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Synthesis and characterization of metallatranes with phenyl substituents in atrane cage

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Abstract

A new series of mono- and diphenylsubstituted silatranes and boratranes $N(CH_2CH_2O)_2(CHR^3CR^1R^2O)MZ$ (M = Si, Z = CH_2Cl, C≡CPh, H, OMenth, R^1, R^2, R^3 = H, Ph; M = B, Z = nothing, R^1, R^2, R^3 = H, Ph) have been synthesized. Both transalkoxylation and stepwise modification of a preformed metallatrane skeleton were used. The chloromethyl derivatives $N(CH_2CH_2O)_2$(CHR-CHRO)$SiCH_2Cl$ (R = H, Ph) react with *tert*-BuOK under intramolecular cycle expansion to give 1-*tert*-butoxy-2-carba-3-oxahomosilatranes $N(CH_2CH_2O)(CH_2CH_2OCH_2)$(CHRCHRO)$SiO^tBu$ (R = H, Ph). The treatment of boratranes $N(CH_2CH_2O)_2$-$(CH_2CR^1R^2O)B$ (R^1,R^2 = H, Ph) with triflic acid and trimethylsilyl triflate results in the products of electrophilic attack at the nitrogen atom. The molecular structures of four silatranes and one boratrane bearing phenyl groups in the atrane skeleton were determined by the X-ray structure analysis.

Keywords: Trialkanolamine ligands; Silatranes; Boratranes; NMR spectroscopy; Crystal structure

1. Introduction

The chemistry of the group 14 element metallatranes (Chart 1) and their analogues has attracted considerable attention from the theoretical point of view, the nature of the intramolecular M ← N interaction being the subject of interest [1]. Due to the impossibility to describe the formation of the M ← N coordination bond in the framework of the classical "octet" rule, several concepts were built up to explain the phenomenon of the so-called hypervalency. According to our recent study, the formation of this bond can be rationalized by an interaction of a lone electron pair of nitrogen atom with the LUMO of MO_3Z fragment [2]. Besides an important contribution to the bonding theory, metallatranes are valuable objects for medicinal chemistry owing to the broad spectrum of bioactivity [3,4].

While most of the research on metallatranes was focused on the variation of the apical substituent Z, the derivatives bearing different substituents at the carbon atoms of atrane moiety have been studied to a very limited extent. Among them the 3,7,10-trimethylsubstituted metallatranes are the most known [1,5,6]. However, the structural study of such derivatives seems important as providing new information concerning the intramolecular bond formation. Furthermore, metallatranes having substituents in the atrane skeleton are known to be less toxic than their unsubstituted analogues and, thus, are more promising as bioactive species.

According to the DFT calculations on nucleophilic substitution in silatranes, the reactions always proceed via a

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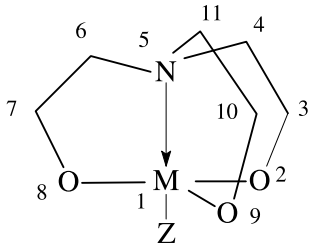


Chart 1.

hexacoordinated silicon atom and in some instances demand a considerable conformational alteration of the atrane skeleton [7]. The latter might be affected by the presence of substituents in the side arms of atrane moiety. In order to clarify whether the presence of such substituents influences the structure and reactivity of atrane molecules, a series of works on metallatranes with phenyl substituents in the atrane cage were commenced in our group.

Recently, we reported the synthesis of germatranes bearing phenyl groups at 3- and/or 4-position of atrane skeleton, and the investigation of their structure both in the solid state and in solution [8,9]. Among the 3-phenylsubstituted silatranes, only six derivatives have been reported so far in the literature [10,11]. Characterization of these compounds was limited by the elemental analysis data. Besides the group 14 metallatranes, boratranes (Chart 1, M = B, Z = nothing) fell into the scope of our interest due to the other type of intramolecular M ← N interaction (classical coordination bond) in comparison with that in silatranes and germatranes. To the best of our knowledge, no phenylboratranes as well as 4-phenylsilatranes or silatranes with two phenyl groups at carbon atoms of atrane cage have been investigated.

In continuation of our studies in atrane chemistry [12–19], we present here the synthesis and characterization of a series of mono- and diphenylsubstituted metallatranes (M = Si, Z = CH_2Cl, C≡CPh, H; M = B, Z = nothing) and their reactions with nucleophilic and electrophilic reagents. The structure of compounds **7**, **9**, **10**, **16**, **18**, and **21** was determined by the single crystal X-ray analysis.

2. Experimental

All manipulations with silicon- and boron-containing compounds were carried out under an argon atmosphere using the standard Schlenk techniques. The solvents were dried by the standard methods and distilled before use. Trimethyl borate and triethoxysilane were purified by distillation at normal pressure, and diethanolamine was purified by distillation in vacuo. (Chloromethyl)trimethoxysilane, potassium *tert*-butoxide (Aldrich), styrene oxide, trimethylsilyl triflate (Merck), and trifluoromethanesulfonic acid (Fluka) were used as supplied. *cis*- and *trans*-stilbene oxides [20,21], 2,2-diphenyloxirane [22], (phenylethynyl)trichlorosilane [23], (phenylethynyl)trimethoxysilane [24], boratrane (**26**), and 1-hydrosilatrane (**19**) [25] were synthesized according to the literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 or Bruker Avance 400 spectrometers, ^{11}B NMR spectra on a Bruker DRX 500, and ^{29}Si NMR spectra on a Bruker DRX 400 or 500 spectrometers. All chemical shifts are given in ppm (δ) relative to Me_4Si (for ^{1}H, ^{13}C, ^{29}Si) or $BF_3 \cdot Et_2O$ (for ^{11}B). IR spectra were obtained in Nujol on a Zeiss UR-20. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department, Moscow State University. Mass spectra (EI-MS, 70 eV) were recorded on a VARIAN CH-7a device (Philipps-Universität Marburg, Germany); all assignments were made with reference to the most abundant isotopes.

2.1. Synthesis of erythro-2-[bis(2-hydroxyethyl)amino]-1, 2-diphenyl-1-ethanol (3)

A mixture of $HN(CH_2CH_2OH)_2$ (1.02 g, 9.68 mmol) and *trans*-stilbene oxide (1.90 g, 9.68 mmol) was stirred for 30 h at 120 °C. The resulting material was diluted with diethyl ether (5 mL), followed by stirring for 2 days at room temperature. The solidified product was filtered, washed with ether (7 mL) and hexane (2 × 7 mL), and dried in vacuo to give **3** (2.02 g, 69%) as a slightly yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$):δ (ppm): 1.80 (br s, 3H, 3OH), 2.32–2.37 (m, 2H), 2.71–2.78 (m, 2H), 3.36–3.41 (m, 2H), 3.44–3.50 (m, 2H) [$(ABXY)_2$ system of NCH_2CH_2O protons], 3.93 (d, J = 9.3 Hz, 1H, NCH(Ph)), 5.19 (d, J = 9.3 Hz, 1H, OCH(Ph)), 7.32–7.47 (m, 10H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 52.68 ($2NCH_2$), 59.56 ($2OCH_2$), 71.32 (NCH(Ph)), 73.65 (OCH(Ph)), 126.87, 127.71, 127.95, 128.19, 128.31, 129.67, 135.87, 142.47 (aromatic carbons). *Anal.* Calc. for $C_{18}H_{23}NO_3$: C, 71.74; H, 7.69; N, 4.65. Found: C, 72.00; H, 7.58; N, 4.62%.

2.2. Synthesis of threo-2-[bis(2-hydroxyethyl)amino]-1, 2-diphenyl-1-ethanol (4)

The reaction between $HN(CH_2CH_2OH)_2$ (2.30 g, 21.8 mmol) and *cis*-stilbene oxide (4.28 g, 21.8 mmol) was performed as described for **3** to give compound **4** (4.91 g, 75%) as a slightly yellow powder, m.p. 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.47–2.52 (m, 2H), 2.95–3.02 (m, 2H), 3.63–3.68 (m, 2H), 3.81–3.87 (m, 2H) [$(ABXY)_2$ system of NCH_2CH_2O protons], 3.80 (d, J = 10.3 Hz, 1H, NCH(Ph)), 5.09 (d, J = 10.3 Hz, 1H, OCH(Ph)), 7.05–7.22 (m, 10H, aromatic protons). ^{13}C NMR (100 MHz, acetone-d_6): δ (ppm): 52.77 ($2NCH_2$), 60.31 ($2OCH_2$), 72.31 (NCH(Ph)), 72.96 (OCH(Ph)), 127.75, 128.12, 128.36, 128.54, 128.63, 130.63, 134.17, 143.32 (aromatic carbons). *Anal.* Calc. for $C_{18}H_{23}NO_3$: C, 71.74; H, 7.69; N, 4.65. Found: C, 71.69; H, 7.54; N, 4.63%.

2.3. Synthesis of 2-[bis(2-hydroxyethyl)amino]-1, 1-diphenyl-1-ethanol (**5**)

A mixture of $HN(CH_2CH_2OH)_2$ (0.76 g, 7.24 mmol) and 2,2-diphenyloxirane (1.42 g, 7.24 mmol) was stirred for 45 h at 90 °C. The resulting oily material was diluted with diethyl ether (3 mL) and kept at −18 °C for 2 weeks. The colourless crystals were filtered and dried under reduced pressure to give **5** (1.11 g, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.65 (t, $J = 5.1$ Hz, 4H, $2NCH_2$), 3.39 (t, $J = 5.1$ Hz, 4H, $2OCH_2$), 3.49 (s, 2H, $NCH_2C(Ph)_2$), 7.17–7.21 (m, 2H), 7.27–7.31 (m, 4H), 7.46–7.48 (m, 4H) (aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 58.90 ($2NCH_2$), 60.61 ($2OCH_2$), 67.27 ($NCH_2C(Ph)_2$), 76.54 ($OC(Ph)_2$), 125.93, 126.84, 128.16, 146.49 (aromatic carbons). *Anal.* Calc. for $C_{18}H_{23}NO_3$: C, 71.74; H, 7.69; N, 4.65. Found: C, 71.42; H, 7.80; N, 4.83%.

2.4. Synthesis of erythro-2-[(2-hydroxyethyl)amino]-1, 2-diphenyl-1-ethanol

A mixture of $H_2NCH_2CH_2OH$ (0.93 g, 12 mmol), *trans*-stilbene oxide (2.15 g, 11 mmol) and toluene (4 mL) was refluxed for 24 h. The removal of the solvent in vacuo left a solid material which was recrystallized from hexane to give *erythro*-$HN(CH_2CH_2OH)CH(Ph)CH(Ph)OH$ (0.73 g, 26%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.13 (br s, 2H, 2IH), 2.78 (br s, 1H, NH), 2.54–2.61 (m, 2H, NCH_2), 3.50–3.55 (m, 2H, OCH_2), 3.85 (d, $J = 6.1$ Hz, 1H, NCH(Ph)), 4.80 (d, $J = 6.1$ Hz, 1H, OCH(Ph)), 7.12–7.22 (m, 10H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 48.88 (NCH_2), 61.09 (OCH_2), 68.58 (NCH(Ph)), 76.72 (OCH(Ph)), 126.73, 127.45, 127.55, 127.95, 128.06, 128.28, 139.17, 140.89 (aromatic carbons).

2.5. Reaction of erythro-2-[(2-hydroxyethyl)amino]-1, 2-diphenyl-1-ethanol with trans-stilbene oxide

A mixture of *erythro*-$HN(CH_2CH_2OH)CH(Ph)CH(Ph)OH$ (0.65 g, 2.5 mmol), *trans*-stilbene oxide (0.4 g, 2.5 mmol) and xylene (5 mL) was refluxed for 55 h. After removal of the solvent, the residue contained only starting materials (^{1}H NMR data). When 1,3,5-triethylbenzene was used as a solvent, a mixture of unidentified products was formed after 8 h of reflux (^{1}H NMR data).

2.6. Reaction of erythro-2-[(2-hydroxyethyl)amino]-1, 2-diphenyl-1-ethanol with styrene oxide

A mixture of *erythro*-$HN(CH_2CH_2OH)CH(Ph)CH(Ph)OH$ (0.5 g, 1.9 mmol), styrene oxide (0.23 g, 1.9 mmol), and xylene (4 mL) was refluxed for 35 h. After removal of the solvent, an oily residue was obtained which contained both starting materials and products of unidentified structure (^{1}H NMR data). The catalytic amount of water in the reaction mixture does not activate the process.

2.7. Synthesis of 2-[(2-hydroxy-1,2-diphenylethyl)amino]-1,2-diphenyl-1-ethanol

A vial with a screw cap was charged with a 2.0 M solution of NH_3 in methanol (5.5 mL, 10 mmol) and *trans*-stilbene oxide (5.89 g, 30 mmol). The reaction mixture was stirred for 12 h at room temperature, followed by heating for 110 h at 60 °C. The precipitate was filtered, washed with hexane (3×10 mL), and dried in vacuo to give $HN[CH(Ph)CH(Ph)OH]_2$ (3.43 g, 84%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.54 (br s, 1H, NH), 3.55 (d, $J = 6.8$ Hz), 3.77 (d, $J = 5.2$ Hz) (2H, 2NCH(Ph)), 4.59 (d, $J = 6.8$ Hz), 4.84 (d, $J = 5.2$ Hz) (2H, 2OCH(Ph)), 6.72–7.21 (m, 20H, aromatic protons). *Anal.* Calc. for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65; N, 3.42. Found: C, 82.40; H, 6.84; N, 3.25%. Two diastereomers.

2.8. Reaction of 2-[(2-hydroxy-1,2-diphenylethyl)amino]-1,2-diphenyl-1-ethanol with styrene oxide

A mixture of $HN[CH(Ph)CH(Ph)OH]_2$ (0.2 g, 0.5 mmol), styrene oxide (0.061 g, 0.5 mmol) and toluene (4 mL) was refluxed for 3 days. After removal of the solvent, the oily residue contained the starting materials along with unidentified products (^{1}H NMR data).

2.9. Reaction of 2-[(2-hydroxy-1,2-diphenylethyl)amino]-1,2-diphenyl-1-ethanol with 2,2-diphenyloxirane

A mixture of $HN[CH(Ph)CH(Ph)OH]_2$ (0.45 g, 1.2 mmol), 2,2-diphenyloxirane (0.23 g, 1.2 mmol), and toluene (6 mL) was refluxed for 40 h. After removal of the solvent in vacuo, the residue contained only starting materials (^{1}H NMR data).

2.10. Synthesis of erythro-1-phenylethynyl-3,4-diphenylsilatrane (**6**)

A solution of $(MeO)_3SiC{\equiv}CPh$ (0.74 g, 3.32 mmol) in methanol (2 mL) was added to a solution of trialkanolamine **3** (1.0 g, 3.32 mmol) in methanol (20 mL). Upon stirring of the reaction mixture for 3 days at room temperature, the formation of a white precipitate was observed. The solvent was partially evaporated, and the solid was filtered, washed with methanol (2 mL) and pentane (2×5 mL), and dried in vacuo to give **6** (0.76 g, 54%) as a white powder; m.p. >255 °C. IR: 2175 (C≡C) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.46–2.51 (m, 1H), 2.79–2.87 (m, 1H), 2.90–2.95 (m, 1H), 3.26–3.34 (m, 1H), 3.82–3.87 (m, 2H), 3.98–4.03 (m, 1H), 4.10–4.17 (m, 1H) [$(ABXY)_2$ system of NCH_2CH_2O protons], 4.43 (d, $J = 7.1$ Hz, 1H, NCH(Ph)), 5.46 (d, $J = 7.1$ Hz, 1H, OCH(Ph)), 6.98–7.00, 7.15–7.36, 7.54–7.57 (3m, 15H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 50.22, 50.31 ($2NCH_2$), 57.47, 58.19 ($2OCH_2$), 66.94 (NCH(Ph)), 75.27 (OCH(Ph)), 96.15 (SiC≡), 96.86 (PhC≡), 124.14, 127.33, 127.46, 127.52, 127.57, 127.60, 128.31, 129.24, 131.32, 131.64,

132.41, 139.02 (aromatic carbons). ^{29}Si NMR (99 MHz, $CDCl_3$): δ (ppm): −94.3. EI-MS: m/z (%) = 427 (17) [M^+], 321 (68) [M^+−PhCHO], 244 (9) [M^+−PhCHO−Ph]. *Anal.* Calc. for $C_{26}H_{25}NO_3Si$: C, 73.04; H, 5.89; N, 3.28. Found: C, 73.28; H, 6.13; N, 3.09%.

2.11. Synthesis of threo-1-phenylethynyl-3,4-diphenylsilatrane (7)

Analogously to that described for **6**, a reaction of trialkanolamine **4** (1.0 g, 3.32 mmol) with $(MeO)_3SiC{\equiv}CPh$ (0.74 g, 3.32 mmol) was performed in methanol (20 mL) to give silatrane **7** (1.03 g, 73%) as a white powder; m.p. >250 °C. IR: 2185 (C≡C) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.24–2.28 (m, 1H), 2.79–2.86 (m, 1H), 2.93–2.97 (m, 1H), 3.35–3.42 (m, 1H), 3.84–3.90 (m, 1H), 4.00–4.09 (m, 2H), 4.13–4.20 (m, 1H) [$(ABXY)_2$ system of NCH_2CH_2O protons], 3.77 (d, J = 10.8 Hz, 1H, NCH(Ph)), 5.37 (d, J = 10.8 Hz, 1H, OCH(Ph)), 7.14–7.19, 7.23–7.29, 7.34–7.36, 7.49–7.52 (4m, 15H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 47.47, 47.75 ($2NCH_2$), 57.28 ($2OCH_2$), 69.11 (NCH(Ph)), 72.54 (OCH(Ph)), 96.07 (SiC≡), 96.83 (PhC≡), 124.20, 126.66, 127.46, 127.61, 127.77, 128.13, 128.95, 129.51, 130.16, 131.36, 132.42, 139.92 (aromatic carbons). ^{29}Si NMR (99 MHz, $CDCl_3$): δ (ppm): −95.5. EI-MS: m/z (%) = 427 (15) [M^+], 321 (100) [M^+−PhCHO], 244 (4) [M^+−PhCHO−Ph]. *Anal.* Calc. for $C_{26}H_{25}NO_3Si$: C, 73.04; H, 5.89; N, 3.28. Found: C, 72.82; H, 5.82; N, 3.29%.

2.12. Synthesis of 1-phenylethynyl-3,3-diphenylsilatrane (8)

Analogously to that described for **6**, a reaction of trialkanolamine **5** (0.60 g, 1.99 mmol) with $(MeO)_3SiC{\equiv}CPh$ (0.44 g, 1.99 mmol) was performed in methanol (12 mL) to give silatrane **8** (0.64 g, 75%) as a white powder; m.p. >250 °C. IR: 2170 (C≡C) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.67–2.79 (m, 4H, $2NCH_2$), 3.65 (s, 2H, $NCH_2C(Ph)_2$), 3.69–3.75 (m, 2H), 3.80–3.86 (m, 2H) ($2OCH_2$), 7.17–7.32, 7.59–7.60 (2m, 15H, aromatic protons). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 51.83 ($2NCH_2$), 56.86 ($2OCH_2$), 59.86 ($NCH_2C(Ph)_2$), 77.01 ($OC(Ph)_2$), 94.26 (SiC≡), 100.89 (PhC≡), 124.40, 124.95, 126.72, 127.54, 128.23, 128.39, 131.32, 147.16 (aromatic carbons). ^{29}Si NMR (99 MHz, $CDCl_3$): δ (ppm): −96.5. EI-MS: m/z (%) = 427 (14) [M^+], 280 (100) [M^+−PhCCSi−H_2O], 245 (61) [M^+−Ph_2CO]. *Anal.* Calc. for $C_{26}H_{25}NO_3Si$: C, 73.04; H, 5.89; N, 3.28. Found: C, 72.65; H, 5.92; N, 2.98%.

2.13. Synthesis of erythro-1-chloromethyl-3,4-diphenylsilatrane (9)

A solution comprising trialkanolamine **3** (0.80 g, 2.65 mmol) and a catalytic amount (~0.01 g) of powdered KOH in methanol (10 mL) was treated with $(MeO)_3SiCH_2Cl$ (0.45 g, 2.65 mmol). Upon stirring of the reaction mixture at room temperature for 4 days, the formation of a white precipitate was observed. When ~1/3 of methanol volume was removed in vacuo, hexane (4 mL) was added. The solid was filtered, washed with hexane (2 × 3 mL), and dried in vacuo to give **9** (0.76 g, 76%) as a white powder; m.p. 210 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.84 (s, 2H, $SiCH_2$), 2.45–2.50 (m, 1H), 2.78–2.87 (m, 1H), 2.90–2.95 (m, 1H), 3.20–3.27 (m, 1H), 3.70–3.82 (m, 2H), 3.92–3.97 (m, 1H), 4.04–4.10 (m, 1H) [$(ABXY)_2$ system of NCH_2CH_2O protons], 4.40 (d, J = 7.2 Hz, 1H, NCH(Ph)), 5.38 (d, J = 7.2 Hz, 1H, OCH(Ph)), 6.98–7.00, 7.11–7.14, 7.18–7.26, 7.31–7.34 (4m, 10H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 31.54 ($SiCH_2$), 50.31, 50.49 ($2NCH_2$), 57.38, 58.00 ($2OCH_2$), 67.11 (NCH(Ph)), 74.74 (OCH(Ph)), 127.33, 127.46, 127.58, 128.31, 129.22, 131.32, 131.80, 139.30 (aromatic carbons). ^{29}Si NMR (99 MHz, $CDCl_3$): δ (ppm): −79.6. EI-MS: m/z (%) = 375 (92) [M^+], 326 (75) [M^+−CH_2Cl], 269 (100) [M^+−PhCHO], 234 (27) [M^+−PhCHO−Cl], 192 (21) [M^+−PhCHO−$SiCH_2Cl$], 148 (22) [$N(CH_2CH_2O)CHPh^+$]. *Anal.* Calc. for $C_{19}H_{22}ClNO_3Si$: C, 60.71; H, 5.90; N, 3.73. Found: C, 60.50; H, 5.88; N, 3.80%.

2.14. Synthesis of threo-1-chloromethyl-3,4-diphenylsilatrane (10)

Analogously to that described for **9**, a reaction of trialkanolamine **4** (0.70 g, 2.32 mmol) with $(MeO)_3SiCH_2Cl$ (0.40 g, 2.32 mmol) was performed in methanol (12 mL) in the presence of KOH (~0.01 g) to give silatrane **10** (0.69 g, 79%) as a white powder; m.p. >255 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.76 (s, 2H, $SiCH_2$), 2.25–2.28 (m, 1H), 2.76–2.84 (m, 1H), 2.91–2.95 (m, 1H), 3.32–3.40 (m, 1H), 3.80–3.86 (m, 1H), 3.94–4.13 (m, 3H) [$(ABXY)_2$ system of NCH_2CH_2O protons], 3.71 (d, J = 10.5 Hz, 1H, NCH(Ph)), 5.30 (d, J = 10.5 Hz, 1H, OCH(Ph)), 7.12–7.21, 7.26–7.28, 7.35–7.37 (3m, 10H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 31.42 ($SiCH_2$), 47.47, 47.76 ($2NCH_2$), 57.05, 57.12 ($2OCH_2$), 69.19 (NCH(Ph)), 71.93 (OCH(Ph)), 126.34, 127.69, 128.15, 128.92, 129.47, 130.12, 131.45, 140.28 (aromatic carbons). ^{29}Si NMR (79 MHz, $CDCl_3$): δ (ppm): −81.0. EI-MS: m/z (%) = 375 (37) [M^+], 326 (59) [M^+−CH_2Cl], 269 (100) [M^+−PhCHO], 234 (9) [M^+−PhCHO−Cl], 220 (6) [M^+−PhCHO−CH_2Cl], 192 (22) [M^+−PhCHO−$SiCH_2Cl$], 148 (23) [$N(CH_2CH_2O)CHPh^+$]. *Anal.* Calc. for $C_{19}H_{22}ClNO_3Si$: C, 60.71; H, 5.90; N, 3.73. Found: C, 60.52; H, 5.76; N, 3.83%.

2.15. Synthesis of 1-chloromethyl-3,3-diphenylsilatrane (11)

Analogously to that described for **9**, a reaction of trialkanolamine **5** (1.53 g, 5.08 mmol) with $(MeO)_3SiCH_2Cl$ (0.87 g, 5.08 mmol) was performed in methanol (12 mL) in the presence of KOH (~0.01 g) to give **11** (1.59 g, 83%) as a white powder; m.p. >255 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.67–2.78 (m, 4H, $2NCH_2$),

2.91 (s, 2H, $SiCH_2$), 3.64 (s, 2H, $NCH_2C(Ph)_2$), 3.64–3.69 (m, 2H), 3.76–3.82 (m, 2H) ($2OCH_2$), 7.15–7.20 (m, 2H), 7.27–7.31 (m, 4H), 7.54–7.57 (m, 4H) (aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 31.70 ($SiCH_2$), 52.65 ($2NCH_2$), 57.38 ($2OCH_2$), 61.34 ($NCH_2C(Ph)_2$), 125.08, 127.02, 128.49, 146.76 (aromatic carbons). ^{29}Si NMR (99 MHz, $CDCl_3$): δ (ppm): −82.2. *Anal*. Calc. for $C_{19}H_{22}ClNO_3Si$: C, 60.71; H, 5.90; N, 3.73. Found: C, 60.58; H, 5.86; N, 3.85%.

2.16. Synthesis of erythro-3,4-diphenylboratrane (12)

Method A: A mixture of trialkanolamine **3** (1.50 g, 4.98 mmol), boric acid (0.31 g, 4.98 mmol), and *iso*-amyl alcohol (5 mL) was refluxed with a water collector for 2 h. During this time, a theoretical amount of water (0.3 mL) was produced. The precipitate was filtered, washed with hexane (3 × 5 mL) and dried in vacuo to give boratrane **12** (1.22 g, 79%) as a white solid; m.p. >295 °C. The product is practically insoluble in the usual organic solvents. ^1H NMR (400 MHz, DMSO-d_6, 100 °C): δ (ppm): 2.80–2.83 (m, 2H), 3.43–3.49 (m, 1H), 3.53–3.57 (m, 2H), 3.70–3.75 (m, 1H), 3.84–3.90 (m, 1H), 3.95–3.99 (m, 1H) [$(ABXY)_2$ system of NCH_2CH_2O protons], 4.84 (d, $J = 5.1$ Hz, 1H, NCH(Ph)), 5.69 (d, $J = 5.1$ Hz, 1H, OCH(Ph)), 7.01–7.05, 7.13–7.18, 7.29–7.32, 7.44–7.47 (4m, 10H, aromatic protons). ^{13}C NMR (100 MHz, DMSO-d_6, 100 °C): δ (ppm): 53.66, 61.27 ($2NCH_2$), 62.11, 63.88 ($2OCH_2$), 75.76 (NCH(Ph)), 77.34 (OCH(Ph)), 123.36, 125.27, 125.34, 126.86, 127.10, 127.95 (aromatic carbons). ^{11}B NMR (160 MHz, $CDCl_3$, 60 °C): δ (ppm): 14.9. EI-MS: m/z (%) = 309 (<1) [M^+], 203 (100) [M^+−PhCHO], 174 (53) [M^+−PhCHO−CH_2O+H], 126 (63) [M^+−PhCHO−Ph]. *Anal*. Calc. for $C_{18}H_{20}BNO_3$: C, 69.93; H, 6.52; N, 4.53. Found: C, 69.56; H, 6.76; N, 4.35%.

Method B: Trimethyl borate (0.30 mL, 2.65 mmol) was added to a solution of trialkanolamine **3** (0.80 g, 2.65 mmol) in chloroform (20 mL). Immediately, a large amount of the precipitate was produced. The reaction mixture was stirred at room temperature for 24 h, then the solid was filtered, washed with chloroform (7 mL), and dried in vacuo to give **12** (0.67 g, 82%) as a white powder.

2.17. Synthesis of 3,3-diphenylboratrane (13)

Method A: Analogously to that described for **12**, a reaction of trialkanolamine **5** (1.19 g, 3.95 mmol) with $B(OH)_3$ (0.24 g, 3.95 mmol) was performed in *iso*-amyl alcohol (5 mL) to give boratrane **13** (0.75 g, 60%) as a white powder; m.p. 277–280 °C (dec.). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.97–3.00 (m, 4H, $2NCH_2$), 3.76–3.81 (m, 2H), 3.92–3.97 (m, 2H) ($2OCH_2$), 3.85 (s, 2H, $NCH_2C(Ph)_2$), 7.14–7.17, 7.25–7.29, 7.55–7.57 (3m, 10H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 60.22 ($2NCH_2$), 62.24 ($2OCH_2$), 67.76 ($NCH_2C(Ph)_2$), 83.24 ($OC(Ph)_2$), 125.54, 126.83, 128.18, 146.17 (aromatic carbons). ^{11}B NMR (160 MHz, $CDCl_3$, 60 °C): δ (ppm): 15.0. EI-MS: m/z (%) = 309 (2) [M^+], 232 (10) [M^+−Ph], 196 (81) [$CH_2C(Ph)_2O^+$], 126 (100) [M^+−Ph_2CO−H]. *Anal*. Calc. for $C_{18}H_{20}BNO_3$: C, 69.93; H, 6.52; N, 4.53. Found: C, 69.65; H, 6.53; N, 4.78%.

Method B: Trimethyl borate (0.18 mL, 1.59 mmol) was added to a solution of trialkanolamine **5** (0.48 g, 1.59 mmol) in chloroform (12 mL). The reaction mixture was stirred at room temperature for 24 h, and a large amount of the precipitate was produced. After a half of the solvent was removed in vacuo, pentane (10 mL) was added to the suspension. The precipitate was filtered, washed with pentane (2 × 5 mL), and dried in vacuo to give **13** (0.44 g, 90%).

2.18. Synthesis of 3-phenylboratrane (14) and 4-phenylboratrane (15)

Analogously to that described for **12**, a reaction of $B(OH)_3$ (5.0 g, 0.08 mol) with the mixture of trialkanolamines **1** + **2** (18.2 g, 0.08 mol) was performed in *iso*-amyl alcohol (60 mL). Recrystallization of the product from ethanol/heptane gave **14** (13.3 g, 70%) as a white solid; m.p. 230 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.62–2.68 (m, 1H), 2.89–2.97 (m, 1H), 3.04–3.11 (m, 1H), 3.19–3.31 (m, 2H), 3.43–3.47 (m, 1H), 3.90–4.05 (m, 4 H), 5.03 (dd, J = 10.6 Hz, $J = 4.0$ Hz, 1 H) [$(ABXY)_2$ and ABX systems of NCH_2CH_2O and $NCH_2CH(Ph)O$ protons], 7.26–7.40 (m, 5 H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 59.44, 59.68 ($2NCH_2$), 61.78, 62.02 ($2OCH_2$), 65.98 ($NCH_2CH(Ph)$), 73.84 (ICH(Ph)), 125.68, 127.80, 128.38, 139.88 (aromatic carbons). ^{11}B NMR (160 MHz, $CDCl_3$, 60 °C): δ (ppm): 14.6. EI-MS: m/z (%) = 233 (18) [M^+], 126 (100) [M^+−PhCHO−H], 114 (54) [M^+−PhC_2H_2O]. *Anal*. Calc. for $C_{12}H_{16}BNO_3$: C, 61.84; H, 6.92; N, 6.01. Found: C, 61.49; H, 6.68; N, 5.98%.

Upon evaporation of the filtrate, a solid precipitated which was filtered, washed with hexane, and dried in vacuo to give 4-phenylboratrane (**15**) (0.15 g, 8%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.41–2.44 (m, 1H), 2.75–2.82 (m, 1H), 2.91–2.98 (m, 1H), 3.04–3.07 (m, 1H), 3.57–3.60 (m, 1H), 3.85–3.89 (m, 2H), 4.05–4.08 (m, 2H), 4.19 (br s, 2H) [$(ABXY)_2$ and ABX systems of NCH_2CH_2O and $NCH(Ph)CH_2O$ protons], 7.29–7.39 (m, 5H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 53.23, 58.32 ($2NCH_2$), 61.62, 61.93 ($2OCH_2$), 64.36 ($OCH_2CH(Ph)$), 68.90 (NCH(Ph)), 127.75, 128.87, 129.22, 131.83 (aromatic carbons).

2.19. Synthesis of threo-3,4-diphenylboratrane (16)

Analogously to that described for **12**, a reaction of trialkanolamine **4** (1.50 g, 4.98 mmol) with boric acid (0.31 g, 4.98 mmol) was performed in *iso*-amyl alcohol (5 mL) to give **16** (1.32 g, 86%) as a white solid; m.p. 255–257 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.28–

2.34 (m, 1H), 2.85–2.95 (m, 1H), 3.11–3.21 (m, 1H), 3.52–3.57 (m, 1H), 3.89–4.06 (m, 2H), 4.14–4.27 (m, 2H) [$(ABXY)_2$ system of NCH_2CH_2O protons], 3.99 (d, $J = 10.6$ Hz, 1H, NCH(Ph)), 5.40 (d, $J = 10.6$ Hz, 1H, OCH(Ph)), 7.15–7.23, 7.36–7.38 (2m, 10H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 53.94, 58.75 ($2NCH_2$), 61.92, 61.99 ($2OCH_2$), 76.17 (NCH(Ph)), 76.37 (OCH(Ph)), 127.00, 127.92, 128.15, 129.04, 129.62, 129.70, 131.47, 138.86 (aromatic carbons). ^{11}B NMR (160 MHz, $CDCl_3$, 60 °C): δ (ppm): 14.0. EI-MS: *m/z* (%) = 309 (<1) [M^+], 203 (100) [$M^+-PhCHO$], 174 (59) [$M^+-PhCHO-CH_2O+H$], 126 (64) [$M^+-PhCHO-Ph$]. *Anal.* Calc. for $C_{18}H_{20}BNO_3$: C, 69.93; H, 6.52; N, 4.53. Found: C, 69.56; H, 6.39; N, 4.55%.

2.20. Synthesis of erythro-1-hydro-3,4-diphenylsilatrane (*17*)

A suspension comprising *erythro*-3,4-diphenylboratrane (**12**) (0.52 g, 1.68 mmol) and a catalytic amount (~0.01 g) of $Al(OEt)_3$ in xylene (25 mL) was treated with $HSi(OEt)_3$ (0.46 mL, 2.52 mmol). After 45 h of reflux, a clear solution was formed and the reaction mixture was refluxed for an additional 15 h. Then the solution was evaporated in vacuo by ~1/3 of the volume. The precipitated solid was filtered, washed with hexane (2 × 3 mL), and dried in vacuo to give **17** (0.41 g, 75%) as a white powder. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.46–2.50 (m, 1H), 2.78–2.85 (m, 1H), 2.90–2.95 (m, 1H), 3.19–3.26 (m, 1H), 3.64–3.69 (m, 1H), 3.73–3.80 (m, 1H), 3.88–3.94 (m, 1H), 4.02–4.08 (m, 1H) [$(ABXY)_2$ system of NCH_2CH_2O protons], 4.24 (s, 1H, SiH), 4.39 (d, $J = 7.1$ Hz, 1H, NCH(Ph)), 5.38 (d, $J = 7.1$ Hz, 1H, OCH(Ph)), 7.00–7.02, 7.12–7.25, 7.30–7.33 (3m, 10H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 50.32, 50.73 ($2NCH_2$), 57.09, 57.81 ($2OCH_2$), 67.34 (NCH(Ph)), 74.80 (OCH(Ph)), 127.24, 127.48, 127.55, 128.28, 129.12, 131.35, 132.12, 139.48 (aromatic carbons). ^{29}Si NMR (99 MHz, $CDCl_3$): δ (ppm): −82.9. EI-MS: *m/z* (%) = 327 (22) [M^+], 221 (100) [$M^+-PhCHO$], 177 (21) [$M^+-PhCHO-CH_2CH_2O$], 130 (6) [$M^+-CH(Ph)CH(Ph)O-H$], 77 (7) [Ph^+]. *Anal.* Calc. for $C_{18}H_{21}NO_3Si$: C, 66.02; H, 6.46; N, 4.28. Found: C, 65.61; H, 6.04; N, 4.04%.

2.21. Synthesis of 1-hydro-3-phenylsilatrane (*18*)

A suspension comprising 3-phenylboratrane (**14**) (0.60 g, 2.57 mmol) and a catalytic amount (~0.01 g) of $Al(OEt)_3$ in xylene (30 mL) was treated with $HSi(OEt)_3$ (0.71 mL, 3.86 mmol). The reaction mixture was refluxed for 6 h with the starting boratrane being totally dissolved in 1 h. On cooling a white solid precipitated, which was filtered, washed with hexane (2 × 5 mL), and dried in vacuo to give **18** (0.52 g, 80%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.55–2.60 (m, 1H), 2.79–2.91 (m, 2H), 2.94–2.98 (m, 1H), 3.02–3.13 (m, 2H), 3.76–3.92 (m, 4H), 4.93 (dd, $J = 10.6$ Hz, $J = 4.6$ Hz, 1H) [$(ABXY)_2$ and ABX systems of NCH_2CH_2O and $NCH_2CH(Ph)O$ protons], 4.07 (s, 1H, SiH), 7.25–7.42 (m, 5H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 51.40, 51.97 ($2N-CH_2$), 57.09, 57.14 ($2OCH_2$), 58.28 ($NCH_2CH(Ph)$), 69.22 (ICH(Ph)), 125.38, 127.81, 128.56, 141.13 (aromatic carbons). ^{29}Si NMR (99 MHz, $CDCl_3$): δ (ppm): −83.4. EI-MS: *m/z* (%) = 251 (23) [M^+], 145 (100) [$M^+-PhCHO$], 101 (6) [$M^+-CH_2CH(Ph)O-CH_2O$], 77 (4) [Ph^+]. *Anal.* Calc. for $C_{12}H_{17}NO_3Si$: C, 57.34; H, 6.82; N, 5.57. Found: C, 56.96; H, 6.60; N, 5.67%.

2.22. Synthesis of 1-menthoxysilatrane (*21*)

A mixture of L-menthol (1.06 g, 6.78 mmol), sodium (0.03 g, 1.47 mmol), and xylene (8 mL) was refluxed until the sodium was completely dissolved. The prepared solution was added dropwise to a refluxing suspension of 1-hydrosilatrane (**19**) (0.40 g, 2.26 mmol) in xylene (10 mL), a vigorous evolution of gas was observed. The reaction mixture was refluxed for 2 h, then a half of the solvent was removed in vacuo, and hexane (10 mL) was added. The precipitated solid was filtered, washed with hexane (2 × 5 mL), and dried in vacuo to give **21** (0.49 g, 66%) as a white powder. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 0.74 (d, $J = 6.8$ Hz), 0.83–0.85 (m), 0.71–0.98 (m), 1.07–1.14 (m), 1.23–1.40 (m), 1.49–1.58 (m), 2.09–2.14 (m), 2.29–2.37 (m), 3.46–3.53 (m) (19H, protons of menthoxy group), 2.78 (t, $J = 6.0$ Hz, 6H, $3NCH_2$), 3.77 (t, $J = 6.0$ Hz, 6H, $3OCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 15.71, 21.52, 22.42, 22.86, 24.98, 31.76, 34.91, 44.76, 50.25, 71.44 (carbons of menthoxy group), 51.54 ($3NCH_2$), 58.04 ($3OCH_2$). EI-MS: *m/z* (%) = 329 (12) [M^+], 244 (100) [$M^+-C_6H_{13}$], 174 (69) [$M^+-MenthO$]. *Anal.* Calc. for $C_{16}H_{31}NO_4Si$: C, 58.32; H, 9.48; N, 4.25. Found: C, 57.89; H, 9.47; N, 3.86%.

2.23. Synthesis of 1-menthoxy-3-phenylsilatrane (*20*)

The compound was prepared analogously to that described for **21** using 1-hydro-3-phenylsilatrane (**18**) (0.40 g, 1.59 mmol), L-menthol (0.75 g, 4.77 mmol), and sodium (0.02 g, 1.04 mmol) in xylene (15 mL). The product (0.17 g, 27%) was isolated as a white powder. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 0.68 (d, $J = 7.1$ Hz, 3H), 0.85 (d, $J = 6.8$ Hz, 6H), 0.71–1.02 (m, 3H), 1.12–1.19 (m, 1H), 1.30–1.40 (m, 1H), 1.50–1.59 (m, 2H), 2.17–2.23 (m, 1H), 2.42–2.46 (m, 1H), 3.56–3.62 (m, 1H) (protons of menthoxy group), 2.42–2.47 (m, 1H), 2.75–2.79 (m, 2H), 2.88–3.00 (m, 2H), 3.05–3.09 (m, 1H), 3.71–3.91 (m, 4H), 4.91 (dd, $J = 10.6$ Hz, $J = 4.5$ Hz, 1H) [$(ABXY)_2$ and ABX systems of NCH_2CH_2O and $NCH_2CH(Ph)O$ protons], 7.23–7.27, 7.30–7.36 (2m, 5H, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 16.02, 21.52, 22.43, 22.98, 24.94, 31.83, 34.97, 44.97, 50.25, 71.68 (carbons of menthoxy group), 51.87, 52.31 ($2NCH_2$), 58.10 ($2OCH_2$), 58.87 ($NCH_2CH(Ph)$), 69.98 (ICH(Ph)), 125.20, 127.45, 128.32,

141.63 (aromatic carbons). ^{29}Si NMR (80 MHz, $CDCl_3$): δ (ppm): −94.6. EI-MS: m/z (%) = 405 (45) [M^+], 320 (100) [$M^+-C_6H_{13}$], 299 (29) [M^+−PhCHO], 250 (98) [M^+−MenthO], 162 (57) [$N(CH_2)_2CH_2CH(Ph)O^+$]. *Anal.* Calc. for $C_{22}H_{35}NO_4Si$: C, 65.15; H, 8.70; N, 3.45. Found: C, 64.89; H, 8.57; N, 3.56%.

2.24. Synthesis of 1-tert-butoxy-2-carba-3-oxahomosilatrane (**24**)

A suspension of 1-chloromethylsilatrane (**22**) (1.76 g, 7.85 mmol) and *tert*-BuOK (0.97 g, 8.64 mmol) in dioxane (50 mL) was refluxed for 12 h. The precipitate was filtered off, and the filtrate was evaporated in vacuo. The residual yellow oil was solidified on keeping at room temperature. The crude product was recrystallized from ether/heptane to give **24** (1.62 g, 79%) as a white powder. ^{1}H NMR (400 MHz, C_6D_6): δ (ppm): 1.50 (s, 9H, *tert*-BuO), 1.92–2.02 (m, 4H), 3.51–3.56 (m, 2H), 3.63–3.68 (m, 2H) [$(ABXY)_2$ system of NCH_2CH_2O protons], 2.25 (br t, J = 4.8 Hz, 2H), 3.07 (br t, J = 4.8 Hz, 2H) [$(AA'XX')$ system of $NCH_2CH_2OCH_2Si$ protons], 3.92 (s, 2H, OCH_2Si). ^{13}C NMR (100 MHz, C_6D_6): δ (ppm): 32.07 ($OC(CH_3)_3$), 53.59 ($2NCH_2$), 58.92 ($NCH_2CH_2OCH_2Si$), 60.26 ($2OCH_2$), 67.63, 67.70 ($NCH_2CH_2OCH_2Si$), 71.25 ($OC(CH_3)_3$). ^{29}Si NMR (80 MHz, $CDCl_3$): δ (ppm): −73.6. EI-MS: m/z (%) = 203 (16) [$M^+-C_4H_{10}$], 188 (100) [M^+−*tert*-BuO], 147 (38). *Anal.* Calc. for $C_{11}H_{23}NO_4Si$: C, 50.54; H, 8.87; N, 5.36. Found: C, 50.12; H, 8.92; N, 5.13%.

2.25. Synthesis of erythro-1-tert-butoxy-2-carba-3-oxa-7,8-diphenylhomosilatrane (**23**)

Analogously to that described for **24**, a reaction of *erythro*-1-chloromethyl-3,4-diphenylsilatrane (**9**) (0.49 g, 1.30 mmol) with *tert*-BuOK (0.16 g, 1.43 mmol) was performed in dioxane (30 mL). The removal of dioxane left an oily material which was diluted with hexane (20 mL), followed by stirring of the mixture at room temperature for 24 h. A precipitate formed was filtered and dried in vacuo to give **23** (0.32 g, 59%) as a white powder. ^{1}H NMR (400 MHz, C_6D_6): δ (ppm): 1.60 (s, 9H, *tert*-BuO), 1.77–1.82, 2.38–2.44, 2.61–2.67, 2.92–2.99, 3.17–3.23, 3.28–3.34, 3.54–3.59, 3.67–3.74 (8m, 8H, $(ABXY)_2$ system of NCH_2CH_2O protons), 3.97–4.16 (m, 2H, AB system of OCH_2Si protons), 4.26 (d, J = 6.4 Hz, 1H, NCH(Ph)), 5.69 (d, J = 6.4 Hz, 1H, OCH(Ph)), 6.91–6.95, 7.03–7.06, 7.26–7.29 (3m, 10H, aromatic protons). ^{13}C NMR (100 MHz, C_6D_6): δ (ppm): 32.34 ($OC(CH_3)_3$), 52.88 (NCH_2CH_2O), 59.66 ($NCH_2CH_2OCH_2Si$), 62.29 (NCH_2CH_2O), 67.37 (OCH_2Si), 68.47 ($NCH_2CH_2OCH_2Si$), 70.64 (NCH(Ph)), 71.67 ($OC(CH_3)_3$), 77.75 (OCH(Ph)), 126.77, 127.24, 127.72, 127.80, 128.03, 131.29, 136.13, 141.59 (aromatic carbons). ^{29}Si NMR (80 MHz, C_6D_6): δ (ppm): −73.1. EI-MS: m/z (%) = 413 (5) [M^+], 383 (8) [M^+-CH_2O], 355 (31) [$M^+-C_4H_{10}$], 340 (100) [M^+−*tert*-BuO], 307 (16) [M^+−PhCHO], 250 (40) [M^+−PhCHO−*tert*-Bu], 234 (17) [M^+−PhCHO−*tert*-BuO], 222 (76), 204 (9) [M^+−PhCHO−*tert*-BuO−CH_2O], 179 (47), 148 (65), 104(41), 91 (78). *Anal.* Calc. for $C_{23}H_{31}NO_4Si$: C, 66.79; H, 7.56; N, 3.39. Found: C, 66.43; H, 7.81; N, 3.15%.

2.26. Reaction of 3,3-diphenylboratrane (**13**) with CF_3SO_2OH

Trifluoromethanesulfonic acid (7.1 μL, 0.081 mmol) was added to a suspension of 3,3-diphenylboratrane (**13**) (0.025 g, 0.081 mmol) in CD_3CN (0.6 mL). After shaking the reaction mixture for 5 min, the starting solid of boratrane was totally dissolved. NMR spectra registered from the solution within an hour revealed the selective formation of the N-protonated derivative **27**. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm): 3.25–3.51 (m, 4H, $2NCH_2$), 3.85–3.94 (m, 2H), 4.21–4.30 (m, 2H) ($2OCH_2$), 4.24 (s, 2H, $NCH_2C(Ph)_2$), 7.33–7.59 (m, 10H, aromatic protons). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm): 55.87 ($2NCH_2$), 58.57 ($2OCH_2$), 75.91 ($NCH_2C(Ph)_2$), 126.62, 129.42, 130.02, 144.18 (aromatic carbons).

2.27. Reaction of 3-phenylboratrane (**14**) with CF_3SO_2OH

Analogously to that described above, a reaction of 3-phenylboratrane (**14**) (0.024 g, 0.103 mmol) with triflic acid (9.1 μL, 0.103 mmol) was performed in CD_3CN (0.6 mL). NMR spectroscopy data revealed the exclusive formation of **28**. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm): 3.04–3.09 (m, 1H), 3.34–3.41 (m, 1H), 3.50–3.70 (m, 3H), 3.85–3.90 (m, 1H), 4.21–4.29 (m, 2H), 4.37–4.46 (m, 2H), 5.25 (dd, J = 10.6 Hz, J = 4.6 Hz, 1H) [$(ABXY)_2$ and ABX systems of NCH_2CH_2O and $NCH_2CH(Ph)O$ protons], 7.34–7.56 (m, 5H, aromatic protons). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm): 58.39, 58.50 ($2NCH_2$), 65.53, 65.58 ($2OCH_2$), 65.29 ($NCH_2CH(Ph)$), 76.85 (OCH(Ph)), 127.05, 129.73, 138.93, 147.82 (aromatic carbons).

2.28. Reaction of 3,3-diphenylboratrane (**13**) with $CF_3SO_2OSiMe_3$

Analogously to that described above, a reaction of 3,3-diphenylboratrane (**13**) (0.028 g, 0.091 mmol) with trimethylsilyl triflate (16.4 μL, 0.091 mmol) was performed in CD_3CN (0.6 mL). According to the NMR spectroscopy data, in a mixture of products, compound **29** was the major component. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm): 0.43 (s, 9H, $SiMe_3$), 3.25–3.31 (m, 2H), 3.39–3.46 (m, 2H) ($2NCH_2$), 3.95–4.01 (m, 2H), 4.25–4.30 (m, 2H) ($2OCH_2$), 4.23 (s, 2H, $NCH_2C(Ph)_2$), 7.33–7.55 (m, 10H, aromatic protons). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm): 59.38 ($2NCH_2$), 65.33 ($2OCH_2$), 68.05 ($NCH_2C(Ph)_2$), 126.14, 127.13, 129.51, 144.24 (aromatic carbons).

2.29. Reaction of 3-phenylboratrane (*14*) with $CF_3SO_2OSiMe_3$

Analogously to that described above, a reaction of 3-phenylboratrane (**14**) (0.030 g, 0.129 mmol) with trimethylsilyl triflate (23.4 μL, 0.129 mmol) was performed in CD_3CN (0.6 mL). According to the NMR spectroscopy data, in a mixture of products, compound **30** was the major component. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm): 0.51 (s, 9H, $SiMe_3$), 3.02–3.08 (m, 1H), 3.39–3.46 (m, 1H), 3.53–3.73 (m, 3H), 3.86–3.91 (m, 1H), 4.23–4.32 (m, 2H), 4.39–4.44 (m, 2H), 5.20 (dd, $J = 10.6$ Hz, $J = 4.5$ Hz, 1H) [$(ABXY)_2$ and ABX systems of NCH_2CH_2O and $NCH_2CH(Ph)O$ protons], 7.35–7.44 (m, 5H, aromatic protons). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm): −0.39 ($SiMe_3$), 57.81, 57.92 ($2NCH_2$), 66.50, 66.86 ($2OCH_2$), 65.50 ($NCH_2CH(Ph)$), 76.56 (OCH(Ph)), 126.98, 129.53, 129.61, 139.16 (aromatic carbons).

2.30. Reaction of boratrane (*26*) with $CF_3SO_2OSiMe_3$

Analogously to that described above, a reaction of boratrane (**26**) (0.030 g, 0.191 mmol) with trimethylsilyl triflate (34.7 μL, 0.191 mmol) was performed in CD_3CN (0.6 mL). According to the NMR spectroscopy data, in a mixture of products, compound **31** was the main component. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm): 0.49 (s, 9H, $SiMe_3$), 3.48 (t, $J = 6.1$ Hz, 6H, $3NCH_2$), 4.19 (t, $J = 6.1$ Hz, 6H, $3OCH_2$). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm): −0.51 ($SiMe_3$), 58.32 ($3NCH_2$), 66.06 ($3OCH_2$).

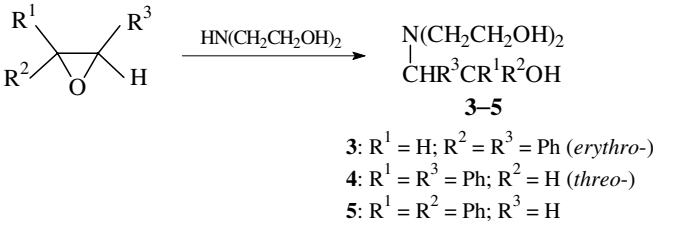
2.31. X-ray crystallography

The crystal data, data collection, structure solution and refinement parameters for compounds **7**, **9**, **10**, **16**, **18**, and **21** are listed in Table 1. All structures were solved by direct methods [26] and refined by full-matrix least-squares on F^2 [27] with anisotropic thermal parameters for all non-hydrogen atoms except disordered solvent $CHCl_3$ molecule in structure **21**. In structures **7**, **9**, **10**, **16** and **18**, all hydrogen atoms were found from different Fourier synthesis and refined with isotropic thermal parameters. In **21**, all hydrogen atoms were placed in calculated positions and refined using a riding model.

3. Results and discussion

3.1. Synthesis of trialkanolamine ligands

Previously, we reported that the reaction of diethanolamine with styrene oxide leads to the mixture of monophenylsubstituted aminoalcohols $N(CH_2CH_2OH)_2CH_2CH(Ph)OH$ (**1**) and $N(CH_2CH_2OH)_2CH(Ph)CH_2OH$ (**2**) in a 9:1 ratio [9]. In this study, a similar approach was developed for the synthesis of novel diphenylsubstituted trialkanolamines *erythro*-$N(CH_2CH_2OH)_2CH(Ph)CH(Ph)OH$ (**3**), *threo*-$N(CH_2CH_2OH)_2CH(Ph)CH(Ph)OH$ (**4**) and $N(CH_2CH_2OH)_2CH_2CPh_2OH$ (**5**). When a mixture of diethanolamine and appropriate oxirane was kept at 90–120 °C for 30–45 h, the desired ligands **3**–**5** were isolated in moderate to good yields (Eq. (1)).



3–5

3: $R^1 = H$; $R^2 = R^3 = Ph$ (*erythro*-)
4: $R^1 = R^3 = Ph$; $R^2 = H$ (*threo*-)
5: $R^1 = R^2 = Ph$; $R^3 = H$

(1)

In contrast to the reaction with styrene oxide [9], in the case of 2,2-diphenyloxirane trialkanolamine **5** was obtained as the sole product. No other products were detected in the reaction mixture by NMR spectroscopy. We attempted to extend this method to the preparation of trialkanolamines containing two or more phenyl groups in different arms. Thus, *erythro*-$HN(CH_2CH_2OH)CH(Ph)CH(Ph)OH$ and $HN[CH(Ph)CH(Ph)OH]_2$ were tested in several reactions with phenylsubstituted oxiranes; however, neither of them was found successful (see Section 2).

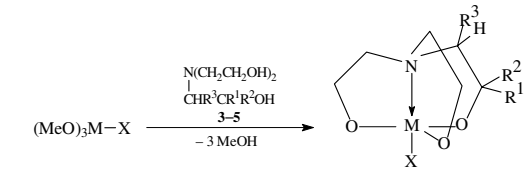
3.2. Synthesis and reactivity of phenylsubstituted metallatranes

In the present study, silatranes and boratranes with phenyl substituents in the atrane skeleton were synthesized using two different methods. The first one implies the formation of the metallatrane cage directly in the course of the reaction. Thus, compounds **6**–**13** were obtained by the treatment of trialkanolamine with the corresponding trialkoxysilane or -borane (Eq. (2)). The transesterification of (phenylethynyl)trimethoxysilane, as well as trimethylborate, with trialkanolamines **3**–**5** proceeds without a catalyst, while (chloromethyl)trimethoxysilane reacts only in the presence of a catalytic amount of KOH. The reaction rate of phenylsubstituted trialkanolamines **3**–**5** is appreciably lower in comparison with the parent $N(CH_2CH_2OH)_3$ [28,29]. So, a prolonged reaction time is required to provide good yields of the products (54–90%).

Boratranes **12**–**16** were also prepared upon treatment of boric acid with the corresponding trialkanolamine (Eq. (3)). This reaction may be considered as a modification of the first method [1,6]. The reaction of $B(OH)_3$ with the mixture **1** + **2** (9:1) (see [9] for detail) afforded compounds **14** and **15** as a mixture of the same ratio, which proved possible to separate via recrystallization. It should be noted that both approaches to boratranes (cf. Eqs. (2) and (3)) give the products with similar high yields. However, the reaction with trimethyl borate proceeds in milder conditions and is more convenient as far as the synthetic aspect is concerned.

Table 1
Crystal data, data collection and refinement parameters for **7**, **9**, **10**, **16**, **18**, and **21**

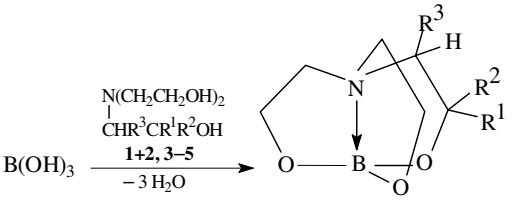
Compound	**7**	**9**	**10**	**16**	**18**	**21**
Empirical formula	$C_{26}H_{25}NO_3Si$	$C_{19}H_{22}ClNO_3Si$	$C_{19}H_{22}ClNO_3Si$	$C_{18}H_{20}BNO_3$	$C_{12}H_{17}NO_3Si$	$C_{17}H_{32}Cl_3NO_4Si$
Formula weight	427.56	375.92	375.92	309.16	251.36	448.88
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
Unit cell dimensions						
a (Å)	10.169(7)	12.286(2)	13.1203(3)	14.657(3)	9.549(3)	10.634(3)
b (Å)	11.051(6)	7.020(2)	12.6304(3)	14.784(5)	9.900(3)	10.681(3)
c (Å)	11.148(3)	20.807(2)	21.6576(4)	14.694(4)	13.085(5)	19.977(11)
α (°)	98.11(3)					
β (°)	94.74(4)	95.78(2)	92.650(1)	101.86(2)	99.36(3)	
γ (°)	114.29(5)					
V (Å^3)	1117(1)	1758.3(6)	3585.1(1)	3116(2)	1220.5(7)	2269(2)
Z	2	4	8	8	4	4
D_{calc} (g cm^{-3})	1.272	1.399	1.393	1.318	1.368	1.314
Absorption coefficient (mm^{-1})	0.133	0.300	0.298	0.088	0.189	0.478
F(000)	452	792	1584	1312	536	952
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Bruker SMART	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Temperature (K)	293(2)	293(2)	120.0(2)	293(2)	293(2)	293(2)
Graphite-monochromated Mo Kα radiation (λ/Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
θ Range (°)	2.06–25.47	1.67–24.97	1.88–28.00	2.20–24.97	2.16–24.98	2.04–24.99
Index ranges	$-12 \leqslant h \leqslant 10$, $-13 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 13$	$-14 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 8$, $0 \leqslant l \leqslant 24$	$-17 \leqslant h \leqslant 14$, $-16 \leqslant k \leqslant 14$, $-28 \leqslant l \leqslant 25$	$-17 \leqslant h \leqslant 17$, $-3 \leqslant k \leqslant 17$, $-3 \leqslant l \leqslant 17$	$-11 \leqslant h \leqslant 11$, $-11 \leqslant k \leqslant 11$, $-3 \leqslant l \leqslant 15$	$-12 \leqslant h \leqslant 2$, $-12 \leqslant k \leqslant 2$, $-23 \leqslant l \leqslant 4$
Reflections collected	4283	3134	12452	8825	5524	4146
Independent reflections (R_{int})	4077 (0.0790)	3134 (0.0000)	4306 (0.0206)	5475 (0.0437)	2147 (0.0327)	3318 (0.0196)
Data/restraints/parameters	4077/0/376	3134/0/315	4306/0/314	5475/0/576	2147/0/223	3318/0/247
Goodness-of-fit on F^2	0.893	0.933	1.077	0.868	1.099	0.961
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0578$, $wR_2 = 0.1555$	$R_1 = 0.0643$, $wR_2 = 0.1318$	$R_1 = 0.0331$, $wR_2 = 0.0890$	$R_1 = 0.0390$, $wR_2 = 0.0785$	$R_1 = 0.0399$, $wR_2 = 0.1019$	$R_1 = 0.0337$, $wR_2 = 0.0831$
R indices (all data)	$R_1 = 0.3055$, $wR_2 = 0.2031$	$R_1 = 0.1355$, $wR_2 = 0.1587$	$R_1 = 0.0399$, $wR_2 = 0.0926$	$R_1 = 0.1616$, $wR_2 = 0.0984$	$R_1 = 0.0605$, $wR_2 = 0.1077$	$R_1 = 0.1150$, $wR_2 = 0.0946$
Flack parameter [39]						0.02(9)
Largest difference in peak and hole (e Å^{-3})	0.270 and −0.293	0.281 and −0.338	0.412 and −0.411	0.227 and −0.172	0.257 and −0.226	0.216 and −0.187



6–13

6: *erythro*, M = Si, X = C≡CPh, R^1=R^3=Ph, R^2= H; **7**: *threo*, M = Si, X = C≡CPh, R^1=H; R^2=R^3= Ph;
8: M = Si, X = C≡CPh, R^1=R^2=Ph, R^3=H; **9**: *erythro*, M = Si, X = CH_2Cl, R^1=R^3=Ph, R^2=H;
10: *threo*, M = Si, X = CH_2Cl, R^1=H, R^2=R^3=Ph; **11**: M = Si, X = CH_2Cl, R^1=R^2=Ph, R^3=H;
12: *erythro*, MX = B, R^1=R^3=Ph, R^2=H; **13**: MX = B, R^1=R^2=Ph, R^3=H

(2)

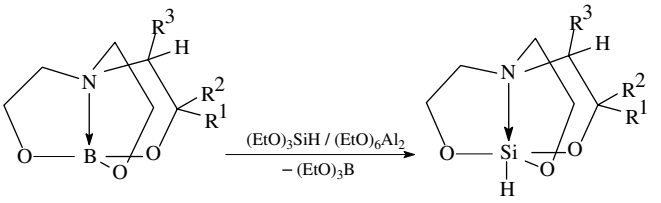


12–16

(3)

12: *erythro*, R^1=R^3=Ph, R^2=H; **13**: R^1=R^2=Ph, R^3=H;
14: R^1=Ph, R^2=R^3=H; **15**: R^1=R^2=H, R^3=Ph;
16: *threo*, R^1=H, R^2=R^3=Ph

The second method consists of successive modification of a preformed metallatrane skeleton. This can be achieved either by a reaction proceeding directly at the element atom or by a transmetallation reaction [1,6]. Such conversions essentially reflect the reactivity of metallatranes. Thus, transmetallation of boratranes **12** and **14** with triethoxysilane in the presence of triethoxyaluminium as a catalyst afforded phenylsubstituted silatranes **17** and **18** (Eq. (4)). The yields amount to 75% and 80%, respectively, and are somewhat lower than previously found for unsubstituted analogue **19** [25].

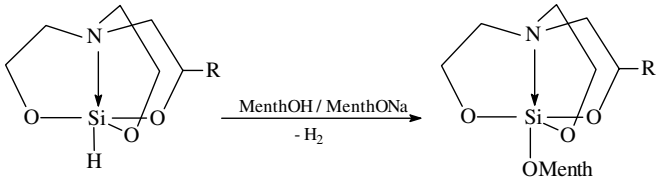


12: *erythro*, R^1=R^3=Ph, R^2=H
14: R^1=Ph, R^2=R^3=H;

17: *erythro*, R^1=R^3=Ph, R^2=H
18: R^1=Ph, R^2=R^3=H;

(4)

The Si–H function in silatrane **19** can be converted into an Si–OR function by the reaction of **19** with alcohols in the presence of the corresponding sodium alkoxide [6]. We have found that hydride **18** and its unsubstituted analogue **19** react with L-(−)-menthol in the presence of sodium to give 1-menthoxysilatranes **20** and **21**, respectively, the yield of **21** being higher (Eq. (5)).



18: R=Ph; **19**: R=H

20: R=Ph; **21**: R=H

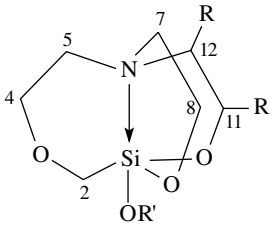
(5)

Remarkably, compound **20**, according to the NMR spectroscopy data, was isolated as one diastereomer and, therefore, presented pure enantiomeric form. The crystallization of only one of two diastereomers in solution accounts for the low yield of the product (27%). Our attempts at growing a single crystal of **20** in order to establish the absolute configuration around C^3 atom in the atrane skeleton failed. To our knowledge, this is the first example of a chemical resolution for racemic mixture of metallatranes.

Modification of a metallatrane structure may also be achieved by reactions in which the atoms of side arms of trialkanolamine moiety are involved. In this study, such transformations were of particular interest since the different nature of phenylsubstituted and unsubstituted arms of the atrane cage could govern the reaction course and, hence, might help in the clarification of the Ph-groups influence on metallatrane reactivity.

A specific reaction of intramolecular cycle expansion was found for 1-chloromethylsilatrane (**22**): the treatment with various sodium alkoxides led to the formation of 1-alkoxy-2-carba-3-oxahomosilatranes [30]. To determine the cycle expansion of whether arm (phenylsubstituted or non-substituted) is more preferable, we subjected *erythro*-3,4-diphenyl derivative **9** to the reaction with potassium *tert*-butoxide. The behaviour of silatrane **22** in similar conditions was studied as well (Eq. (6)). In case of **9**, the formation of the sole product was observed with the ring expansion taking place exclusively in an unsubstituted arm of atrane moiety. The product was assigned the structure of **23** on the basis of the ^{13}C NMR spectroscopy data. The comparison of the ^{13}C chemical shifts of 2-homosilatranes **23** and **24** with each other and with the starting **9** and **22** as well as with the previously described $N(CH_2CH_2O)_2(CH_2CH_2OCH_2)SiOEt$ (**25**) [30] (Table 2) revealed the following. In the products **23**–**25**, the ^{13}C NMR resonances of the unchanged five-membered rings carbons are downfield shifted by 2–4 ppm, as compared with those of the corresponding 1-chloromethylsilatrane, while the carbons of the expanded five-membered ring show considerably more pronounced downfield shifts of 7–11 ppm. The unambiguous assignment of the signals of **23** was made using ^{13}C APT and ^{13}C proton-coupled NMR spectra. The character of signals splitting in the latter is in full agreement with the supposed structure. To our opinion, the preferable cycle expansion of the unsubstituted arm of atrane moiety in **23** is caused by the comparative steric undifficulty and

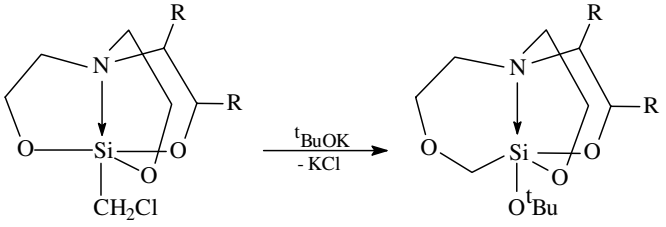
Table 2
^{13}C NMR chemical shifts of atrane cage carbons for **9** and **22**–**25**



	22	R′ = Et; R = H (**25**)[a]	R′ = *t*-Bu; R = H (**24**)	R′ = *t*-Bu; R = Ph (**23**)	**9**
C^2		65.40	67.63	67.37	
C^4	57.3	66.35	67.70	68.47	57.38
C^5	51.1	58.05	58.92	59.66	50.49
C^7	51.1	53.0	53.59	52.88	50.31
C^8	57.3	59.6	60.26	62.29	58.00
C^{11}	57.3	59.6	60.26	77.75	74.74
C^{12}	51.1	53.0	53.59	70.64	67.11

[a] Values taken from [30].

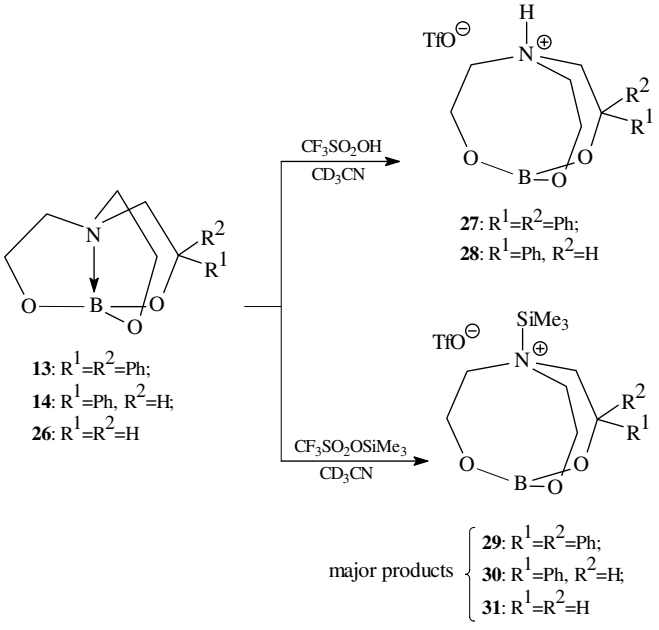
greater flexibility of the NCH_2CH_2O fragment together with the greater negative charge on the oxygen atom in NCH_2CH_2O group.



9: *erythro*, R=Ph; **22**: R=H **23**: *erythro*, R=Ph; **24**: R=H

(6)

According to the literature, electrophilic reagents such as HOTf, MeOTf, or Me_3SiOTf may react with the atrane-type compounds through an attack at the apical nitrogen atom, at apical substituent or at equatorial atoms [31–33]; the reaction pathway is determined by the nature of these groups and reagent as well as by the strength of the transannular M ← N interaction. We have tested the phenylsubstituted boratranes **13** and **14**, and their unsubstituted analogue **26** in reactions with triflic acid and Me_3Si-triflate (Eq. (7)). The treatment of boratranes **13** and **14** with HOTf resulted in the exclusive formation of N attack derivatives **27** and **28**. The attack at the N atom also prevailed in the reactions of boratranes **13**, **14** and **26** with Me_3SiOTf. In this case, however, the formation of minor products was observed. The corresponding signals in the ^{1}H and ^{13}C NMR spectra could be assigned with caution to the products of attack at the O atom ($[Me_3SiO\text{-}CH_2CH_2N(CH_2CH_2O)_2B]^+OTf^-$ in the case of **26**, for **13** and **14** regiochemistry of minor products cannot be established due to the small concentration). The formation of minor products might be explained by the greater thermodynamic preference of Si–O bond formation, as compared with Si–N bond.



(7)

The identity of compounds **27**–**31** was confirmed by ^{1}H and ^{13}C NMR spectroscopy. The signals of all atrane cage protons of products **27**–**31** are downfield shifted by 0.3–0.5 ppm in comparison with those of the starting boratranes. At the same time, the general appearance of the spectra and the signals multiplicity remain unchanged. The latter suggests that products **27**–**31** retain the symmetry of the starting boratrane molecules, and only the bridgehead N and B atoms undergo transformations in the course of an electrophilic attack.

It should be noted that the reactions of the unsubstituted boratrane **26** with triflic acid and methyl triflate were previously reported by Alder and Jin [34]. The similar process of N-protonation was found upon treatment of **26** with HOTf. In contrast, the reaction with MeOTf affor-

ded the product of O-methylation, $[MeOCH_2CH_2N(CH_2CH_2O)_2B]^+OTf^-$.

The novel compounds **3**–**21**, **23**, **24**, **27**–**31** were characterized by elemental analyses, IR, ^1H, ^{13}C, ^{11}B, ^{29}Si NMR spectroscopy and mass spectrometry.

3.3. NMR spectra

The ^1H NMR spectra of unsubstituted metallatranes comprising two broad triplets of $(AA'XX')_3$ system for $N(CH_2CH_2O)_3M$ protons are well known. The presence of one or two phenyl groups in one arm of the atrane cage complicates the spectra entailing non-equivalence of all skeleton protons [9]. A typical ^1H NMR spectrum of phenylsubstituted metallatrane shows a set of multiplets of $(ABXY)_2$ system for $N(CH_2CH_2O)_2M$ protons as well as (a) multiplets of ABX system for NCH_2CHPhO protons, or (b) two doublets of AX system for NCHPhCHPhO protons, or (c) a broad singlet or multiplet of AB system for NCH_2CPh_2O protons.

Due to the complex pattern of ^1H NMR spectra for Ph-substituted metallatranes, the ^{13}C NMR spectra proved very useful to analyse crude reaction mixtures. The ^{13}C NMR spectra of 3-Ph-substituted and 3,4-Ph_2-substituted derivatives display six signals of atrane skeleton carbons, whereas the spectra of 3,3-Ph_2-substituted compounds show four signals, two higher field ones arising from the carbon atoms of unsubstituted $N(CH_2CH_2O)_2M$ rings.

The ^{11}B chemical shifts for the prepared boratranes range between 14.0 and 15.0 ppm. These values are close to those of the previously studied $N(CH_2CH_2O)_3B$ (**26**) and $N(CH_2CHMeO)_3B$ (14.2 ppm) and correspond to the tetracoordination of boron atoms [1]. The ^{29}Si NMR spectra of the studied silatranes show single resonances in the range −79.6 to −96.5 ppm. These values testify to the pentacoordinated nature of Si atom in solution [6].

3.4. Crystal structures

To the best of our knowledge, compounds **7**, **9**, **10**, **16** and **18** are the first structurally characterized silatrane and boratrane derivatives bearing Ph substituents in the atrane cage. The molecular structures of **7**, **9**, **10**, **16** (one independent molecule), **18**, and **21** are shown in Figs. 1–6, the selected bond lengths and angles are listed in Table 3.

The coordination polyhedron of the silicon atom in studied silatranes **7**, **9**, **10**, **18**, and **21** represents a distorted trigonal bipyramid with N atom and C atom (for compounds **7**, **9**, **10**), H atom (for compound **18**) or O atom (for compound **21**) in the axial positions and three oxygen atoms occupying the equatorial sites. The $N–Si–C(H,O)_{ax}$ fragment is almost linear (173.81(5)–179.0(3)°) in all these compounds. According to the Cambridge Structural Database (ver. 5.27, January 2006) [35], the values of Si ← N distance in **7**, **9**, **10**, **18**, and **21** lie within the typical range for silatranes (1.964–2.420 Å) and clearly verify the existence of Si–N transannular bond. The silicon atom is displaced by 0.17–0.18 Å (ΔSi) towards the apical substituent from the equatorial plane defined by three oxygen atoms. It should be noted that the Si ← N distances in **7** (2.132(5) Å), **9** (2.136(4) Å), and **10** (2.124(1) Å) are close to those previously found in the unsubstituted analogues:

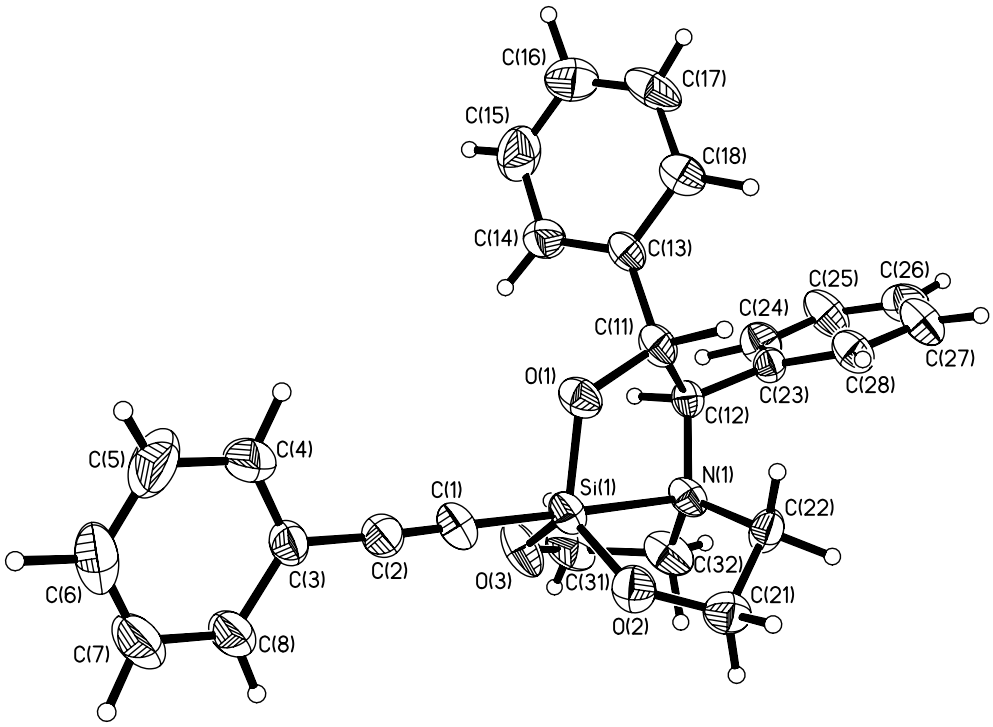


Fig. 1. Molecular structure of **7**.

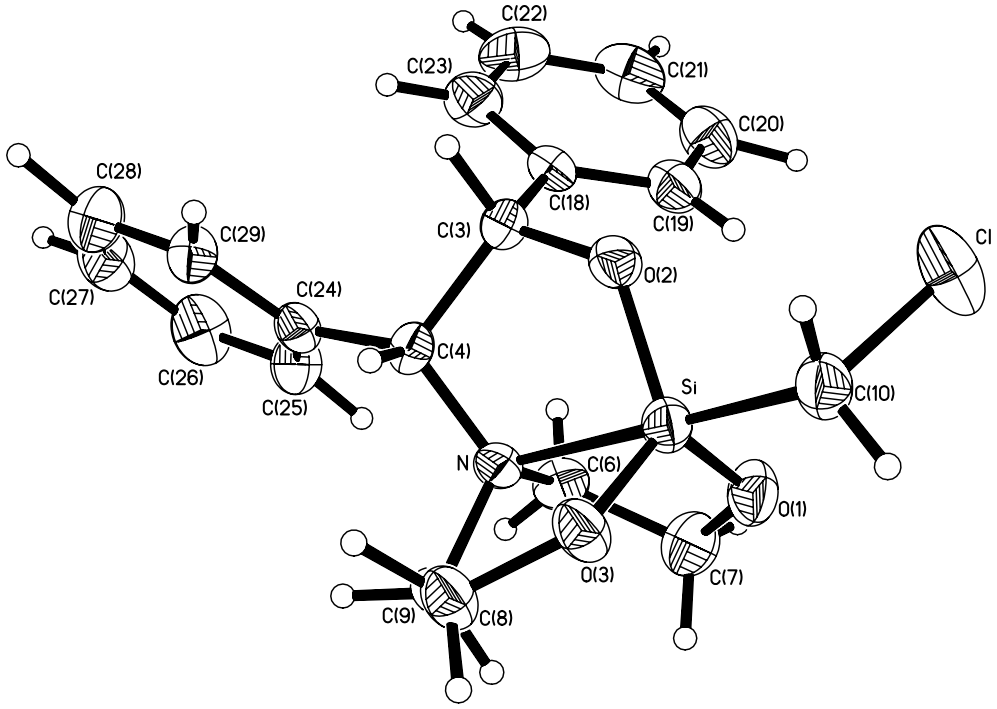


Fig. 2. Molecular structure of **9**.

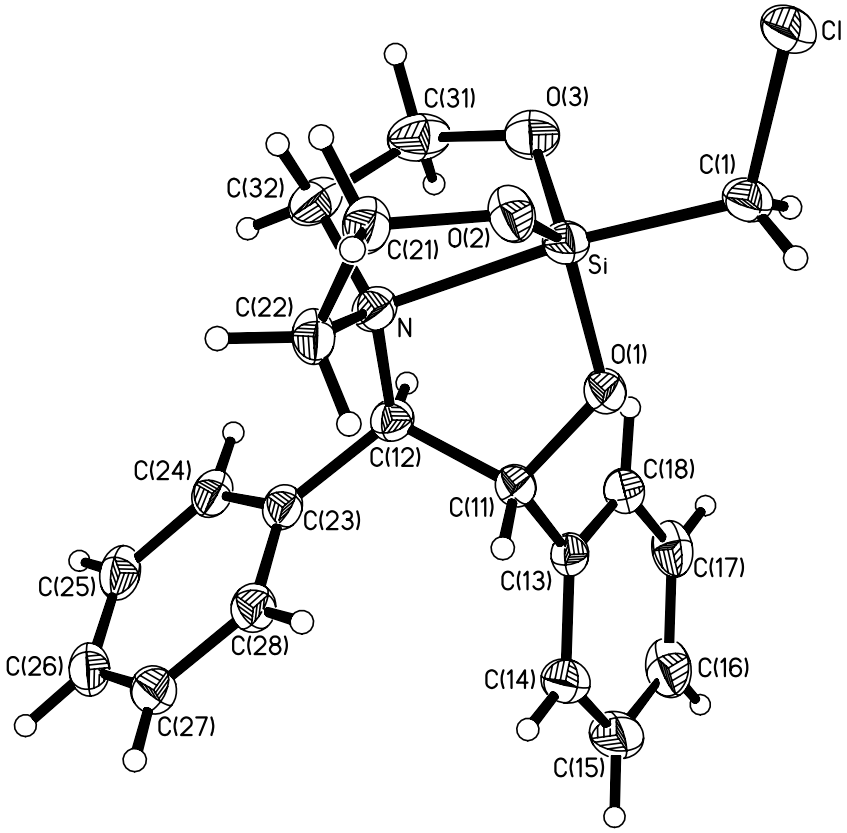


Fig. 3. Molecular structure of **10**.

$N(CH_2CH_2O)_3SiC{\equiv}CPh$ (2.094(2) Å) [12], $N(CH_2CH_2O)_3SiCH_2Cl$ (2.120(8) Å) [36]. While the structural data for $N(CH_2CH_2O)_3SiH$, unsubstituted analogue of **18**, have so far not been reported in the literature, some data concerning the X-ray investigation of $N(CH_2CHMeO)_3SiH$ are available in a review by Hencsei [37]. The value of Si ← N

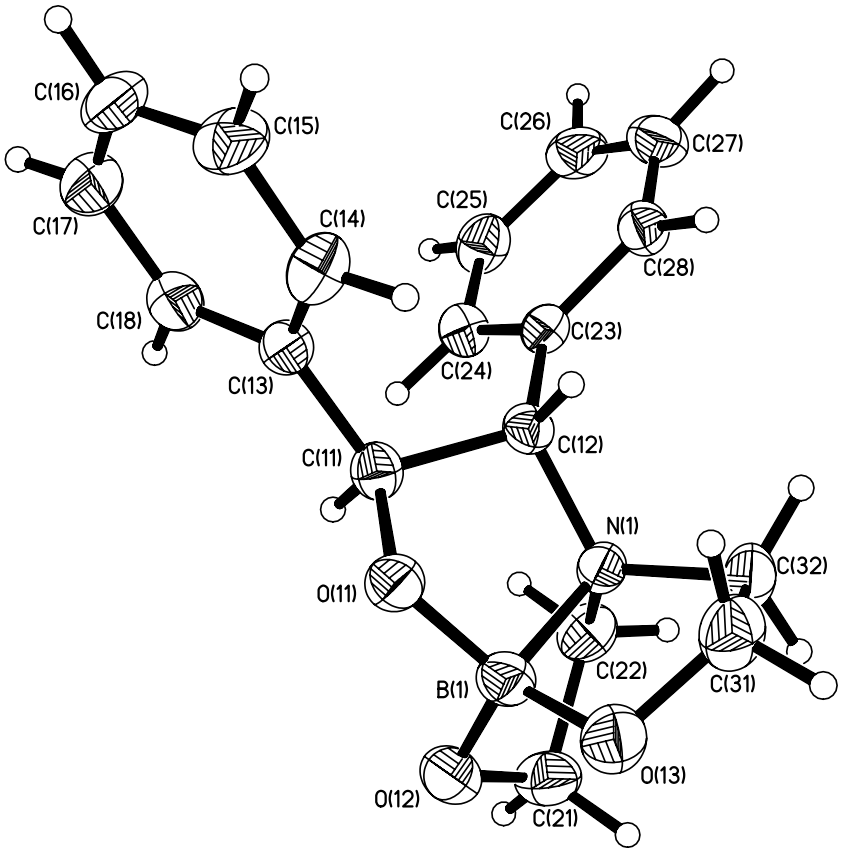


Fig. 4. Molecular structure of **16**. One independent molecule is shown.

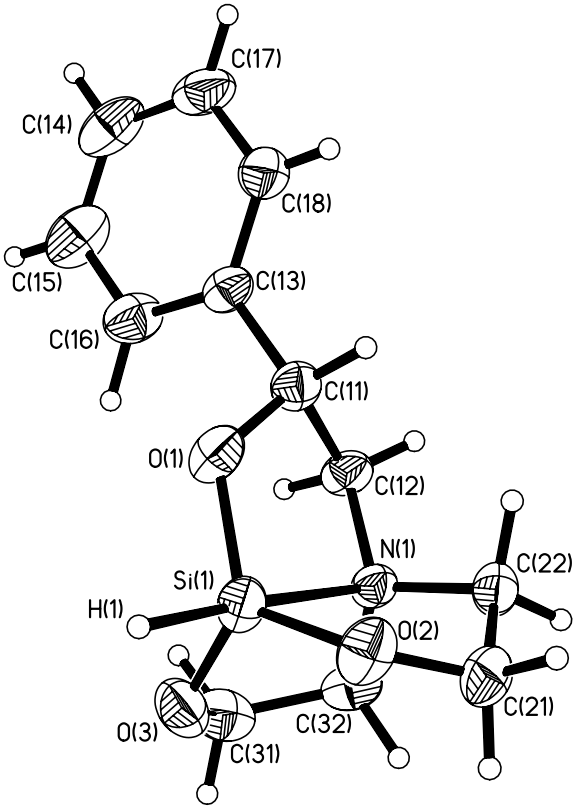


Fig. 5. Molecular structure of **18**.

distance in **18** (2.135(2) Å) is close to that in $N(CH_2CH\text{-}MeO)_3SiH$ (2.146 Å) as well. Previously we have shown that the M ← N distance alterations in germatranes bearing the same apical substituents and different substituents at carbon atoms of the atrane skeleton are caused mainly by the steric requirements and crystal packing effects [8,9].

The $Si–O_{eq}$ distances in Ph-substituted arms of atrane moiety are slightly longer than the $Si–O_{eq}$ distances in the unsubstituted arms within the same molecule (see Table 3). All five-membered rings of silatrane skeleton in **7**, **9**, **10**, **18**, and **21** adopt an "envelope"-like conformation, the carbon atoms in α-positions to the N atom occupy the "flap" sites. In the substituted five-membered rings of compounds **7**, **9**, **18**, and **21**, the phenyl groups occupy the equatorial positions. In silatrane **10**, the Ph-group that is bound to the carbon atom in α-position to the N atom occupies the axial position.

The structure of boratrane **16** essentially differs from that of silatranes. The coordination polyhedron of the B atom in **16** represents a distorted tetrahedron with the boron being displaced by 0.31, 0.32 Å (ΔB) towards the nitrogen atom from the equatorial plane defined by three oxygen atoms. The N-B-O angles vary within the range 102.1(2)–103.2(2)°, while the O–B–O angles vary within the range 113.3(2)–116.3(2)°. All five-membered rings of the boratrane skeleton adopt an "envelope"-like conformation. The carbon atoms lying in β-positions to the N atom

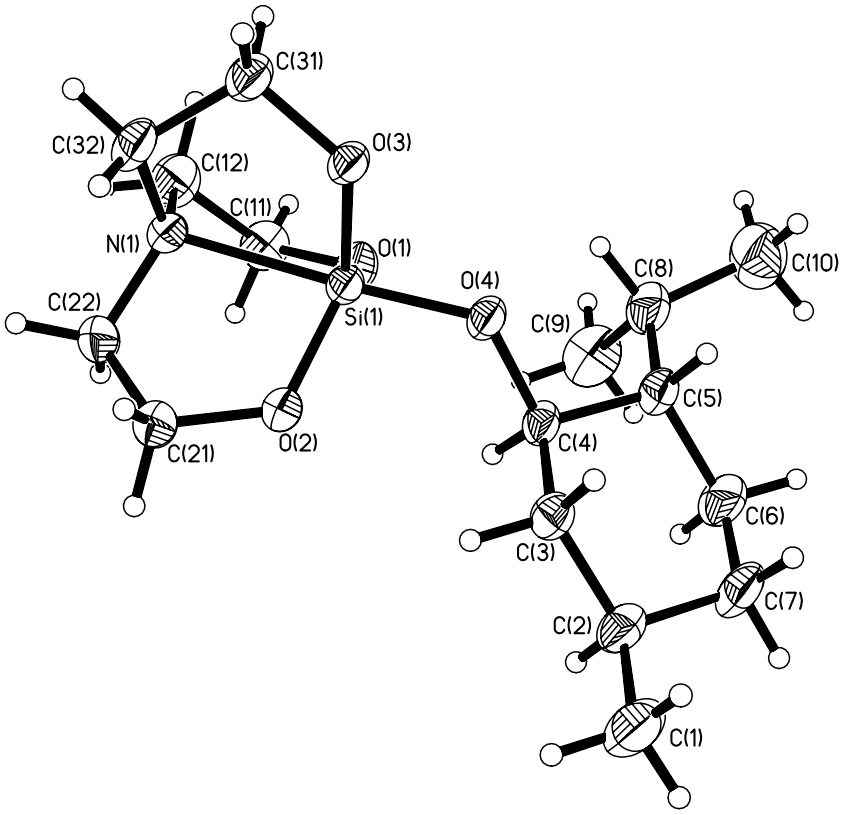


Fig. 6. Molecular structure of **21**.

Table 3
The main geometrical parameters for **7**, **9**, **10**, **16**, **18**, and **21**

Compound	d(M···N) (Å)	d(M–X) (Å)	ΔM (Å)	ΔN (Å)	d(M–O) (Å)		∠N–M–X (°)
					Unsubstituted arm	Substituted arm	
7	2.132(5)	1.856(7)	0.17	0.35	1.648(5) 1.652(5)	1.666(4)	179.0(3)
9	2.136(4)	1.874(6)	0.17	0.35	1.643(3) 1.659(3)	1.659(3)	177.4(2)
10	2.124(1)	1.894(2)	0.17	0.38	1.662(1) 1.665(1)	1.666(1)	173.81(5)
16[a]	1.684(3)		0.32	0.32	1.425(3) 1.436(3)	1.446(3)	
	1.687(3)		0.31	0.34	1.423(3) 1.429(3)	1.437(4)	
18	2.135(2)	1.50(2)	0.18	0.38	1.659(2) 1.654(2)	1.660(2)	176.6(8)
21	2.130(3)	1.657(2)	0.18	0.38	1.654(2) 1.651(2) 1.657(3)		176.4(1)

[a] Two independent molecules.

occupy the "flap" sites. The B ← N distances in **16** (1.684(3) Å, 1.687(3) Å, two independent molecules) are slightly longer than that in the parent boratrane $N(CH_2CH_2O)_3B$ (1.6764(3) Å) [38].

Summarizing the results, a series of silatranes and boratranes based on the C-phenylsubstituted trialkanolamines have been prepared using two different approaches. The presence of phenyl groups in the ligands reduces the rate of atrane skeleton formation and in most cases decreases the product yields in comparison with those found for the unsubstituted analogues. We have shown that in the reaction of *erythro*-1-chloromethyl-3,4-diphenylsilatrane with *tert*-BuOK, the unsubstituted NCH_2CH_2O arm exclusively undergoes the intramolecular cycle expansion. The chemical behaviour of the prepared boratranes was examined in the reactions with triflic acid and Me_3Si-triflate. Irrespective of boratrane structure, the electrophilic attack takes place mainly at the bridgehead nitro-

gen atom. The presence of phenyl substituents in the atrane cage of the studied metallatranes results in only a slight elongation of the M ← N coordination bond in the solid state, as compared with the corresponding unsubstituted counterparts. Taking into account the earlier investigations [8,9], such M ← N distance alteration should be referred to the crystal packing effects.

Acknowledgements

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Appendix A. Supplementary data

The crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications Nos. CCDC 247418 for **7**, 247419 for **9**, 247416 for **10**, 247417 for **16**, 247414 for **18** and 247419 for **21**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (int. code) + 44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.07.109.

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