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One-Step Conversion of Methoxysilanes to Aminosilanes: A Convenient Synthetic Strategy to *N*,*O*-Functionalised Organosilanes

Jonathan O. Bauer and Carsten Strohmann*

Anorganische Chemie, Technische Universität Dortmund, Otto-Hahn-Straße 6, 44227 Dortmund, Germany

Fax: (+49) 231-755-3797; Tel: (+49) 231-755-3807; E-mail: mail@carsten-strohmann.de

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1. Experimental Procedures and Characterisation Data

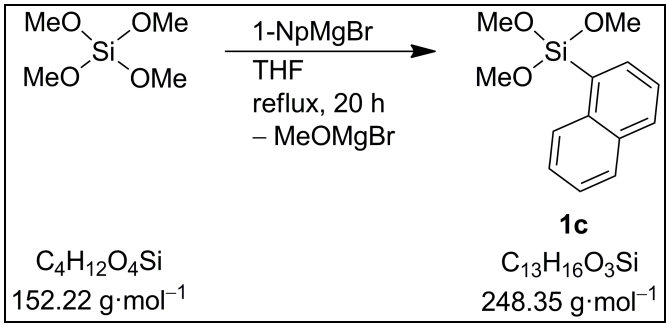
1.1 General remarks

All reactions with oxygen- and moisture-sensitive compounds were performed under an atmosphere of argon in dried solvents, which were distilled prior to use. The NMR solvent C_6D_6 was dried over sodium. All commercially available reagents were used without further purification.

The NMR spectra were measured on a *Bruker Avance DPX-300*, a *Bruker Avance DRX-400* and on a *Bruker Avance DRX-500* NMR spectrometer. Chemical shifts (δ) are indicated in ppm relative to the external standard of tetramethylsilane (δ = 0.0). For the assignment of the multiplicities the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Aromatic carbon and hydrogen atoms were assigned as follows: i = ipso, o = ortho, m = meta, p = para. Melting points were obtained using a *Büchi M-560* melting point apparatus. Elemental analysis was performed on a *Leco Instrument CHNS-932* apparatus. Mass spectra were obtained using a *HP 5973 MSD*, *6890 GC* system and an *Agilent Technologies 5975C VL MSD*, 7890 *GC* system. Single crystal structure determination was performed on an *Oxford Diffraction Xcalibur S* diffractometer.

1.2 Synthesis of the Starting Compounds

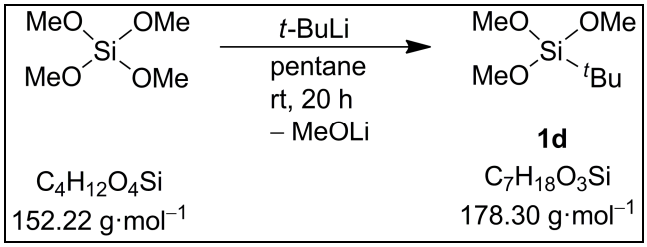
(Trimethoxy)naphthylsilane (1c)



1-Naphthylmagnesiumbromide was prepared starting with magnesium turnings (0.9 eq., 1.93 g, 79.2 mmol) and 1-naphthylbromide (1.0 eq., 18.2 g, 88.0 mmol) in THF (100 ml). After the mixture had been heated under refluxation for further 30 min it was added dropwise to a stirred solution of tetramethoxysilane (1.2 eq., 16.1 g, 106 mmol) in THF (250 ml) at 0 °C and heated for 20 h under refluxation. All insoluble components were filtered off and the filtrate was liberated from all volatiles under reduced pressure. The residue was again solved in pentane (300 ml) and filtered. After the solvent had been removed under reduced pressure the crude product was finally purified by Kugelrohr distillation (temperature: 80 °C; pressure: $1.0 \cdot 10^{-3}$ mbar) to yield **1c** (13.3 g, 53.6 mmol, 68%) as a colourless oil that crystallises at room temperature.

^{1}H-NMR (500.1 MHz, C_6D_6): δ = 3.49 [s, 9H; Si(OC*H*$_3$)$_3$], 7.25-7.32 (m, 2H; C*H*-naphthyl), 7.38-7.41 (m, 1H; C*H*-naphthyl), 7.63, 7.65 (d, 1H; C*H*-naphthyl), 7.69, 7.71 (d, 1H; C*H*-naphthyl), 8.15-8.17 (dd, 1H; C*H*-naphthyl), 8.64, 8.66 (d, 1H; C*H*-naphthyl). **{^{1}H}^{13}C-NMR** (100.6 MHz, C_6D_6): δ = 50.9 (3C) [Si(O*C*H$_3$)$_3$], 125.7 (1C) (*C*-naphthyl), 126.4 (1C) (*C*-naphthyl), 127.2 (1C) (*C*-naphthyl), 129.3 (1C) (*C*-naphthyl), 129.4 (1C) (*C*-naphthyl), 129.4 (1C) (*C*-naphthyl), 132.0 (1C) (*C*-naphthyl), 134.3 (1C) (*C*-naphthyl), 136.9 (1C) (*C*-naphthyl), 138.1 (1C) (*C*-naphthyl). **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –52.7 (1Si) [*Si*(OCH$_3$)$_3$]. **CHN Analysis:** $C_{13}H_{16}O_3Si$ calculated: C 62.87%, H 6.49%; found: C 62.5%, H 6.3%. **GC/EI-MS** [50 °C (1 min) – 300 °C (5 min) with 40 °C·min^{-1}], (70 eV, t_R = 6.05 min): m/z (%) = 248 (100) [M^+], 217 (25) [(M – OMe)$^+$], 187 (8) [{NpSi(OMe)H}$^+$], 128 (61) [(NpH)$^+$], 121 (32) [(M – Np)$^+$].

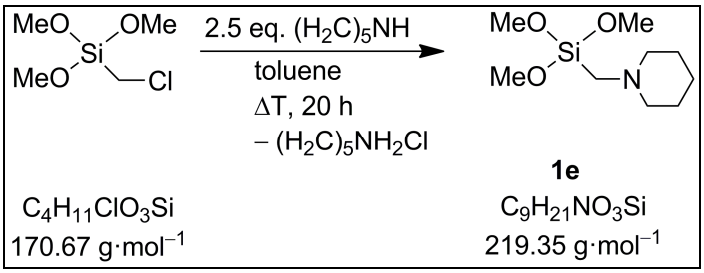
(*tert*-Butyl)trimethoxysilane (1d)



tert-Butyllithium (1.2 eq., 36.8 ml of a 1.9 M solution in pentane, 70.0 mmol) was added to a stirred solution of tetramethoxysilane (1.0 eq., 8.87 g, 58.3 mmol) in pentane (250 ml) at –78 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred for further 20 h. After all insoluble components had been filtered off the filtrate was concentrated under reduced pressure. Finally, the crude product was purified by Kugelrohr distillation (temperature: 60 °C; pressure: 25 mbar) to yield **1d** (7.83 g, 43.9 mmol, 75%) as a colourless liquid.

^{1}H-NMR (400.1 MHz, C_6D_6): δ = 1.13 [s, 9H; C(C*H*$_3$)$_3$], 3.47 (s, 9H; Si(OC*H*$_3$)$_3$]. **{^{1}H}^{13}C-NMR** (100.6 MHz, C_6D_6): δ = 18.5 (1C) [*C*(CH$_3$)$_3$], 27.0 (3C) [C(*C*H$_3$)$_3$], 51.4 (3C) [Si(O*C*H$_3$)$_3$]. **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –45.6 (1Si) [*Si*(OCH$_3$)$_3$]. **CHN Analysis:** $C_7H_{18}O_3Si$ calculated: C 47.15%, H 10.18%; found: C 47.0%, H 10.2%. **GC/EI-MS** [50 °C (1 min) – 300 °C (5 min) with 40 °C·min^{-1}], (70 eV, t_R = 2.75 min): m/z (%) = 178 (11) [M^+], 147 (2) [(M – OMe)$^+$], 121 (100) [(M – *t*-Bu)$^+$], 91 (90) [{HSi(OMe)$_2$}$^+$].

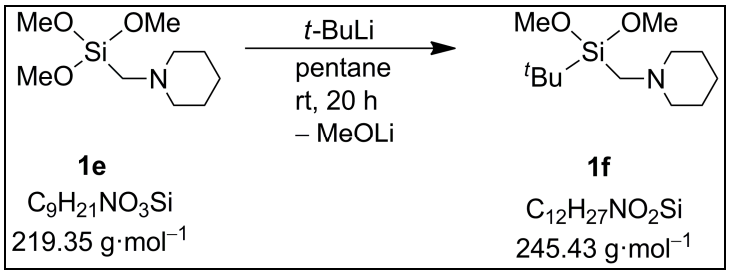
Trimethoxy(piperidinomethyl)silane (1e)



According to a procedure by *Tacke et al.*,[1] a stirred solution of trimethoxy(chloromethyl)silane (1.0 eq., 20.0 g, 117 mmol) and piperidine (2.5 eq., 24.9 g, 293 mmol) in toluene (200 ml) was heated under refluxation for 20 h. After all volatiles had been removed under reduced pressure the residue was again solved in pentane (100 ml). All insoluble components were filtered off and the filtrate was liberated from the solvent under reduced pressure. Finally, the crude product was purified by Kugelrohr distillation (temperature: 90 °C; pressure: $1.0 \cdot 10^{-3}$ mbar) to yield **1e** (15.4 g, 70.2 mmol, 60%) as a colourless liquid.

^{1}H-NMR (400.1 MHz, C_6D_6): δ = 1.20-1.30 (m, 2H; $NCH_2CH_2CH_2$), 1.48-1.53 (m, 4H; $NCH_2CH_2CH_2$), 2.04 (s, 2H; $SiCH_2N$), 2.30-2.50 (m, 4H; $NCH_2CH_2CH_2$), 3.50 [s, 9H; $Si(OCH_3)_3$]. **{^{1}H}^{13}C-NMR** (100.6 MHz, C_6D_6): δ = 24.6 (1C) ($NCH_2CH_2CH_2$), 27.2 (2C) ($NCH_2CH_2CH_2$), 45.2 (1C) ($SiCH_2N$), 50.8 (3C) [$Si(OCH_3)_3$], 58.9 (2C) ($NCH_2CH_2CH_2$). **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –48.9 (1Si) [$Si(OCH_3)_3$]. **CHN Analysis:** $C_9H_{21}NO_3Si$ calculated: C 49.28%, H 9.65%, N 6.39%; found: C 49.2%, H 9.5%, N 6.7%. **GC/EI-MS** [50 °C (1 min) – 300 °C (5 min) with 40 °C·min^{-1}], (70 eV, t_R = 4.46 min): m/z (%) = 219 (21) [M^+], 204 (9) [$(M - Me)^+$], 121 (16) [$(M - H_2CNC_5H_{10})^+$], 98 (100) [$(H_2CNC_5H_{10})^+$], 91 (19) [$\{HSi(OMe)_2\}^+$].

(*tert*-Butyl)dimethoxy(piperidinomethyl)silane (1f)

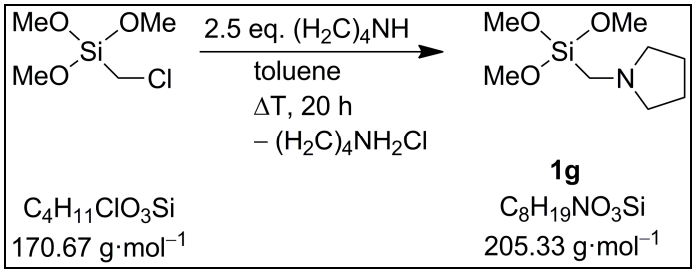


tert-Butyllithium (1.0 eq., 4.08 ml of a 1.9 M solution in pentane, 7.75 mmol) was added to a stirred solution of **1e** (1.0 eq., 1.70 g, 7.75 mmol) in pentane (30 ml) at –60 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred for further 20 h. After all insoluble components had been filtered off the filtrate was liberated from all volatiles under reduced pressure.

Finally, the crude product was purified by Kugelrohr distillation (temperature: 75 °C; pressure: $1.0 \cdot 10^{-3}$ mbar) to yield **1f** (1.69 g, 6.89 mmol, 89%) as a colourless liquid.

^{1}H-NMR (400.1 MHz, C_6D_6): δ = 1.15 [s, 9H; C(C*H*$_3$)$_3$] 1.24-1.35 (m, 2H; NCH$_2$CH$_2$C*H*$_2$), 1.47-1.53 (m, 4H; NCH$_2$C*H*$_2$CH$_2$), 2.00 (s, 2H; SiC*H*$_2$N), 2.22-2.55 (m, 4H; NC*H*$_2$CH$_2$CH$_2$), 3.47 [s, 6H; Si(OC*H*$_3$)$_2$]. **{^{1}H}^{13}C-NMR** (100.6 MHz, C_6D_6): δ = 20.0 (1C) [*C*(CH$_3$)$_3$], 24.7 (1C) (NCH$_2$CH$_2$*C*H$_2$), 26.9 (3C) [C(*C*H$_3$)$_3$], 27.2 (2C) (NCH$_2$*C*H$_2$CH$_2$), 45.6 (1C) (Si*C*H$_2$N), 51.3 (2C) [Si(O*C*H$_3$)$_2$], 59.1 (2C) (N*C*H$_2$CH$_2$CH$_2$). **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –12.4 (1Si) [*Si*(OCH$_3$)$_2$]. **CHN Analysis:** $C_{12}H_{27}NO_2Si$ calculated: C 58.72%, H 11.09%, N 5.71%; found: C 58.9%, H 11.2%, N 5.6%. **GC/EI-MS** [50 °C (5 min) – 280 °C (20 min) with 10 °C·min^{-1}], (70 eV, t_R = 15.56 min): m/z (%) = 245 (3) [M^+], 230 (1) [(M – Me)$^+$], 188 (7) [(M – *t*-Bu)$^+$], 98 (100) [(H$_2$CNC$_5$H$_{10}$)$^+$].

Trimethoxy(pyrrolidinomethyl)silane (1g)

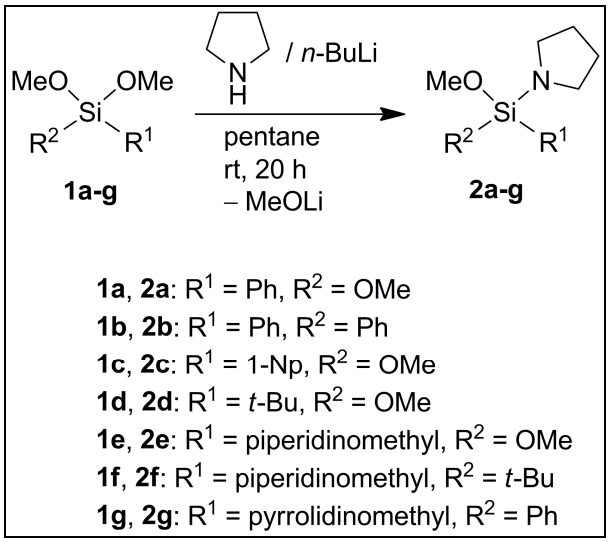


According to a procedure by *Tacke et al.*,[1] a stirred solution of trimethoxy(chloromethyl)silane (1.0 eq., 21.4 g, 125 mmol) and pyrrolidine (2.5 eq., 22.3 g, 313 mmol) in toluene (200 ml) was heated under refluxation for 20 h. After all volatiles had been removed under reduced pressure the residue was again solved in pentane (200 ml). All insoluble components were filtered off and the filtrate was liberated from the solvent under reduced pressure. Finally, the crude product was purified by Kugelrohr distillation (temperature: 50 °C; pressure: $1.0 \cdot 10^{-3}$ mbar) to yield **1g** (20.7 g, 101 mmol, 81%) as a colorless liquid.

^{1}H-NMR (300.1 MHz, C_6D_6): δ = 1.58-1.62 (m, 4H; NCH$_2$C*H*$_2$), 2.14 (s, 2H; SiC*H*$_2$N), 2.44-2.49 (m, 4H; NC*H*$_2$CH$_2$), 3.49 [s, 9H; Si(OC*H*$_3$)$_3$]. **{^{1}H}^{13}C-NMR** (75.5 MHz, C_6D_6): δ = 24.8 (2C) (NCH$_2$*C*H$_2$), 40.4 (1C) (Si*C*H$_2$N), 50.8 (3C) [Si(O*C*H$_3$)$_3$], 58.5 (2C) (N*C*H$_2$CH$_2$). **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –48.5 (1Si) [*Si*(OCH$_3$)$_3$]. **CHN Analysis:** $C_8H_{19}NO_3Si$ calculated: C 46.80%, H 9.33%, N 6.82%; found: C 46.7%, H 9.4%, N 7.1%. **GC/EI-MS** [50 °C (1 min) – 300 °C (5 min) with 40 °C·min^{-1}], (70 eV, t_R = 4.15 min): m/z (%) = 205 (30) [M^+], 204 (81) [(M – H)$^+$], 190 (7) [(M – Me)$^+$], 121 (20) [(M – H$_2$CNC$_4$H$_8$)$^+$], 91 (23) [{HSi(OMe)$_2$}$^+$], 84 (100) [(H$_2$CNC$_4$H$_8$)$^+$].

1.3 Synthesis of the Aminosilanes 2a-g

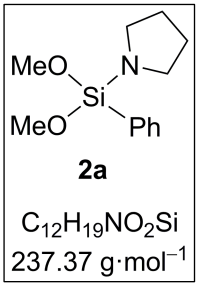
General Procedure



n-Butyllithium (1.0 eq.) was added to a stirred solution of pyrrolidine (1.0 eq.) in pentane at –30 °C. The reaction mixture was stirred for 1 h at 0 °C and then the respective methoxysilane (**1a-g**, 1.0 eq.) was added to the suspension of the lithium amide at –60 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred for further 20 h. After all insoluble components had been filtered off the filtrate was liberated from all volatiles under reduced pressure. Finally, the crude product was purified by Kugelrohr distillation to yield a colourless or pale yellow oil.

(Dimethoxy)(phenyl)pyrrolidinosilane (2a)

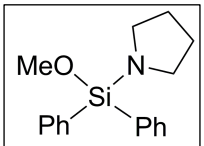
According to the general procedure, *n*-BuLi (4.04 ml of a 2.5 M solution in hexane, 10.1 mmol), pyrrolidine (718 mg, 10.1 mmol) and **1a** (2.0 g, 10.1 mmol) in pentane (50 ml) gave **2a** (1.92 g, 8.09 mmol, 80%) as a colourless liquid after Kugelrohr distillation (temperature: 75 °C; pressure: $1.0 \cdot 10^{-3}$ mbar).



^{1}H-NMR (400.1 MHz, C_6D_6): δ = 1.49-1.57 (m, 4H; NCH_2CH_2), 3.08-3.13 (m, 4H; NCH_2CH_2), 3.49 [s, 6H; $Si(OCH_3)_2$], 7.23-7.28 (m, 3H; *CH*-m, *CH*-p), 7.79-7.85 (m, 2H; *CH*-o). **{^{1}H}^{13}C-NMR** (75.5 MHz, C_6D_6): δ = 27.3 (2C) (NCH_2CH_2), 47.1 (2C) (NCH_2CH_2), 50.6 (2C) [$Si(OCH_3)_2$], 128.5 (2C) (*C*-m), 130.6 (1C) (*C*-p), 133.7 (1C) (*C*-i), 135.7 (2C) (*C*-o). **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –43.8 (1Si) [*Si*$(OCH_3)_2$]. **GC/EI-MS** [50 °C (1 min) – 300 °C (5 min) with 40 °C·min^{-1}], (70 eV, t_R = 5.34 min): m/z (%) = 237 (41) [M^+], 236 (100) [$(M - H)^+$], 167 (73) [$(M - NC_4H_8)^+$], 137 (24) [{PhSi(OMe)H}$^+$], 91 (21) [{$HSi(OMe)_2$}$^+$], 77 (3) [Ph^+], 70 (5) [$(NC_4H_8)^+$].

Methoxy(diphenyl)pyrrolidinosilane (2b)

According to the general procedure, *n*-BuLi (4.91 ml of a 2.5 M solution in hexane, 12.28 mmol), pyrrolidine (873 mg, 12.28 mmol) and **1b** (3.0 g, 12.28 mmol) in pentane (25 ml) gave **2b** (2.98 g, 10.51 mmol, 86%) as a colourless oil after Kugelrohr distillation (temperature: 135 °C; pressure: $1.0 \cdot 10^{-3}$ mbar).



2b

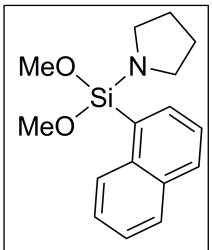
$C_{17}H_{21}NOSi$

283.44 g·mol^{-1}

^{1}H-NMR (400.1 MHz, C_6D_6): δ = 1.49-1.56 (m, 4H; NCH_2CH_2), 3.05-3.10 (m, 4H; NCH_2CH_2), 3.57 (s, 3H; $SiOCH_3$), 7.21-7.26 (m, 6H; C*H*-m, C*H*-p), 7.78-7.83 (m, 4H; C*H*-o). **{^{1}H}^{13}C-NMR** (75.5 MHz, C_6D_6): δ = 27.4 (2C) (NCH_2CH_2), 48.1 (2C) (NCH_2CH_2), 51.1 (1C) ($SiOCH_3$), 128.5 (4C) (*C*-m), 130.4 (2C) (*C*-p), 135.7 (2C) (*C*-i), 135.9 (4C) (*C*-o). **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –25.2 (1Si) ($SiOCH_3$). **CHN Analysis:** $C_{17}H_{21}NOSi$ calculated: C 72.04%, H 7.47%, N 4.94%; found: C 72.0%, H 7.7%, N 4.3%. **GC/EI-MS** [50 °C (5 min) – 290 °C (10 min) with 10 °C·min^{-1}], (70 eV, t_R = 10.97 min): m/z (%) = 283 (100) [M^+], 213 (77) [(M – NC_4H_8)$^+$], 183 (52) [(Ph_2SiH)$^+$], 137 (10) [{PhSi(OMe)H}$^+$], 70 (17) [(NC_4H_8)$^+$].

(Dimethoxy)(naphth-1-yl)pyrrolidinosilane (2c)

According to the general procedure, *n*-BuLi (6.48 ml of a 2.5 M solution in hexane, 16.19 mmol), pyrrolidine (1.15 g, 16.19 mmol) and **1c** (4.02 g, 16.19 mmol) in pentane (100 ml) gave **2c** (3.57 g, 12.42 mmol, 77%) as a pale yellow oil after Kugelrohr distillation (temperature: 140 °C; pressure: $1.0 \cdot 10^{-3}$ mbar).



2c

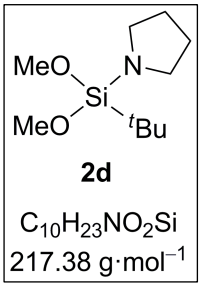
$C_{16}H_{21}NO_2Si$

287.43 g·mol^{-1}

^{1}H-NMR (300.1 MHz, C_6D_6): δ = 1.43-1.57 (m, 4H; NCH_2CH_2), 3.08-3.17 (m, 4H; NCH_2CH_2), 3.52 [s, 6H; $Si(OCH_3)_2$], 7.27-7.46 (m, 3H; C*H*-naphthyl), 7.66-7.74 (m, 2H; C*H*-naphthyl), 8.25, 8.27 (d, 1H; C*H*-naphthyl), 8.64, 8.67 (d, 1H; C*H*-naphthyl). **{^{1}H}^{13}C-NMR** (75.5 MHz, C_6D_6): δ = 27.3 (2C) (NCH_2CH_2), 47.0 (2C) (NCH_2CH_2), 50.6 (2C) [$Si(OCH_3)_2$], 125.8 (1C) (*C*-naphthyl), 126.2 (1C) (*C*-naphthyl), 126.8 (1C) (*C*-naphthyl), 129.3 (1C) (*C*-naphthyl), 129.5 (1C) (*C*-naphthyl), 131.5 (1C) (*C*-naphthyl), 131.7 (1C) (*C*-naphthyl), 134.3 (1C) (*C*-naphthyl), 137.0 (1C) (*C*-naphthyl), 138.4 (1C) (*C*-naphthyl). **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –42.8 (1Si) [$Si(OCH_3)_2$]. **CHN Analysis:** $C_{16}H_{21}NO_2Si$ calculated: C 66.86%, H 7.36%, N 4.87%; found: C 67.0%, H 7.4%, N 4.8%. **GC/EI-MS** [50 °C (1 min) – 300 °C (5 min) with 40 °C·min^{-1}], (70 eV, t_R = 6.77 min): m/z (%) = 287 (75) [M^+], 286 (100) [(M – H)$^+$], 217 (68) [(M – NC_4H_8)$^+$], 187 (15) [{NpSi(OMe)H}$^+$].

tert-Butyl(dimethoxy)pyrrolidinosilane (2d)

According to the general procedure, *n*-BuLi (3.34 ml of a 2.5 M solution in hexane, 8.36 mmol), pyrrolidine (595 mg, 8.36 mmol) and **1d** (1.49 g, 8.36 mmol) in pentane (50 ml) gave **2d** (726 mg, 3.34 mmol, 40%) as a colourless liquid after Kugelrohr distillation (temperature: 60 °C; pressure: $1.0 \cdot 10^{-3}$ mbar).



2d

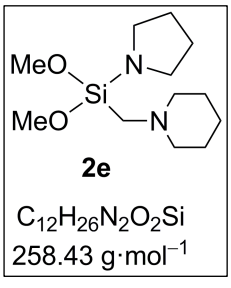
$C_{10}H_{23}NO_2Si$

217.38 g·mol^{-1}

^{1}H-NMR (400.1 MHz, C_6D_6): δ = 1.18 [s, 9H; C(CH_3)$_3$], 1.53-1.56 (m, 4H; NCH$_2$CH_2), 3.06-3.09 (m, 4H; NCH_2CH$_2$), 3.47 [s, 6H; Si(OCH_3)$_2$]. **{^{1}H}^{13}C-NMR** (100.6 MHz, C_6D_6): δ = 20.1 (1C) [*C*(CH$_3$)$_3$], 27.2 (2C) (NCH$_2$*C*H$_2$), 27.5 (3C) [C(*C*H$_3$)$_3$], 47.6 (2C) (N*C*H$_2$CH$_2$), 51.1 (2C) [Si(O*C*H$_3$)$_2$]. **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –34.6 (1Si) [*Si*(OCH$_3$)$_2$]. **CHN Analysis:** $C_{10}H_{23}NO_2Si$ calculated: C 55.25%, H 10.66%, N 6.44%; found: C 55.1%, H 10.7%, N 6.1%. **GC/EI-MS** [50 °C (1 min) – 300 °C (5 min) with 40 °C·min^{-1}], (70 eV, t_R = 4.25 min): m/z (%) = 217 (20) [M^+], 202 (1) [(M – Me)$^+$], 186 (1) [(M – OMe)$^+$], 160 (100) [(M – *t*-Bu)$^+$], 91 (33) [{HSi(OMe)$_2$}$^+$], 70 (41) [(NC$_4$H$_8$)$^+$].

Dimethoxy(piperidinomethyl)pyrrolidinosilane (2e)

According to the general procedure, *n*-BuLi (3.65 ml of a 2.5 M solution in hexane, 9.12 mmol), pyrrolidine (649 mg, 9.12 mmol) and **1e** (2.0 g, 9.12 mmol) in pentane (50 ml) gave **2e** (1.93 g, 7.47 mmol, 82%) as a colourless liquid after Kugelrohr distillation (temperature: 90 °C; pressure: $1.0 \cdot 10^{-3}$ mbar).



2e

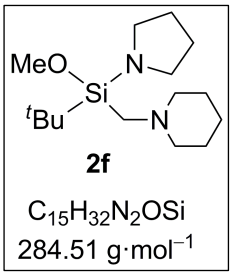
$C_{12}H_{26}N_2O_2Si$

258.43 g·mol^{-1}

^{1}H-NMR (300.1 MHz, C_6D_6): δ = 1.25-1.34 (m, 2H; NCH$_2$CH$_2$CH_2), 1.48-1.60 (m, 4H; NCH$_2$CH_2CH$_2$), 1.55-1.59 (m, 4H; NCH$_2$CH_2), 2.06 (s, 2H; SiCH_2N), 2.30-2.50 (m, 4H; NCH_2CH$_2$CH$_2$), 3.09-3.15 (m, 4H; NCH_2CH$_2$), 3.50 [s, 6H; Si(OCH_3)$_2$]. **{^{1}H}^{13}C-NMR** (75.5 MHz, C_6D_6): δ = 24.8 (1C) (NCH$_2$CH$_2$*C*H$_2$), 27.3 (2C) (NCH$_2$*C*H$_2$), 27.4 (2C) (NCH$_2$*C*H$_2$CH$_2$), 46.1 (1C) (Si*C*H$_2$N), 46.8 (2C) (N*C*H$_2$CH$_2$), 50.5 (2C) [Si(O*C*H$_3$)$_2$], 59.0 (2C) (N*C*H$_2$CH$_2$CH$_2$). **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –37.6 (1Si) [*Si*(OCH$_3$)$_2$]. **CHN Analysis:** $C_{12}H_{26}N_2O_2Si$ calculated: C 55.77%, H 10.14%, N 10.84%; found: C 55.3%, H 10.7%, N 10.3%. **GC/EI-MS** [50 °C (1 min) – 300 °C (5 min) with 40 °C·min^{-1}], (70 eV, t_R = 5.55 min): m/z (%) = 258 (26) [M^+], 243 (7) [(M – Me)$^+$], 188 (10) [(M – NC$_4$H$_8$)$^+$], 160 (18) [(M – H$_2$CNC$_5$H$_{10}$)$^+$], 98 (100) [(H$_2$CNC$_5$H$_{10}$)$^+$], 91 (16) [{HSi(OMe)$_2$}$^+$], 84 (12) [(NC$_5$H$_{10}$)$^+$], 70 (18) [(NC$_4$H$_8$)$^+$].

(*tert*-Butyl)methoxy(piperidinomethyl)pyrrolidinosilane (2f)

According to the general procedure, *n*-BuLi (0.71 ml of a 2.5 M solution in hexane, 1.77 mmol), pyrrolidine (126 mg, 1.77 mmol) and **1f** (434 mg, 1.77 mmol) in pentane (50 ml) gave **2f** (176 mg, 0.62 mmol, 35%) as a colourless oil after Kugelrohr distillation (temperature: 80 °C; pressure: $1.0 \cdot 10^{-3}$ mbar).



2f

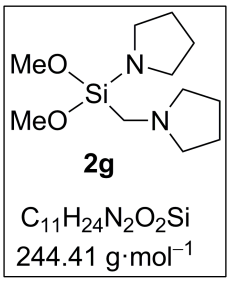
$C_{15}H_{32}N_2OSi$

284.51 g·mol^{-1}

^{1}H-NMR (400.1 MHz, C_6D_6): δ = 1.23 [s, 9H; C(CH_3)$_3$], 1.27-1.36 (m, 2H; NCH$_2$CH$_2$CH_2), 1.50-1.59 (m, 8H; NCH$_2$CH_2CH$_2$, NCH$_2$CH_2), 2.06 + 2.12 (AB-system, $^2J_{AB}$ = 14.8 Hz, 2H; SiCH_2N), 2.27-2.60 (m, 4H; NCH_2CH$_2$CH$_2$), 3.00-3.10 (m, 4H; NCH_2CH$_2$), 3.46 (s, 3H; SiOCH_3). **{^{1}H}^{13}C-NMR** (75.5 MHz, C_6D_6): δ = 21.5 (1C) [*C*(CH$_3$)$_3$], 24.8 (1C) (NCH$_2$CH$_2$*C*H$_2$), 27.3 (2C) (NCH$_2$*C*H$_2$), 27.3 (2C) (NCH$_2$*C*H$_2$CH$_2$), 27.6 (3C) [C(*C*H$_3$)$_3$], 46.3 (1C) (Si*C*H$_2$N), 48.0 (2C) (N*C*H$_2$CH$_2$), 50.8 (1C) (SiO*C*H$_3$), 59.1 (2C) (N*C*H$_2$CH$_2$CH$_2$). **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –9.6 (1Si) (*Si*OCH$_3$). **CHN Analysis:** $C_{15}H_{32}N_2OSi$ calculated: C 63.32%, H 11.34%, N 9.85%; found: C 63.0%, H 11.2%, N 9.4%. **GC/EI-MS** [50 °C (1 min) – 300 °C (5 min) with 40 °C·min^{-1}], (70 eV, t_R = 6.01 min): m/z (%) = 284 (19) [M^+], 227 (46) [(M – *t*-Bu)$^+$], 214 (7) [(M – NC$_4$H$_8$)$^+$], 186 (36) [(M – H$_2$CNC$_5$H$_{10}$)$^+$], 158 (16) [{HSi(OMe)(CH$_2$NC$_5$H$_{10}$)}$^+$], 144 (62) [{MeSi(OMe)(NC$_4$H$_8$)}$^+$], 98 (100) [(H$_2$CNC$_5$H$_{10}$)$^+$], 84 (6) [(NC$_5$H$_{10}$)$^+$].

Dimethoxy(pyrrolidinomethyl)pyrrolidinosilane (2g)

According to the general procedure, *n*-BuLi (13.64 ml of a 2.5 M solution in hexane, 34.1 mmol), pyrrolidine (2.43 g, 34.1 mmol) and **1g** (7.0 g, 34.1 mmol) in pentane (100 ml) gave **2g** (7.19 g, 29.4 mmol, 86%) as a colourless liquid after Kugelrohr distillation (temperature: 85 °C; pressure: $1.0 \cdot 10^{-3}$ mbar).



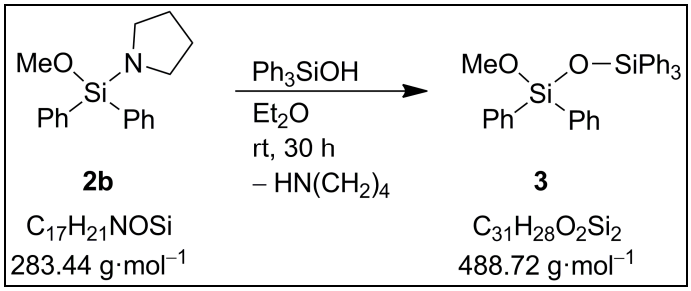
2g

$C_{11}H_{24}N_2O_2Si$

244.41 g·mol^{-1}

^{1}H-NMR (400.1 MHz, C_6D_6): δ = 1.54-1.58 (m, 4H; SiNCH$_2$CH_2), 1.63-1.66 (m, 4H; CH$_2$NCH$_2$CH_2), 2.24 (s, 2H; SiCH_2N), 2.52-2.55 (m, 4H; CH$_2$NCH_2CH$_2$), 3.13-3.17 (m, 4H; SiNCH_2CH$_2$), 3.53 [s, 6H; Si(OCH_3)$_2$]. **{^{1}H}^{13}C-NMR** (100.6 MHz, C_6D_6): δ = 24.8 (2C) (CH$_2$NCH$_2$*C*H$_2$), 27.3 (2C) (SiNCH$_2$*C*H$_2$), 41.5 (1C) (Si*C*H$_2$N), 46.8 (2C) (SiN*C*H$_2$CH$_2$), 50.5 (2C) [Si(O*C*H$_3$)$_2$], 58.5 (2C) (CH$_2$N*C*H$_2$CH$_2$). **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –37.7 (1Si) [*Si*(OCH$_3$)$_2$]. **GC/EI-MS** [50 °C (1 min) – 300 °C (5 min) with 40 °C·min^{-1}], (70 eV, t_R = 5.27 min): m/z (%) = 244 (15) [M^+], 229 (6) [(M – Me)$^+$], 174 (13) [(M – NC$_4$H$_8$)$^+$], 160 (17) [(M – H$_2$CNC$_5$H$_{10}$)$^+$], 91 (17) [{HSi(OMe)$_2$}$^+$], 84 (100) [(H$_2$CNC$_4$H$_8$)$^+$], 70 (22) [(NC$_4$H$_8$)$^+$].

1.4 Synthesis of 1-Methoxy-1,1,3,3,3-pentaphenyldisiloxane (3)



2b
$C_{17}H_{21}NOSi$
283.44 g·mol^{-1}

3
$C_{31}H_{28}O_2Si_2$
488.72 g·mol^{-1}

A solution of **2b** (1.0 eq., 530 mg, 1.87 mmol) and triphenylsilanol (1.0 eq., 517 mg, 1.87 mmol) in diethylether (10 ml) was stirred for 30 h at room temperature until reaction was completed. After all volatiles had been removed under reduced pressure product **3** was achieved in spectroscopically pure form (904 mg, 1.85 mmol, 99%). Colourless crystals of **3** were formed at 0 °C after recrystallisation from pentane/diethylether (2:1) overnight.

^{1}H-NMR (400.1 MHz, C_6D_6): δ = 3.38 (s, 3H; SiOC*H*$_3$), 7.06-7.15 (m, 15H; C*H*-m, C*H*-p), 7.73-7.78 (m, 10H; C*H*-o). **{^{1}H}^{13}C-NMR** (100.6 MHz, C_6D_6): δ = 51.3 (1C) (SiO*C*H$_3$), 128.5 (4C) (*C*-m), 128.6 (6C) (*C*-m), 130.6 (3C) (*C*-p), 130.8 (2C) (*C*-p), 134.7 (2C) (*C*-i), 135.5 (4C) (*C*-o), 135.9 (6C) (*C*-o), 136.2 (3C) (*C*-i). **{^{1}H}^{29}Si-NMR** (59.6 MHz, C_6D_6): δ = –36.0 (1Si) [*Si*Ph$_2$(OCH$_3$)], –17.9 (1Si) (*Si*Ph$_3$). **CHN Analysis:** $C_{31}H_{28}O_2Si_2$ calculated: C 76.18%, H 5.77%; found: C 75.9%, H 5.8%. **GC/EI-MS** [50 °C (1 min) – 300 °C (5 min) with 40 °C·min^{-1}], (70 eV, t_R = 11.71 min): m/z (%) = 488 (4) [M^+], 411 (100) [(M – Ph)$^+$], 334 (10) [(M – 2Ph)$^+$], 319 (9) [{M – (2Ph + Me)}$^+$], 303 (66) [{M – (2Ph + OMe}$^+$], 257 (20) [(M – 3Ph)$^+$]. **Melting Point:** 95 °C.

Single Crystal X-Ray Diffractional Analysis of 1-Methoxy-1,1,3,3,3-pentaphenyldisiloxane (3)

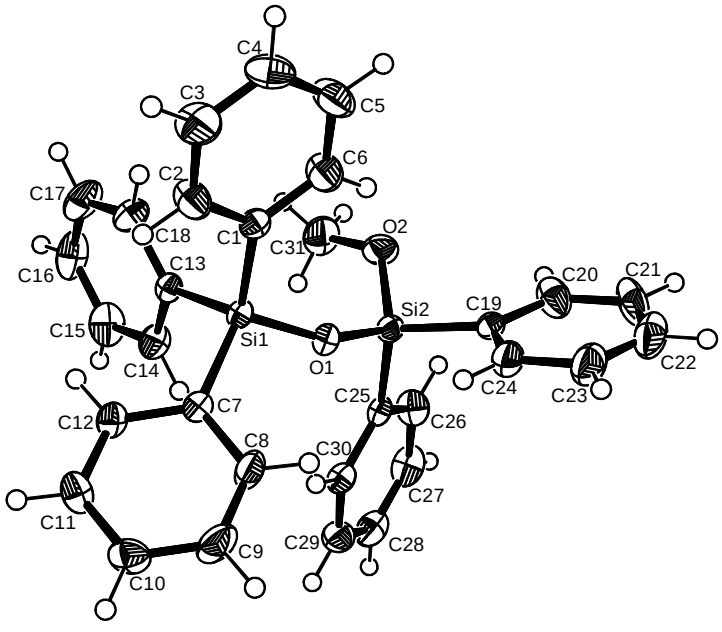


Figure 1. ORTEP plot[2] of the molecular structure of 1-methoxy-1,1,3,3,3-pentaphenyldisiloxane (**3**) in the crystal with the displacement ellipsoids drawn at the 50% probability level.

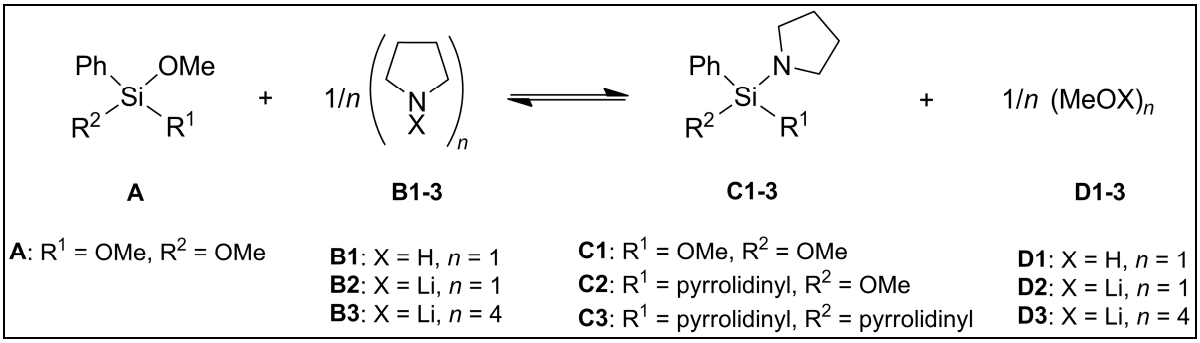
Table 1. Crystal data and structure refinement for 1-methoxy-1,1,3,3,3-pentaphenyldisiloxane (**3**).

Molecular structure in the crystal	**3**
Empirical formula	$C_{31}H_{28}O_2Si_2$
Formula weight [g·mol^{-1}]	488.71
Temperature [K]	173(2)
Wavelength [Å]	0.71073
Crystal system	Triclinic
Space group (Nr.)	$P\bar{1}$, (2)
a [Å]	8.1738(3)
b [Å]	10.1328(4)
c [Å]	16.4692(6)
α [°]	98.523(3)
β [°]	92.493(3)
γ [°]	103.426(3)
Volume [Å^3]	1307.80(9)
Z	2
Density (calculated) [g·cm^{-3}]	1.241
Absorption coefficient [mm^{-1}]	0.162
F(000)	516
Crystal size [mm^3]	0.20 x 0.20 x 0.05
Theta range for data collection [°]	2.26 – 26.00
Index ranges	$-10 \le h \le 10$ $-12 \le k \le 12$ $-20 \le l \le 20$
Reflections collected	22177
Independent reflections	5131 (R_{int} = 0.0461)
Refinement method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	5131/ 0 / 317
Goodness-of-fit on F^2	1.001
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0436, w$R2$ = 0.0958
R indices (all data)	$R1$ = 0.0680, w$R2$ = 0.0999
Largest diff. peak and hole [e·Å^{-3}]	0.435 and –0.325

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 874664. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

2. Computational Details

Optimisation and additional harmonic vibrational frequency analyses were performed with the software package Gaussian 03 (Revision E.01) on the B3LYP/6-31+G(d) level.[3] The total (SCF) and zero-point energies (ZPE) of the isolated calculated systems can be found in Table 2. Table 3 summarises the total (SCF) and zero-point energies (ZPE) of the calculated systems by applying the Polarisable Continuum Model (PCM) (Solvent: THF). The calculated standard orientations of the optimised structures can be found in Tables 4-21.



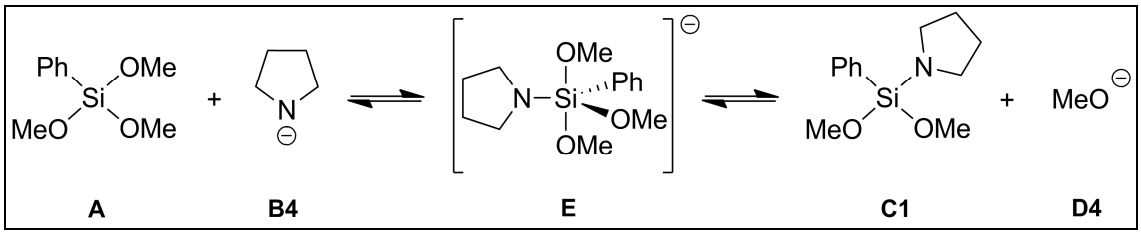


Table 2. Total (SCF) and zero-point energies (ZPE) of the optimised structures as isolated systems.

Optimised structure	Method/Basis	SCF [Hartree]	ZPE [Hartree]
A	B3LYP/6-31+G(d)	–866.690777008	–866.470815
B1	B3LYP/6-31+G(d)	–212.591036602	–212.461053
B2	B3LYP/6-31+G(d)	–219.513268875	–219.395456
B3	B3LYP/6-31+G(d)	–878.279139424	–877.799068
B4	B3LYP/6-31+G(d)	–211.956428025	–211.844233
C1	B3LYP/6-31+G(d)	–963.537486417	–963.240484
C2	B3LYP/6-31+G(d)	–1060.37833306	–1060.003877
C3	B3LYP/6-31+G(d)	–1157.21840383	–1156.766960
D1	B3LYP/6-31+G(d)	–115.725192403	–115.673893
D2	B3LYP/6-31+G(d)	–122.685636427	–122.644423
D3	B3LYP/6-31+G(d)	–491.011905403	–490.838481
D4	B3LYP/6-31+G(d)	–115.111530981	–115.076401
E	B3LYP/6-31+G(d)	–1078.70501210	–1078.368100

Table 3. Total (SCF) and zero-point energies (ZPE) of the optimised structures resulting from PCM calculations.

Optimised structure	Method/Basis	SCF [Hartree]	ZPE [Hartree]
A-PCM	B3LYP/6-31+G(d)	– 866.697673915	– 866.477916
B4-PCM	B3LYP/6-31+G(d)	– 212.043522780	– 211.930087
C1-PCM	B3LYP/6-31+G(d)	– 963.542517628	– 963.246144
D4-PCM	B3LYP/6-31+G(d)	– 115.218410809	– 115.181514
E-PCM	B3LYP/6-31+G(d)	– 1078.76315612	– 1078.425113

Table 4. Standard orientation of **A** [B3LYP/6-31+G(d)].

atomic symbol	x	y	z
C	1.18339800	–0.77024500	2.50260600
C	2.63432900	–1.73659700	–1.09724400
C	2.53741500	2.16825800	–0.53845700
H	0.11245300	–0.80438900	2.74137600
H	1.73192400	–0.43388200	3.38776300
H	1.52038200	–1.78133100	2.23876100
H	3.27584700	–1.66871700	–0.20841000
H	2.62972000	–2.77224000	–1.45062600
H	2.71328800	2.20111200	0.54210600
H	2.36775100	3.18339700	–0.91112500
H	3.04791100	–1.09679600	–1.88732900
H	3.42476400	1.75580600	–1.03569600
O	1.44623700	0.15355900	1.45218400
O	1.29132000	–1.37072400	–0.80258500
O	1.38636500	1.39123800	–0.85319300
Si	0.81872700	0.04714800	–0.08630000
C	–1.04148900	0.03286700	–0.13707600
C	–1.76650200	1.21321000	0.11520600
C	–1.76542800	–1.14630000	–0.39492300
C	–3.16333100	1.21670300	0.11362300
H	–1.23409100	2.14267500	0.30436800
C	–3.16327400	–1.14793300	–0.39589700
H	–1.22863000	–2.06698600	–0.60775200
C	–3.86431200	0.03384500	–0.14084900
H	–3.70408800	2.14031900	0.30589400
H	–3.70382500	–2.06916700	–0.60017700
H	–4.95179200	0.03470100	–0.14414200

Table 5. Standard orientation of **B1** [B3LYP/6-31+G(d)].

atomic symbol	x	y	z
C	–1.16393000	–0.44931800	0.17082400
C	1.16534400	–0.44591200	0.17064500
C	0.77783000	1.03119800	–0.05674300
C	–0.78096000	1.02880700	–0.05695400
H	–2.07381900	–0.74633400	–0.36207000
H	–1.32607400	–0.63280100	1.25078600
H	1.32823500	–0.62910800	1.25054600
H	2.07599600	–0.74014600	–0.36247300
H	1.19638200	1.68029800	0.71958200
H	1.16068500	1.38171800	–1.02063800
H	–1.20167300	1.67698000	0.71897800
H	–1.16461000	1.37774900	–1.02110400
N	0.00171300	–1.17175000	–0.35051600
H	0.00318200	–2.15476300	–0.08662800

Table 6. Standard orientation of **B2** [B3LYP/6-31+G(d)].

atomic symbol	x	y	z
C	0.25284800	–1.13510100	0.32014200
C	0.25283900	1.13512600	0.32009100
C	–1.16430300	0.77718100	–0.21529700
C	–1.16425800	–0.77721400	–0.21535000
H	0.63843800	–2.07376800	–0.10583500
H	0.18048700	–1.29104900	1.42009100
H	0.18053300	1.29116300	1.42002900
H	0.63839100	2.07376300	–0.10598300
H	–1.96308100	1.19806000	0.40922000
H	–1.30067200	1.16810500	–1.23088400
H	–1.96308400	–1.19819400	0.40903800
H	–1.30047200	–1.16806800	–1.23098600
N	1.10081000	0.00000700	–0.01041300
Li	2.70700800	–0.00000200	–0.72310700

Table 7. Standard orientation of **B3** [B3LYP/6-31+G(d)].

atomic symbol	x	y	z
Li	1.25879100	–0.25264400	0.56087600
Li	0.32030300	0.90851500	–1.34487700
Li	–0.76632400	0.99417600	0.77331500
Li	–0.68557900	–1.09831100	–0.50281800
C	0.33427100	–1.96988200	2.13415700
C	–1.55666200	–0.74632200	2.39785500

C	–0.69002200	–3.00627000	2.67522800
H	0.90185200	–1.56209000	3.00041800
H	1.06790100	–2.43771800	1.45761700
C	–1.98645100	–2.16959000	2.84977900
H	–2.39457000	–0.19103700	1.94626900
H	–1.24133800	–0.17818500	3.30147800
H	–0.83749100	–3.81483900	1.94979800
H	–0.35419700	–3.46494600	3.61294300
H	–2.78870200	–2.54908200	2.20632000
H	–2.36019200	–2.17970000	3.88069100
C	–2.91595100	–0.05066100	–1.12172400
C	–1.91932800	1.87557100	–1.78399800
C	–4.05691300	0.99787700	–1.00848000
H	–3.02261200	–0.85233600	–0.37289600
H	–2.98620100	–0.53211700	–2.12255400
C	–3.37805500	2.31485100	–1.47422100
H	–1.85238500	1.64732900	–2.87155600
H	–1.19748700	2.68273800	–1.57728400
H	–4.92671500	0.73052500	–1.62052000
H	–4.39815400	1.07907000	0.03006300
H	–3.86896400	2.75618500	–2.34982500
H	–3.39078100	3.06771600	–0.67762300
C	0.67882200	–1.73031700	–2.51666000
C	2.54993200	–1.22743900	–1.33264800
C	1.39082000	–3.10423100	–2.36862600
H	0.96935100	–1.28573400	–3.49157300
H	–0.42070700	–1.82907300	–2.56031800
C	2.66801100	–2.76052200	–1.55601300
H	3.02563300	–0.91426700	–0.38444100
H	3.12178700	–0.70577500	–2.12805500
H	0.75810200	–3.81425800	–1.82270800
H	1.61860100	–3.55454700	–3.34214300
H	2.67625700	–3.29162500	–0.59708000
H	3.59049500	–3.02819400	–2.08484500
C	2.04181200	2.50900300	–0.40430600
C	1.02709700	2.49590800	1.62509700
C	3.17697300	2.93755800	0.56733600
H	1.56528500	3.43046400	–0.80654500
H	2.43409300	1.94687900	–1.26731300
C	2.48411700	2.92143900	1.95727100
H	0.57197100	1.92318000	2.45016500
H	0.41859300	3.41859600	1.49433800

H	4.00435600	2.21946700	0.53128700
H	3.58663200	3.92220800	0.31198700
H	2.95357300	2.18733600	2.62236300
H	2.52514700	3.89429800	2.46162100
N	1.12115200	–0.90437500	–1.38508500
N	1.10631300	1.70559000	0.38998100
N	–1.66369200	0.69152500	–0.95286400
N	–0.45256600	–0.93524400	1.45084700

Table 8. Standard orientation of **B4** [B3LYP/6-31+G(d)].

atomic symbol	x	y	z
C	–1.10660300	–0.52326600	0.15633900
C	1.10661200	–0.52325400	0.15632500
C	0.77780600	1.00134700	–0.05811900
C	–0.77782100	1.00133300	–0.05813500
H	–2.06151900	–0.81329200	–0.31382600
H	–1.25542200	–0.65191100	1.27980000
H	1.25545600	–0.65191200	1.27978000
H	2.06152300	–0.81326100	–0.31386300
H	1.19692900	1.64982700	0.73118000
H	1.17701800	1.34838600	–1.02164600
H	–1.19697600	1.64983400	0.73112900
H	–1.17701400	1.34832700	–1.02168600
N	0.00000500	–1.25756500	–0.36133300

Table 9. Standard orientation of **C1** [B3LYP/6-31+G(d)].

atomic symbol	x	y	z
C	0.34323400	2.57923200	1.93201100
C	–1.31265700	2.52605400	–1.69576200
H	1.37048800	2.23071600	2.10224300
H	–0.07214600	2.93096500	2.88160100
H	0.36845600	3.41789800	1.22364400
H	–1.57333700	3.30341900	–0.96494800
H	–1.04367800	3.00813300	–2.64110400
H	–2.19168400	1.88842100	–1.85959900
O	–0.48779700	1.52512400	1.46012500
O	–0.19447000	1.76395000	–1.25931300
Si	–0.23405000	0.70690900	0.03138000
C	1.44824800	–0.11477900	–0.03864200
C	1.80175800	–1.06222800	0.94226900
C	2.39270500	0.17653500	–1.04065000

C	3.04855100	–1.69258100	0.92756400
H	1.09229000	–1.31281800	1.72917200
C	3.64120200	–0.45292500	–1.06260600
H	2.14339600	0.90325600	–1.80899900
C	3.97158000	–1.38808600	–0.07788400
H	3.29946800	–2.41987300	1.69625600
H	4.35512700	–0.21346900	–1.84741800
H	4.94234000	–1.87814000	–0.09355200
C	–1.60399200	–1.51251500	–1.00757300
C	–2.70395500	–0.44435500	0.87781200
C	–2.98160400	–2.16105000	–0.77160200
H	–0.79561600	–2.24031200	–0.83952600
H	–1.50044900	–1.14558900	–2.03794900
C	–3.26030300	–1.86504600	0.70975900
H	–3.46331500	0.29760400	0.57847300
H	–2.41292600	–0.21495000	1.90721100
H	–3.74093200	–1.67581000	–1.39863800
H	–2.98394400	–3.22949800	–1.01247200
H	–4.32151600	–1.93545400	0.97311400
H	–2.70505400	–2.56495400	1.34791600
N	–1.53439300	–0.41262800	–0.02134500

Table 10. Standard orientation of **C2** [B3LYP/6-31+G(d)].

atomic symbol	x	y	z
C	0.15075200	–1.25620400	2.81159700
H	–0.89330400	–1.59371700	2.73974900
H	0.36767500	–1.01594800	3.85775000
H	0.80764700	–2.07972600	2.49857500
O	0.38025900	–0.09033500	2.03872800
Si	0.20512800	–0.00025800	0.37383000
C	–1.64174500	–0.04883700	–0.01269000
C	–2.58426700	0.31953700	0.96787200
C	–2.13017400	–0.35657100	–1.29743300
C	–3.95193400	0.36981400	0.68347500
H	–2.24178200	0.57329500	1.96885100
C	–3.49591300	–0.30622000	–1.59124400
H	–1.43311600	–0.64339700	–2.08210600
C	–4.41154800	0.05564100	–0.59885400
H	–4.65796300	0.65344700	1.46083100
H	–3.84522700	–0.54968700	–2.59220600
H	–5.47498400	0.09286600	–0.82327200
C	1.07876400	2.03831800	–1.35570200

C	1.39124800	2.50896100	1.00452900
C	1.96359500	3.28447000	–1.20340700
H	0.08937400	2.32300200	–1.75347700
H	1.50885200	1.30281300	–2.04753600
C	1.56971900	3.80140900	0.18833900
H	2.33701200	2.21989600	1.48748400
H	0.64723400	2.62304100	1.80098600
H	3.02332500	2.99728400	–1.21494500
H	1.80181900	4.01519900	–2.00342500
H	2.31339800	4.47416100	0.62966000
H	0.61833600	4.34626100	0.12842200
N	0.98278900	1.49353400	0.00935600
C	2.39476300	–1.34259600	–0.82192800
C	0.42352900	–2.59217800	–0.84575100
C	2.82082800	–2.73835600	–0.31153200
H	2.93783900	–0.52013600	–0.34824800
H	2.56828500	–1.27358900	–1.91033300
C	1.52229300	–3.59013000	–0.39076500
H	0.25888800	–2.69326400	–1.93231200
H	–0.53954600	–2.76104300	–0.35619600
H	3.63833900	–3.15911800	–0.90789900
H	3.17325900	–2.66860600	0.72374600
H	1.61441500	–4.42507400	–1.09447800
H	1.27728900	–4.01856600	0.58747200
N	0.95858500	–1.26145600	–0.54072600

Table 11. Standard orientation of **C3** [B3LYP/6-31+G(d)].

atomic symbol	x	y	z
Si	0.05696300	0.05571100	–0.08901100
C	–1.82861500	0.21535100	–0.13722700
C	–2.67641400	–0.86297400	0.18443000
C	–2.43975300	1.42868600	–0.50426200
C	–4.06754900	–0.74177200	0.13212700
H	–2.24168700	–1.81397800	0.48789500
C	–3.83124700	1.56135700	–0.55857600
H	–1.81867200	2.28759600	–0.74780000
C	–4.64919000	0.47391500	–0.24177500
H	–4.69743000	–1.59162000	0.38594200
H	–4.27548700	2.51196600	–0.84543400
H	–5.73147400	0.57293600	–0.28180100
C	1.11470400	2.41658900	–1.32344400
C	1.31790800	2.32227500	1.07040200

C	2.33306000	3.26395600	–0.93475600
H	0.26187100	3.08164500	–1.55641200
H	1.28481600	1.79017000	–2.20449700
C	2.04396300	3.58513300	0.54123400
H	1.98926300	1.69258800	1.66942300
H	0.47875400	2.60765900	1.72366700
H	3.24667300	2.66290200	–1.02824100
H	2.44815200	4.16024800	–1.55483800
H	2.94568400	3.81733300	1.11821400
H	1.38045700	4.45662200	0.60727000
N	0.87213200	1.59296600	–0.13432800
C	1.96836500	–0.90915300	–1.97599800
C	–0.17798200	–1.75580500	–2.31237100
C	2.18382000	–2.40674000	–2.32227200
H	2.67869800	–0.53135400	–1.23427000
H	2.09617100	–0.30095000	–2.88966500
C	0.74844800	–2.98290500	–2.47856200
H	–0.38987100	–1.31109500	–3.30135000
H	–1.13901900	–2.00195800	–1.85527800
H	2.78046500	–2.52023000	–3.23454800
H	2.72338000	–2.91905600	–1.51791700
H	0.59660800	–3.48104600	–3.44292700
H	0.54244000	–3.71877100	–1.69303600
N	0.58964800	–0.81878900	–1.49160500
C	1.67858000	–1.50643400	1.62650400
C	–0.24400000	–0.51524200	2.70096900
C	1.43509800	–2.24401800	2.94948800
H	2.56397100	–0.84929200	1.72225900
H	1.86692700	–2.18920400	0.79035300
C	0.64681600	–1.20298200	3.75879700
H	–1.25145000	–0.95349200	2.68777500
H	–0.36614000	0.55400200	2.92580700
H	0.82165800	–3.13661700	2.77076000
H	2.36340500	–2.55996700	3.43853500
H	0.06019400	–1.63832000	4.57516400
H	1.33991600	–0.47590700	4.20146900
N	0.43938800	–0.74820400	1.40898900

Table 12. Standard orientation of **D1** [B3LYP/6–31+G(d)].

atomic symbol	x	y	z
C	–0.66901300	–0.02081700	0.00000000
H	–1.02889500	–0.54669400	0.89609400

H	–1.02889400	–0.54670400	–0.89608800
H	–1.08099200	0.99121400	–0.00000600
O	0.74964600	0.12298300	0.00000000
H	1.15569300	–0.75677800	0.00000000

Table 13. Standard orientation of **D2** [B3LYP/6–31+G(d)].

atomic symbol	x	y	z
C	–0.93653900	–0.00078600	0.00000000
H	–1.35504200	–0.51429000	0.88798400
H	–1.35504200	–0.51429900	–0.88797800
H	–1.35808200	1.02372700	–0.00000600
O	0.44399500	0.00214500	0.00000000
Li	2.04514600	–0.00252900	0.00000000

Table 14. Standard orientation of **D3 [**B3LYP/6–31+G(d)].

atomic symbol	x	y	z
Li	–0.00081200	0.86624700	1.22412300
Li	–0.00081200	0.86624700	–1.22412300
Li	–1.22338200	–0.86684300	0.00000000
Li	1.22430600	–0.86510500	0.00000000
O	–1.44030500	1.01769100	0.00000000
O	0.00049000	–1.01773200	1.44035200
O	1.43927400	1.01801900	0.00000000
O	0.00049000	–1.01773200	–1.44035200
C	–2.59027200	1.81617700	0.00000000
H	–2.34860200	2.89522100	0.00000000
H	–3.22456400	1.63284200	–0.88709100
H	–3.22456400	1.63284200	0.88709100
C	2.58956400	1.81604500	0.00000000
H	2.34831500	2.89518200	0.00000000
H	3.22381500	1.63252300	0.88709300
H	3.22381500	1.63252300	–0.88709300
C	0.00049000	–1.81625800	–2.59025800
H	0.88613600	–1.63113300	–3.22605600
H	0.00328500	–2.89526800	–2.34839100
H	–0.88808800	–1.63508100	–3.22310800
C	0.00049000	–1.81625800	2.59025800
H	–0.88808800	–1.63508100	3.22310800
H	0.00328500	–2.89526800	2.34839100
H	0.88613600	–1.63113300	3.22605600

Table 15. Standard orientation of **D4** [B3LYP/6–31+G(d)].

atomic symbol	x	y	z
C	0.54359600	0.00000500	0.00000000
H	1.03682100	–0.51552300	–0.89225900
H	1.03679500	–0.51498800	0.89257700
H	1.03674200	1.03052500	–0.00030500
O	–0.79649100	–0.00000600	–0.00000200

Table 16. Standard orientation of **E** [B3LYP/6–31+G(d)].

atomic symbol	x	y	z
Si	0.28087100	0.61318400	0.23706900
O	0.36718200	–0.02039600	1.90699200
C	–0.37689300	0.49240200	2.97018100
H	–0.03242500	1.49419800	3.27406100
H	–1.45632400	0.57264600	2.73994300
H	–0.27679700	–0.18720100	3.83532600
O	0.26728600	2.20682900	0.92318900
C	–0.21415300	3.40125400	0.37552100
H	–0.83916600	3.91511900	1.12601300
H	0.61559500	4.08139100	0.11402600
H	–0.81883200	3.24563900	–0.52849200
O	0.21287200	1.25634000	–1.45176300
C	1.20996300	2.05358300	–2.01579600
H	1.62486800	1.58126000	–2.92522500
H	0.80570000	3.03737800	–2.31982400
H	2.05574500	2.24059600	–1.33157500
C	2.75275200	–0.84813500	0.80352100
C	2.16475000	–0.83159200	–1.42083200
C	2.92287200	–2.32657300	0.36555900
H	2.40770000	–0.73366900	1.82999800
H	3.73224000	–0.33217300	0.70159800
C	2.52908000	–2.31514100	–1.13817000
H	3.06148800	–0.31857100	–1.83024700
H	1.35928900	–0.71976100	–2.14881400
H	3.94570900	–2.69380000	0.53219200
H	2.24390200	–2.96856600	0.93991800
H	3.34003300	–2.66872600	–1.79073000
H	1.65917300	–2.95876900	–1.31722200
N	1.78965100	–0.28046300	–0.12776300
C	–1.43384400	–0.24744400	–0.10025900
C	–2.37415000	0.23808600	–1.03324700
C	–1.79876600	–1.42068300	0.59143000

C	–3.60358100	–0.39445700	–1.25408700
H	–2.11763100	1.12145300	–1.60985700
C	–3.01502700	–2.07660400	0.36648900
H	–1.10537700	–1.81869300	1.32777700
C	–3.93074400	–1.56192900	–0.55666800
H	–4.30382600	0.02001800	–1.97959500
H	–3.25036800	–2.98726900	0.91747000
H	–4.88273000	–2.06262100	–0.73057700

Table 17. Standard orientation of **A-PCM** [B3LYP/6–31+G(d)].

atomic symbol	x	y	z
C	1.22581600	–1.03193500	2.39083100
C	2.66863100	–1.61047300	–1.19965000
C	2.51208300	2.23246900	–0.36581600
H	0.15728200	–1.14465100	2.61234600
H	1.75256200	–0.77673000	3.31430700
H	1.61496300	–1.98448300	2.01101500
H	3.26088800	–1.63460200	–0.27682800
H	2.68882000	–2.60189300	–1.65990800
H	2.67005800	2.20964000	0.71673900
H	2.35219900	3.26542000	–0.68737600
H	3.11335600	–0.88843300	–1.89485300
H	3.40221500	1.83799500	–0.86985400
O	1.44808000	0.02658400	1.45536700
O	1.30200600	–1.27969500	–0.93367000
O	1.35484000	1.47700900	–0.73507000
Si	0.81465900	0.05931800	–0.08404100
C	–1.04699100	0.04120400	–0.13182400
C	–1.77532600	1.21124300	0.16092100
C	–1.76966900	–1.13213700	–0.42196900
C	–3.17314900	1.21087200	0.16352000
H	–1.24606400	2.13534900	0.38184900
C	–3.16830100	–1.13825200	–0.42031300
H	–1.23440200	–2.04756800	–0.65920900
C	–3.87225900	0.03437300	–0.12775700
H	–3.71530400	2.12623200	0.38764400
H	–3.70673600	–2.05435200	–0.65128300
H	–4.95949100	0.03226600	–0.12869300

Table 18. Standard orientation of **B4–PCM** [B3LYP/6–31+G(d)].

atomic symbol	x	y	z
C	–1.11275000	–0.52070400	0.16299100
C	1.12130500	–0.50888600	0.15280700
C	0.77004600	1.00434300	–0.05199400
C	–0.78396100	0.99217200	–0.06492200
H	–2.06668500	–0.81548400	–0.30227500
H	–1.25363200	–0.65213700	1.27613700
H	1.28215100	–0.65038300	1.26171000
H	2.07154400	–0.78613500	–0.33053900
H	1.17819700	1.64536000	0.74419900
H	1.17289400	1.36856800	–1.00620600
H	–1.21768500	1.64561400	0.70748800
H	–1.17443100	1.32494300	–1.03560800
N	0.00568700	–1.26884200	–0.35831400

Table 19. Standard orientation of **C1–PCM** [B3LYP/6–31+G(d)].

atomic symbol	x	y	z
C	0.38054600	2.62100700	1.86477700
C	–1.35966000	2.49297700	–1.67403700
H	1.41991200	2.29071600	1.98789100
H	0.01151800	2.98789500	2.82685600
H	0.35318400	3.44273700	1.13821700
H	–1.60324900	3.26954200	–0.93771800
H	–1.12792500	2.97347400	–2.62914300
H	–2.23377400	1.84288700	–1.80593400
O	–0.46031900	1.54012900	1.45823500
O	–0.21398500	1.74248500	–1.26904800
Si	–0.23069800	0.69718900	0.03543600
C	1.45597600	–0.11928700	–0.04229800
C	1.81097100	–1.06837600	0.93755000
C	2.40183600	0.17430700	–1.04301600
C	3.05958800	–1.69695100	0.92333100
H	1.10169700	–1.32379400	1.72293500
C	3.65273400	–0.45253200	–1.06542800
H	2.15495100	0.90049700	–1.81255400
C	3.98419900	–1.38908900	–0.08104500
H	3.31046300	–2.42530600	1.69082700
H	4.36658800	–0.21038000	–1.84931200
H	4.95573400	–1.87723300	–0.09638200
C	–1.60923100	–1.52198100	–0.98172700
C	–2.69110400	–0.45398200	0.91653900

C	–3.01461800	–2.11691900	–0.78292700
H	–0.83593600	–2.28340700	–0.79600400
H	–1.46472100	–1.15350900	–2.00610100
C	–3.29903400	–1.84759800	0.70211800
H	–3.42313100	0.32542100	0.64882000
H	–2.39040200	–0.27851700	1.95410600
H	–3.74305100	–1.58333500	–1.40711100
H	–3.05692300	–3.17804900	–1.05018900
H	–4.36489600	–1.88113700	0.95228000
H	–2.77981300	–2.58596400	1.32710300
N	–1.52274900	–0.42907700	0.01268400

Table 20. Standard orientation of **D4–PCM** [B3LYP/6–31+G(d)].

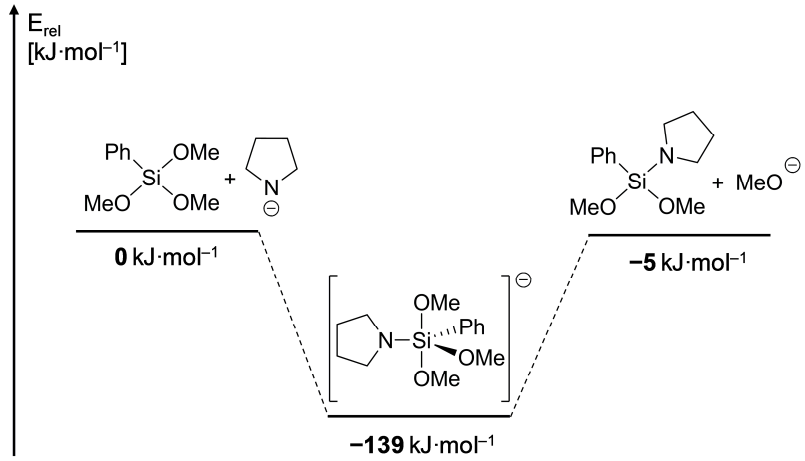
atomic symbol	x	y	z
C	–0.56772600	0.00006300	–0.00008500
H	–1.02381600	–0.15454800	1.01160000
H	–1.02438600	–0.79944200	–0.63877000
H	–1.02585600	0.95289400	–0.37183400
O	0.81005200	0.00009000	–0.00006100

Table 21. Standard orientation of **E–PCM** [B3LYP/6–31+G(d)].

atomic symbol	x	y	z
Si	0.26358100	0.63328400	0.23160700
O	0.29191700	0.04773300	1.93342300
C	–0.67215900	0.45877800	2.86012800
H	–0.55447700	1.51787100	3.14262300
H	–1.70438600	0.33518900	2.48348000
H	–0.58375800	–0.15333600	3.77261700
O	0.19853900	2.24733400	0.87733400
C	–0.34052800	3.40852800	0.29241900
H	–1.00861100	3.89982600	1.01745600
H	0.45434100	4.12551600	0.03091700
H	–0.91333600	3.19676900	–0.61866500
O	0.19756700	1.22933400	–1.47998600
C	1.17728500	2.07258700	–2.02737900
H	1.63485800	1.61431000	–2.92087500
H	0.73950700	3.03533900	–2.34278100
H	1.99380700	2.29547400	–1.32124300
C	2.73530600	–0.76480600	0.92334600
C	2.28364200	–0.72256700	–1.33501400
C	2.99083800	–2.22381500	0.46473700

H	2.32218500	–0.69230700	1.92766300
H	3.69720000	–0.21173700	0.89934900
C	2.67696600	–2.19707800	–1.05628600
H	3.18308200	–0.17114700	–1.67852600
H	1.52194100	–0.62573100	–2.10971800
H	4.01752100	–2.54883900	0.67817800
H	2.31389800	–2.90940700	0.98900200
H	3.52945700	–2.51557500	–1.67024000
H	1.83758600	–2.86223800	–1.29161700
N	1.81051800	–0.20344900	–0.05610100
C	–1.39748200	–0.29652600	–0.12384400
C	–2.51330400	0.30637600	–0.73711700
C	–1.54460300	–1.64765600	0.24842500
C	–3.70823900	–0.38996200	–0.96443000
H	–2.44552700	1.34423800	–1.05422100
C	–2.72288300	–2.36527800	0.00934600
H	–0.71364600	–2.14377500	0.74535400
C	–3.81649900	–1.73601600	–0.59766500
H	–4.55090100	0.11521800	–1.43447900
H	–2.79111800	–3.41239300	0.30123700
H	–4.73762300	–2.28569700	–0.78147100

Additional explanation concerning the formation of a pentacoordinate silicon species



Quantum chemical calculations for an isolated system with naked anions involved raise the energetic level of the substitution products. Concomitantly the pentacoordinate silicon compound becomes the energetically most favoured species by –139 kJ·mol^{-1} and hence represents the global minimum of this reaction. As presented in the article, the anionic pentavalent species may be better described by PCM computations without the consideration of metal cations due to complications in localising the charge

distribution between the molecular anion and the metal cation correctly. Furthermore, in the here presented diagram, the educts are considered virtually as stable as the products formed, taking both the strong silicon–oxygen bond and the stabilized anionic component of the starting material into account. From this point of view, the reaction seems to be an almost thermodynamically indifferent process that is drastically changed when involving solvent effects by PCM calculations or metal ion effects (as seen in the argumentation of the article).

3. Literature

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