally similar compounds **20** and **21**.



X-Ray Crystallography

Compounds **5**, **8**, **10**, **17**, and **20** were subjected to single crystal X-ray diffraction analysis. Isotetrasilane **5** (Fig. 1) appears as an almost C_3 symmetric propeller

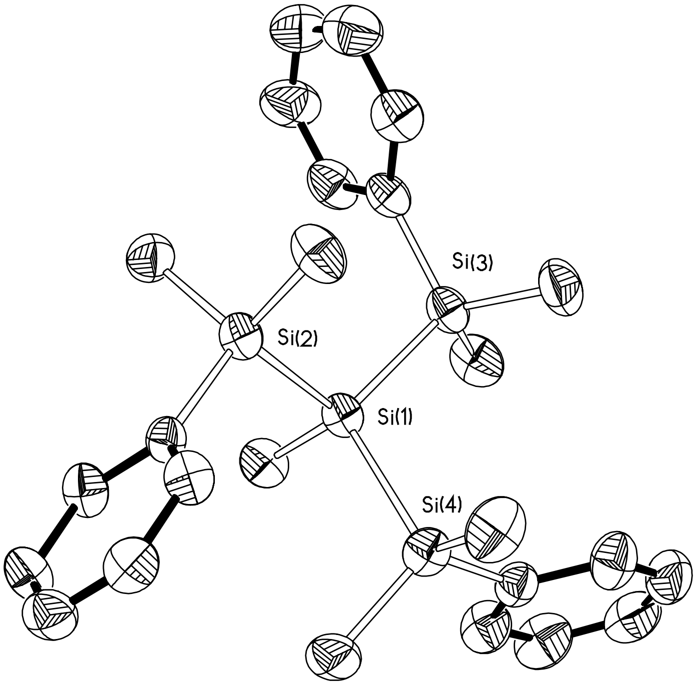


Fig. 1. Molecular structure of **5** with selected bond distances [Å] and angles [°] with estimated standard deviations. Si(1)–Si(2) 2.3362(18), Si(1)–Si(4) 2.3371(19), Si(1)–Si(3) 2.3390(19), Si(2)–Si(1)–Si(4) 110.51(7), C(1)–Si(1)–Si(3) 107.97(16), Si(2)–Si(1)–Si(3) 112.11(7), Si(4)–Si(1)–Si(3) 111.00(7)

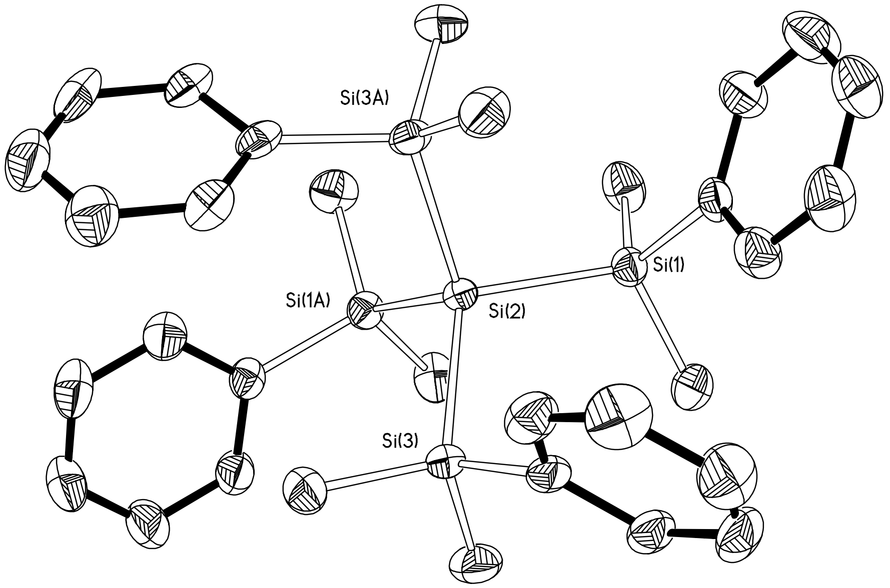


Fig. 2. Molecular structure of **8** with selected bond distances [Å] and angles [°] with estimated standard deviations: Si(2)–Si(1A) 2.3693(13), Si(2)–Si(3) 2.3718(12), Si(1A)–Si(2)–Si(1) 106.72(7), Si(1A)–Si(2)–Si(3) 105.77(4), Si(1)–Si(2)–Si(3) 110.49(3), Si(3)–Si(2)–Si(3A) 117.22(7)

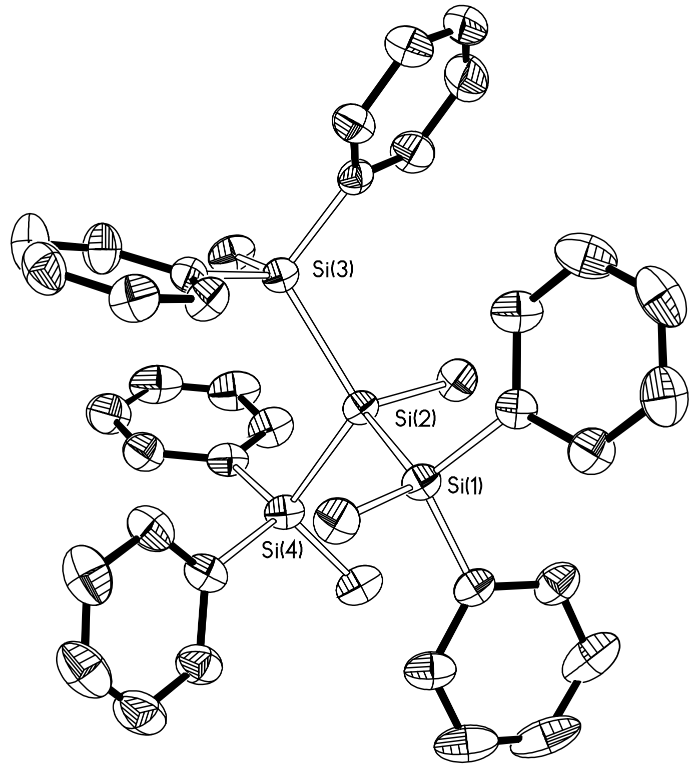


Fig. 3. Molecular structure of **10** with selected bond distances [Å] and angles [°] with estimated standard deviations: Si(1)–Si(3) 2.3692(9), Si(1)–Si(4) 2.3707(10), Si(1)–Si(2) 2.3712(11), Si(3)–Si(1)–Si(4) 120.35(4), C(1)–Si(1)–Si(2) 106.24(8), Si(3)–Si(1)–Si(2) 106.65(3), Si(4)–Si(1)–Si(2) 111.70(4)

shaped molecule with not much steric interaction between the three side-chains. As a consequence Si–Si bond lengths in the molecule are relatively short (2.33–2.34 Å). The angles around the central silicon atom reflect the slightly larger steric demand of the dimethylphenylsilyl group displaying Si–Si–Si bond angles between 110.5 and 112.1°. The corresponding neopentasilane **8** (Fig. 2) with four dimethylphenylsilyl substituents experiences more steric strain. Si–Si bond lengths are elongated to 2.37 Å, which is longer than in tetrakis(trimethylsilyl)silane (2.346(1) Å) [14]. Two dimethylphenylsilyl groups are arranged in a way that the phenyl moieties point away from the center of the molecule. This allows for a relatively small angle of 106.7° between these groups. The remaining dimethylphenylsilyl substituents accommodate the phenyl in a way closer to the central silicon atom thus widening the bond angle to 117.2°. For compound **10** (Fig. 3) a propeller shaped arrangement as was found for **5** does not seem to be possible for steric reasons. Si–Si bond lengths are close to 2.37 Å and the tetrahedron around Si(2) is severely distorted with fairly different Si–Si–Si angles of 106.6, 111.7, and 120.4°. Compound **17** (Fig. 4) again shows the propeller shaped arrangement. The terminal methyldiphenylsilyl groups, however, display different spatial orientations. All Si–Si bond lengths are close to 2.36 Å. Si–Si–Si angles around the central silicon atom Si(3) are ranging from 109.1 to 112.3°. In order to accommodate the disilanyl branches around the central silicon atom the bond angles of

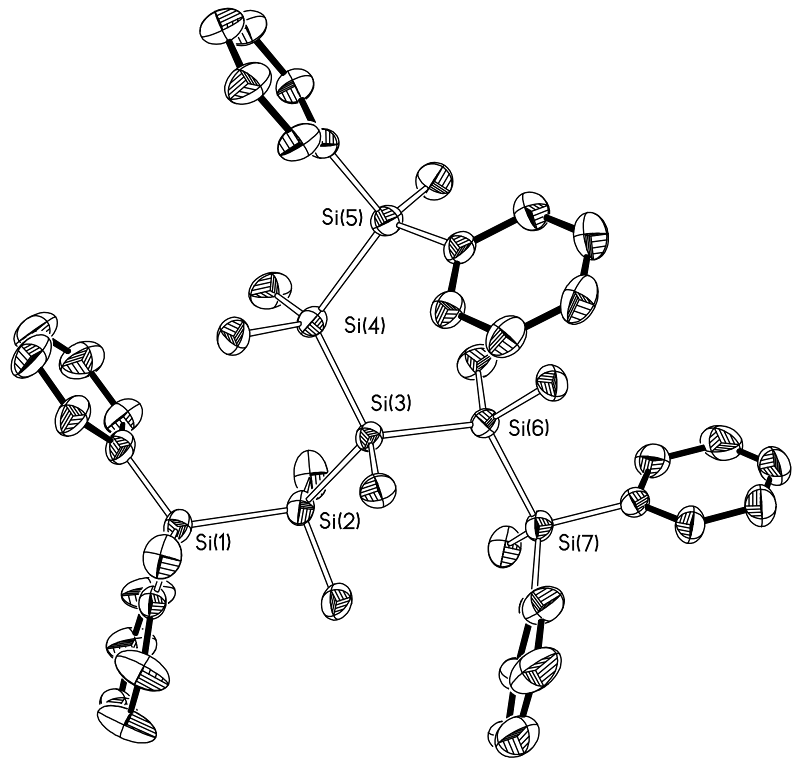


Fig. 4. Molecular structure of **17** with selected bond distances [Å] and angles [°] with estimated standard deviations: Si(1)–Si(2) 2.3519(10), Si(2)–Si(3) 2.3581(9), Si(3)–Si(6) 2.3576(9), Si(3)–Si(4) 2.3661(8), Si(4)–Si(5) 2.3590(11), Si(6)–Si(7) 2.3572(8), Si(1)–Si(2)–Si(3) 117.43(4), Si(6)–Si(3)–Si(2) 109.11(4), Si(6)–Si(3)–Si(4) 112.30(3), Si(2)–Si(3)–Si(4) 111.69(3), Si(5)–Si(4)–Si(3) 117.82(3), Si(7)–Si(6)–Si(3) 117.13(4)

the trisilanyl units are all widened to values close to 117°. For compound **20** (Fig. 5) two independent molecules with similar structural features are found in the asymmetric unit. Again the molecule exhibits the propeller shaped arrangement with symmetry close to C_3. As was found before for **17**, the bond angles around the central silicon atom are close to a perfect tetrahedron. The higher steric demand of the *tert*-butyl groups of **20** in comparison to the methyl groups in **17** forces the bond angles of the trisilanyl units to be widened to close to 120°. The higher steric strain also causes an elongation of the Si–Si bonds to values close to 2.38 Å.

Experimental

All reactions were carried out under an atmosphere of dry Ar or N_2. Solvents were dried over Na/K alloy and distilled freshly before use. HBr was dried over P_2O_5. *PhMe*$_2$SiLi [15], *Ph*$_2$*Me*SiLi [16], 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane [17] and **2a** [6] were prepared using known procedures.

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded either on a Bruker MSL 300 or on Varian INOVA 300 or 500 spectrometers. Samples for ^{29}Si spectra were either dissolved in C_6D_6 or in cases of reaction samples measured with a D_2O capillary in order to provide an external lock frequency signal. To compensate for the low isotopic abundance of ^{29}Si the INEPT pulse sequence was used for the amplification of the signal [18].

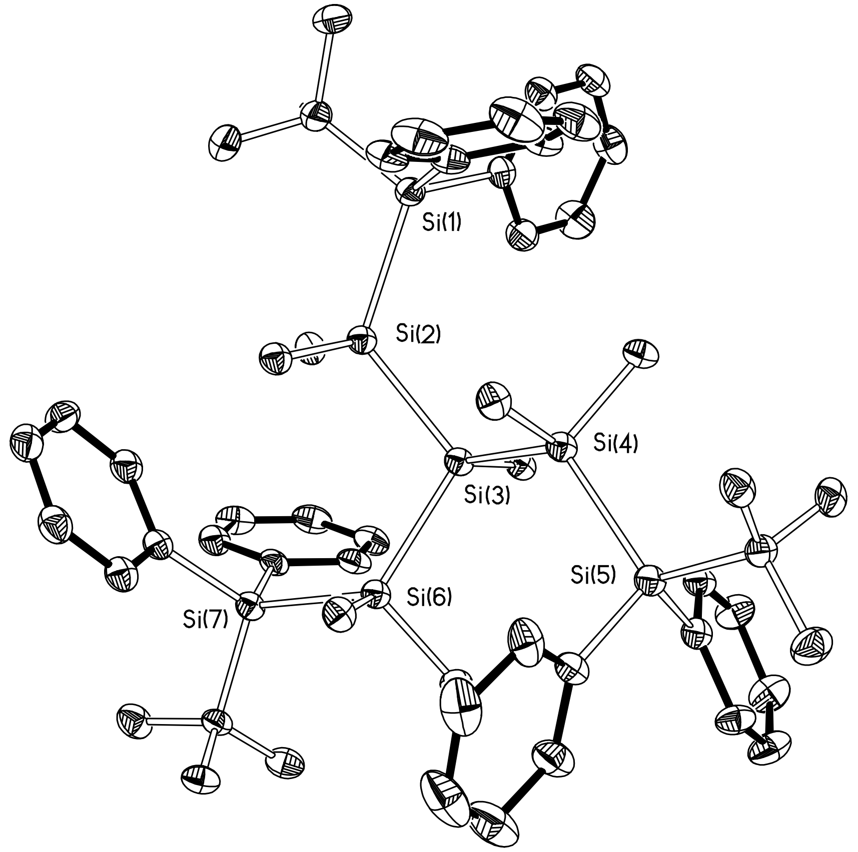


Fig. 5. Molecular structure of **20** with selected bond distances [Å] and angles [°] with estimated standard deviations (only one of two independent molecules shown): Si(1)–Si(2) 2.376(2), Si(2)–Si(3) 2.374(2), Si(3)–Si(4) 2.376(2), Si(3)–Si(6) 2.379(2), Si(4)–Si(5) 2.385(2), Si(6)–Si(7) 2.387(2), Si(3)–Si(2)–Si(1) 122.72(9), Si(2)–Si(3)–Si(4) 109.35(9), Si(2)–Si(3)–Si(6) 109.21(9), Si(4)–Si(3)–Si(6) 109.59(8), Si(3)–Si(4)–Si(5) 118.82(9), Si(3)–Si(6)–Si(7) 118.60(9)

IR spectra were measured with a Perkin Elmer 883 instrument. GC/MS were recorded on a HP 5890/II gas chromatograph with HP 5971/A MSD, a HP1 (cross-linked methyl silicone) column, and He as carrier gas. High resolution mass spectra were obtained on a Kratos Profile instrument. Elemental analyses (C, H) were carried out using a Heraeus Elementar vario EL instrument, the results were in good agreement with the calculated values.

Tris(bromodimethylsilyl)methylsilane (**2b**, $C_7H_{21}Br_3Si_4$)
In a 50 cm^3 flask equipped with a reflux condenser cooled to −75°C 5.00 g **5** (11.1 mmol) were placed. The flask was cooled to −80°C and about 20 cm^3 HBr were condensed onto the material. After the condensation was complete the bath was removed and the HBr was allowed to reflux for 3 h. After removal of all volatiles in vacuum, *n*-pentane was distilled onto the residue to dissolve the product. At −35°C 4.70 g **2b** (10.3 mmol, 92%) were obtained as colourless crystals. ^{1}H NMR (C_6D_6): $\delta = 0.78$ (s, 18H), 0.34 (s, 3H) ppm; ^{29}Si NMR (toluene): $\delta = 19.7$, −72.9 ppm.

Bis(chlorodimethylsilyl)dimethylphenylsilylmethylsilane (**3**, $C_{13}H_{26}Cl_2Si_4$)
and *Chlorodimethylsilylbis(dimethylphenylsilyl)methylsilane* (**4**, $C_{19}H_{31}ClSi_4$)
To a solution of 30.0 g **2a** (92.8 mmol) in 500 cm^3 petrol ether, cooled to −70°C, a solution of 90.0 mmol phenyllithium in 300 cm^3 diethyl ether (prepared from 14.1 g bromobenzene and excess

Li) was added slowly over a period of 2 h. After separation from the salts by filtration, the solvents were removed by evaporation in vacuum and replaced by 300 cm^3 diethyl ether. A solution of approx. 100 mmol $LiAlH_4$ in 200 cm^3 diethyl ether was added slowly at -30°C. The reaction mixture was refluxed for a couple of hours and then added dropwise to 1000 cm^3 aqueous 1 *N* H_2SO_4 at 0°C. The organic phase was separated and dried (Na_2SO_4) overnight. Diethyl ether was then removed, and the oily residue, which contained $(HMe_2Si)MeSi(SiMe_2Ph)_2$ (**6**) and $(HMe_2Si)_2MeSi(SiMe_2Ph)$ (**7**) besides some **5** was subjected to fractional distillation. Details relating to the properties of **6** and **7** are given below.

To a solution of 5.6 g **6** (15.5 mmol) in 50 cm^3 petrol ether at 0°C 3.2 g PCl_5 (15.5 mmol) were added, and the reaction mixture was stirred for 2 h. The solvent and PCl_3 were then removed by evaporation in vacuum and the residue was purified by fractional distillation using a short column. At 135°C and 0.05 mbar 4.6 g **4** (72.8%) were obtained as a viscous, oily liquid which solidified slowly upon standing. ^{29}Si NMR: $\delta = +30.9, -15.0, -85.9$ ppm.

The reaction with PCl_5 was also used for the preparation of $(ClMe_2Si)_2MeSi(SiMe_2Ph)$ (**3**) in an analogous way: 3.2 g **7** (10.8 mmol) were treated with 4.5 g PCl_5 (21.6 mmol) and the fractional distillation gave 3.1 g **3** (78.5%) at 100–110°C/0.05 mbar. ^{29}Si NMR: $\delta = +28.9, -16.1, -78.8$ ppm.

Tris(dimethylphenylsilyl)methylsilane (**5**, $C_{25}H_{36}Si_4$)

A solution of 7.00 g methyltrichlorosilane (46.9 mmol) in 120 cm^3 diethylether was cooled to -70°C. Dimethylphenylsilyllithium (prepared from 25.0 g dimethylphenylchlorosilane (146.5 mmol) and 6.0 g lithium powder) in 200 cm^3 *THF* was added slowly. The reaction was allowed to warm up to room temperature, stirred for another 12 h and poured on 2 *N* H_2SO_4/ice. The aqueous layer was extracted several times with toluene, dried (Na_2SO_4), and the solvent removed in vacuum. The remaining residue was dissolved in *n*-pentane and cooled to -70°C whereupon crystallisation occurred and pure 12.6 g **5** (60%) were obtained as colourless crystals. ^1H NMR ($CDCl_3$): $\delta = 7.31$ (m, 15H), 0.23 (s, 21H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 140.53, 134.06, 128.63, 127.96, -1.53, -11.40$ ppm; ^{29}Si NMR (toluene): $\delta = -15.5, -86.1$ ppm; EIMS: m/z (rel.int.%) = 448 (5, $M^{+\bullet}$), 313 (12, $(M\text{-}SiMe_2Ph)^{+\bullet}$), 236 (40, $(M\text{-}SiMe_2Ph_2)^{+\bullet}$), 135 (100, $(SiMe_2Ph)^{+\bullet}$).

Dimethylsilylbis(dimethylphenylsilyl)methylsilane (**6**, $C_{19}H_{32}Si_4$) and *Bis(dimethylsilyl)(dimethylphenylsilyl)methylsilane* (**7**, $C_{13}H_{28}Si_4$)

The synthesis of **6** by partial phenylation of **2a** and subsequent reduction with $LiAlH_4$ was described above. Compounds **6** and **7** were also obtained *via* an alternative route by reaction of **5** with one or two equivalents of CF_3SO_3H, which proceeded selectively with formation of $(TfOMe_2Si)MeSi(SiMe_2Ph)_2$ and $(TfOMe_2Si)_2MeSi(SiMe_2Ph)$ ($TfO = -OSO_2CF_3$).

To a solution of 20.0 g **5** (44.6 mmol) in 100 cm^3 toluene, cooled to -50°C either 6.7 g (44.6 mmol) or 13.4 g (89.2 mmol) CF_3SO_3H were added dropwise at that temperature. After complete addition, the reaction mixtures were allowed to warm up to room temperature and stirred for 2 h. They were then again cooled down to -30°C, and stoichiometric solutions of $LiAlH_4$ in diethyl ether were added slowly. After stirring for 2 h at rt, the reaction mixtures were added dropwise to 1000 cm^3 2 *N* H_2SO_4. The organic phases were then subjected to the work-up procedures as described above. Typically, achieved yields were 80–90%. ^{29}Si NMR: $(TfOMe_2Si)MeSi(SiMe_2Ph)_2$: $\delta = +53.0, -16.4, -85.0$ ppm; $TfOMe_2Si)_2MeSi(SiMe_2Ph)$: $\delta = +48.4, -15.4, -85.5$ ppm; **6** $(HMe_2Si)MeSi(SiMe_2Ph)_2$: $\delta = -15.4, -34.4, -87.3$ ppm; **7** $(HMe_2Si)_2MeSi(SiMe_2Ph)$: $\delta = -15.3, -34.5, -80.0$ ppm.

Tetrakis(dimethylphenylsilyl)silane (**8**)

Compound **8** was prepared as described in Ref. [8] by the reaction of phenyldimethylchlorosilane and $SiCl_4$ with Li in a yield of less than 10%. An alternative reaction attempt with phenyldimethylsilyllithium and $SiCl_4$ did not give an improved yield. Detailed spectroscopic data were recorded and single crystals suitable for X-ray structure analysis were grown from acetone. ^1H NMR (C_6D_6): $\delta = 7.22$–7.30 (m, 8H), 7.10–7.18 (m, 12H), 0.41 (s, 24H) ppm; ^{13}C NMR (C_6D_6): $\delta = 140.9, 134.7, 128.7, 128.0, 1.5$ ppm; ^{29}Si NMR (C_6D_6): $\delta = -12.8, -129.7$ ppm.

Tris(dimethylsilyl)methylsilane (**9**, $C_7H_{24}Si_4$)

A solution of 4.00 g **2b** (7.00 mmol) in 100 cm^3 diethyl ether was cooled to 0°C and 4.4 cm^3 2.4 *M* $LiAlH_4$ (10.56 mmol) solution in diethyl ether were added dropwise. After complete addition the reaction was stirred at ambient temperature for another 16 h after which the solution was cautiously (!) added dropwise to a mixture of diethyl ether/ice/2 *N* H_2SO_4. The aqueous layer was saturated with NaCl and extracted twice with diethyl ether. The combined organic phases were dried (Na_2SO_4) and evaporated to leave 1.35 g **9** (6.1 mmol, 87%) as a colourless oil. ^{1}H NMR (C_6D_6): $\delta = 3.92$ (m, 3H), 0.23 (s, 18H), 0.21 (s, 3H) ppm; ^{29}Si NMR (C_6D_6): $\delta = -35.2$ (d, $J = 195$ Hz), -88.9 ppm.

Tris(methyldiphenylsilyl)methylsilane (**10**, $C_{40}H_{42}Si_4$)

A solution of 6.20 g methyltrichlorsilane (41.2 mmol) in 150 cm^3 ether was cooled to −70°C. Methyldiphenylsilyllithium (prepared from 30.0 g methyldiphenylchlorosilane (128.9 mmol) and 6.0 g Li) in 200 cm^3 *THF* was added dropwise. The reaction was allowed to warm up to room temperature, and was heated to reflux for another 24 h. The solution was poured on 2 *N* H_2SO_4/ice and the aqueous layer extracted several times with ether, dried (Na_2SO_4), and the solvent removed in vacuum. The remaining residue was dissolved in *n*-pentane and after crystallisation at −70°C 8.6 g **10** (33%) were obtained as colourless crystals. ^{1}H NMR ($CDCl_3$): $\delta = 7.33$ (m, 12H), 7.21 (m, 18H), 0.55 (d, $J = 2$ Hz, 3H), 0.32 (d, $J = 2$ Hz, 9H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 137.6$, 135.3, 129.0, 128.0, −3.0, −8.5 ppm; ^{29}Si NMR (C_6D_6): $\delta = -17.3$, -84.90 ppm.

Tris(dibromomethylsilyl)methylsilane (**11**, $C_4H_{12}Br_6Si_4$)

Under the same conditions as described above for the synthesis of **2b** 2.50 g **10** (3.94 mmol) were converted to **11**. After crystallisation from *n*-pentane at −35°C 1.82 g **11** (2.79 mmol, 71%) were obtained as colourless crystals. ^{1}H NMR (C_6D_6): $\delta = 1.33$ (s, 9H), 0.51 (s, 3H) ppm; ^{29}Si NMR (C_6D_6): $\delta = 14.6$, -59.4 ppm.

Tris(methylsilyl)methylsilane (**13**, $C_4H_{18}Si_4$)

The reaction of 1.50 g **11** (2.30 mmol) with 2.9 cm^3 2.4 *M* $LiAlH_4$ (6.96 mmol) solution in diethyl ether was carried out in the same way as described above for the synthesis of **9**. After work-up 0.38 g **13** (2.14 mmol, 92%) were obtained as a colourless oil. ^{1}H NMR (C_6D_6): $\delta = 3.58$ (m, 6H), 0.28 (s, 3H), 0.21 (s, 9H) ppm; ^{29}Si NMR (C_6D_6): $\delta = -62.1$ (t, $J = 185$ Hz), -90.9 ppm.

Tris(methylphenylsilyl)methylsilane (**14**, $C_{22}H_{30}Si_4$)

To a solution of 0.60 g **10** (0.74 mmol) in 5 cm^3 toluene at 0°C 0.355 g CF_3SO_3H (2.36.1 mmol) were added dropwise. After stirring for 16 at rt complete conversion to **12** was detected by ^{29}Si NMR spectroscopy. **12** (as a mixture of two diasteromers): ^{29}Si NMR (C_6D_6): $\delta = 31.3$, 30.5, 30.4, 30.1, −82.3 ppm. After the addition of 5 cm^3 diethyl ether the mixture was cooled to 0°C and 0.6 cm^3 of a 2.0 *M* $LiAlH_4$ (1.20 mmol) solution in diethyl ether was added dropwise. After work-up of the reaction in a way analogous to the preparation of **9**, 0.21 g **13** (0.52 mmol, 70%) were obtained as a colourless solid. ^{29}Si NMR (C_6D_6): $\delta = -31.6$, -88.3 ppm; EIMS: m/z (rel.int.%) = 406 (3, $M^{+\bullet}$), 284 (74), 239 (77), 135 (76), 105 (100); HRMS: $^{12}C_{22}{}^1H_{30}{}^{28}Si_4$ calcd 406.14246, found 406.14232.

2,5-Bis(dimethylphenylsilyl)-1,6-diphenyldecamethylhexasilane (**15**, $C_{38}H_{62}Si_8$)

To a solution of 7.2 g **4** (17.7 mmol) in 100 cm^3 toluene 2.0 g Na (87 mmol) were added and the mixture was refluxed for 24 h. After filtration the solvent was removed in vacuum and the remaining residue distilled at 0.01 mm Hg. The fraction from 230 to 250° consisted of 4.2 g pure **15** (63.8%). ^{29}Si NMR (toluene): $\delta = -15.3$, -33.6, -80.5 ppm.

2,5-Bis(chlorodimethylsilyl)-1,6-dichlordecamethylhexasilane (**16**, $C_{14}H_{42}Cl_4Si_8$)

To a solution of 3.9 g **15** (5.2 mmol) in 50 cm^3 toluene 3.8 g CF_3SO_3H (25.1 mmol) were added dropwise maintaining −30°C. After completion, all volatiles were removed in vacuum and the residue was dissolved in 50 cm^3 diethyl ether. An ample excess of dry LiCl (approx 1–2 g) was added at room temperature, and the reaction mixture was stirred overnight. Diethyl ether was then removed in vacuum and 50 cm^3 petrol ether was added. Lithium salts were separated by filtration, the solvent was removed by evaporation in vacuum, and the oily residue was subjected to a fractional distillation using a short, air-cooled column. At 150–170°C (0.05 mbar), 1.7 g (57%) pure **16** solidified. The residue also contained **16**, but all attempts to obtain crystals failed. ^{29}Si NMR (toluene): **16**: $\delta = 28.6$, -34.7, -74.0 ppm; $((TfOMe_2Si)_2MeSiSiMe_2)_2$: ^{29}Si NMR: (Toluene) $\delta = +49.3$, -34.8, -79.9 ppm.

Tris(2,2-diphenyltrimethyldisilanyl)methylsilane (**17**, $C_{46}H_{60}Si_7$)
Starting with 40.1 g **2a** (124 mmol) and 37.9 g diphenylmethylsilyllithium (185 mmol) the same procedure as described for **5** was followed yielding 48.6 g **17** (97%) as colourless crystals. ^{1}H NMR (C_6D_6): $\delta = 7.52$ (m, 12H), 7.14 (m, 18H), 0.64 (s, 9H), 0.23 (s, 18H), 0.13 (s, 3H) ppm; ^{13}C NMR (C_6D_6): $\delta = 138.2$, 135.8, 128.8, 128.6, -1.2, -2.8, -7.0 ppm; ^{29}Si NMR (C_6D_6): $\delta = -18.4$, -39.2, -69.0 ppm; EIMS: m/z (rel.int.%) = 611 ($M^+ - Ph_2MeSi$, 7) 553 (3), 487 (5), 457 (9), 415 (11), 313 (14), 197 (100), 135 (63).

Tris(2,2-dibromotrimethyldisilanyl)methylsilane (**18**, $C_{10}H_{30}Br_6Si_7$)
Compound **17** (2.90 g, 3.58 mmol) was treated with about 15 cm^3 HBr as described above for **2a**. After crystallisation from *n*-pentane 2.90 g **18** (3.51 mmol, 98%) were obtained as colourless crystals. ^{1}H NMR (C_6D_6): $\delta = 1.01$ (s, 9H), 0.46 (s, 3H), 0.35 (s, 18H) ppm; ^{13}C NMR (C_6D_6): $\delta = 10.1$, -2.0, -8.4 ppm; ^{29}Si NMR (toluene): $\delta = 25.7$, -29.7, -75.8 ppm.

*Tris(1,1,2-trimethyldisilanyl)methylsilane (***19,** $C_{10}H_{36}Si_7$)
As described above for **9** a solution of 1.80 g **18** (2.18 mmol) in 20 cm^3 diethyl ether was treated with 8.7 cm^3 1.5 *M* $LiAlH_4$ (13.0 mmol) solution in diethyl ether. After work-up 0.68 g **19** (1.92 mol, 88%) were obtained as a colourless oil. ^{1}H NMR (C_6D_6): $\delta = 3.80$ (m, 6H), 0.32 (s, 18H), 0.28 (s, 3H), 0.14 (s, 9H) ppm; ^{13}C NMR (C_6D_6): $\delta = -2.5$, -10.5, -11.1 ppm; ^{29}Si NMR (C_6D_6): $\delta = -39.9$, -61.8 (t, $J = 184$ Hz), -77.0 ppm; EIMS: m/z (rel.int.%) = 352 (3, $M^{+\bullet}$), 307 (29), 247 (42), 233 (83), 155 (31), 125 (34), 73 (100); IR (neat): $\tilde{\nu} = 2113\,cm^{-1}$; HRMS: $^{12}C_{10}{}^1H_{36}{}^{28}Si_7$ calcd 352.12019, found 352.12023.

Tris(2,2-diphenyl-2-tert-butyl-dimethyldisilanyl)methylsilane (**20**, $C_{55}H_{78}Si_7$)
To ice cold Na (6.0 g, 348 mmol)/K (24.0 g, 614 mmol) alloy suspended in 500 cm^3 diethyl ether 64.0 g 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane (134 mmol) were added over a period of 4 h. The stirring was continued for 12 h. To remove excess alloy, 5 cm^3 Hg were slowly added at 0°C. The solution was transferred into a dropping funnel and added to 28.6 g ice cold **2a** (88 mmol) in 400 cm^3 diethyl ether over a period of 3 h. Stirring was continued for 12 h at rt and another 6 h at reflux. After cooling to rt the mixture was diluted with toluene and poured onto ice cold 10% H_2SO_4. After several extractions of the aqueous layer with toluene, the combined organic layers were dried (Na_2SO_4), and the solvent was removed in vacuum. The remaining residue was treated with ether and 43.2 g pure **20** (52%) were obtained as white crystals. ^{29}Si NMR (toluene): $\delta = -8.4$, -36.8, -52.4 ppm.

Tris(2,2-dibromo-2-tert-butyl-dimethyldisilanyl)methylsilane (**21**, $C_{19}H_{48}Br_6Si_7$)
A sealed glass tube charged with 9.8 g **20** (10.5 mmol) and 10 cm^3 HBr (262 mmol) was first kept at -50°C for 5 h, because the protodearylation with HBr is exothermic. Then the tube was placed in a refrigerator at -30°C for a week. By this time, all **20** was dissolved in the benzene, which had been formed. The tube was opened under N_2, and the excess of HBr and benzene were removed in vacuum. The crystalline residue was dissolved in *n*-pentane. At -70°C 6.2 g pure **21** (62%) were obtained as colourless needles. ^{1}H NMR (C_6D_6): $\delta = 1.17$ (s, 27H), 0.78 (s, 3H) 0.64 (s, 18H) ppm; ^{13}C NMR (C_6D_6): $\delta = 26.9$, 26.1, 0.6, -7.3 ppm; ^{29}Si NMR (toluene): $\delta = 34.9$, -26.1, -66.9 ppm; HRMS: $^{12}C_{19}{}^1H_{48}{}^{79}Br_6{}^{28}Si_7$ calcd 945.72411, found 945.72412.

Table 1. Crystallographic data

	5	**8**	**10**	**17**	**20**
Empirical formula	$C_{25}H_{36}Si_4$	$C_{32}H_{44}Si_5$	$C_{40}H_{42}Si_4$	$C_{46}H_{60}Si_7$	$C_{55}H_{78}Si_7$
M_w	448.90	569.12	635.10	809.57	935.80
Temperature/K	243(1)	293(2)	213(1)	213(1)	100(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Size/mm	0.40×0.05×0.05	0.70×0.50×0.40	0.58×0.43×0.28	0.47×0.43×0.28	0.50×0.35×0.05
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2(1)/c$	$C2/c$	P-1	$C2/c$	$P2(1)/c$
a/Å	15.650(3)	16.4476(2)	10.634(2)	20.297(4)	32.910(7)
b/Å	20.166(4)	9.93780(10)	12.445(3)	20.089(4)	13.956(3)
c/Å	8.8766(18)	22.30910(10)	14.973(3)	25.972(5)	25.287(5)
α/°	90	90	77.44(3)	90	90
β/°	96.80(3)	110.8940(10)	75.32(3)	105.69(3)	104.58(3)
γ/°	90	90	76.46(3)	90	90
V/Å^3	2781.8(10)	3406.70(6)	1837.0(7)	10195(4)	11241(4)
Z	4	4	2	8	4
ρ_{calc}/(g/cm^3)	1.072	1.110	1.148	1.055	1.106
Absorption coefficient/mm^{-1}	0.223	0.228	0.188	0.215	0.203
F(000)	968	1224	676	3472	4048
θ range/°	$1.65 < \theta < 23.29$	$1.95 < \theta < 20.82$	$1.71 < \theta < 24.71$	$1.52 < \theta < 24.71$	$1.68 < \theta < 23.26$
Reflections collected/unique	12332/3996	1785/1785	12748/6236	35126/8691	67674/16123
Completeness to θ/%	99.7	99.8	99.3	99.9	99.8
Absorption correction	SADABS	none	SADABS	SADABS	SADABS
Data/restraints/ parameters	3996/0/270	1785/0/169	6236/0/401	8691/0/488	16123/0/1149
Goodness of fit on F^2	0.968	1.128	1.060	1.047	1.028
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0634$, $wR2 = 0.1231$	$R1 = 0.0548$, $wR2 = 0.1500$	$R1 = 0.0431$, $wR2 = 0.1170$	$R1 = 0.0447$, $wR2 = 0.1233$	$R1 = 0.0822$, $wR2 = 0.1704$
R indices (all data)	$R1 = 0.1230$, $wR2 = 0.1441$	$R1 = 0.0568$, $wR2 = 0.1530$	$R1 = 0.0498$, $wR2 = 0.1221$	$R1 = 0.0537$, $wR2 = 0.1290$	$R1 = 0.1390$, $wR2 = 0.1958$
Largest diff. peak/hole/(e$^-$/Å^3)	0.192/−0.204	0.424/−0.334	0.300/−0.182	0.359/−0.180	0.329/−0.317

X-Ray Structure Analysis

Crystals were mounted onto the tip of a glass fibre, and data collection was performed on BRUKER-AXS SMART 1000 or SMART APEX CCD diffractometers (Table 1). Data were reduced to F_0^2 and corrected for absorption effects with SAINT [19] and SADABS [20]. All structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97) [21].

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