Utilization of industrial waste materials. Part 20.[1] Stereoselective cycloaddition of silylenes and a disilene to an enantiomerically pure cyclic ketimine derived from an industrial waste material

Nikolai Graf von Keyserlingk, Jürgen Martens,* Detlev Ostendorf, Wolfgang Saak and Manfred Weidenbruch *

Department of Chemistry, University of Oldenburg, 26111 Oldenburg, Germany. E-mail: juergen.martens@uni-oldenburg.de

Received (in Cambridge, UK) 30th October 2000, Accepted 1st February 2001
First published as an Advance Article on the web 2nd March 2001

A new enantiomerically pure aromatic cyclic ketimine with two stereogenic centres derived from an industrial waste material has been used as a reactant in novel stereoselective cycloadditions of silylenes and disilenes. The products obtained are chiral non-aromatic organosilanes.

Introduction

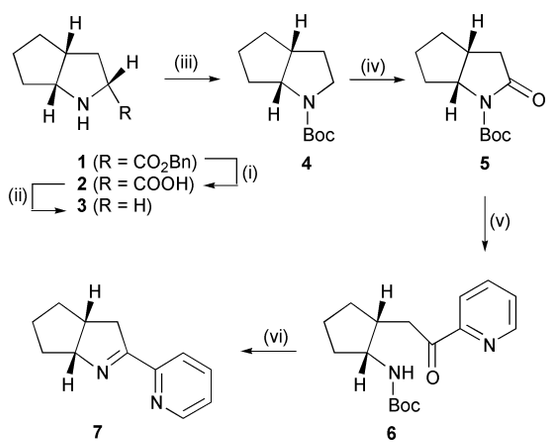
The widespread use of chiral nitrogen-containing ligands is mainly based on their successful practical application in several fields of organometallic chemistry *e.g.* enantioselective catalysis[2] and ligand exchange chromatography.[3] Dinitrogen ligands, namely chiral oxazolinylpyridines, have been shown to be highly enantioselective in several test reactions. Thus, the pyridine structure plays an important role in coordination chemistry[4] and in enantioselective catalysis. For the latter application many optically active pyridines with different side-chains (amines,[5] imines[6] and oxazolines[7]) have been developed in the last few years. As previously shown, reactions of pyridine-2-carbaldimines bearing an open-chain substituent on the aldimine nitrogen atom with silylenes R_2Si**:** proceed through [4+1] cycloaddition of the reactive species to both nitrogen atoms and furnish products in which the hetero-aromatic pyridine ring has been converted into a system of non-aromatic, conjugated double bonds.[8]

In the context of our studies on the utilization of industrial waste materials we used the enantiomerically pure amine **3** as the starting material for the synthesis of the α-substituted imine **7**. We were interested in investigating if the chiral ketimine **7** in which both nitrogen atoms are incorporated in rings would undergo cycloadditions with silylenes. The bicyclic optically active pyrrolidine analogue **3** (Scheme 1) is available from the nonrecyclable enantiomerically pure waste material **1**[9] from the production of the ACE inhibitor ramipril.[10] In the industrial synthesis of ramipril only the (all-*S*)-enantiomer of the (all-*R*)-amino acid **2** can be used. Until now there have been no industrial applications for the (all-*R*)-amino acid **2** or its benzyl ester **1**.

Results and discussion

For introduction of the 2-pyridyl subunit the 3-position of the amine **3** has to be activated towards nucleophilic attack. The oxidative conversion[11] of the Boc-protected bicyclic amine **4** into the new five-membered lactam **5** and subsequent reaction with 2-pyridyllithium turned out to be an effective synthetic protocol. The resulting ketone **6** was then treated with trifluoroacetic acid to remove the protecting group. Upon direct intramolecular dehydration the new chiral cyclic imine **7**[12] is obtained.

The pyrrolidine analogue **3** was converted into its Boc-derivative **4**[13] by treatment with Boc_2O–triethylamine in THF. The oxidation to the Boc-protected lactam **5** was achieved by



Scheme 1 Four-step synthesis of the optically active imine **7** starting from the bicyclic amine **3**. *Reagents, conditions and yields*: (i) Pd/C, cyclohexene, 2 h reflux;[10] (ii) cyclohex-2-enone, tetraglyme, 2 h 170 °C;[9] (iii) Boc_2O, NEt_3, in THF, 18 h room temp., 80%; (iv) RuO_2, $NaIO_4$, in H_2O–ethyl acetate, 3 h room temp., 76%; (v) 2-bromopyridine, *n*-BuLi in Et_2O, 4 h −78 °C, 50%; (vi) trifluoroacetic acid, in CH_2Cl_2, 3 h room temp., 79%.

reaction with a catalytic amount of RuO_2 in an aqueous solution of $NaIO_4$ as oxidizing agent and ethyl acetate as solvent.[14] In the next step the Boc-protected lactam **5** was allowed to react at −78 °C with 2-pyridyllithium[15] in Et_2O to afford the ketone **6**. We were not able to isolate the ketone **6** in an analytically pure form. However, after chromatographic purification **6** was directly converted into the cyclic imine **7** by cleavage of the Boc protecting group with trifluoroacetic acid and subsequent alkaline and extractive work-up. The optically active cyclic imine **7** was purified by column chromatography and obtained as a slightly yellow oil which solidified on standing to afford a low melting, nearly colourless solid.

Photolysis of the trisilane **8**,[16] conditions that afford dimesitylsilylene, in the presence of **7** resulted in the formation of a red solution from which dark red crystals were isolated in a yield of 38% (Scheme 2). The high sensitivity of these crystals to air and moisture suggests that the heteroaromatic ring of **7** has been transformed into a system of conjugated double bonds. This assumption was confirmed by the ^1H and ^{13}C NMR spectral data as well as by an X-ray crystallographic analysis (Fig. 1).

Compound **9** crystallises in the chiral space group $P2_12_12_1$. The average values of 1.34 and 1.45 Å, respectively, for the C=C double and C–C single bonds are in the typical ranges for a

 DOI: 10.1039/b008708o

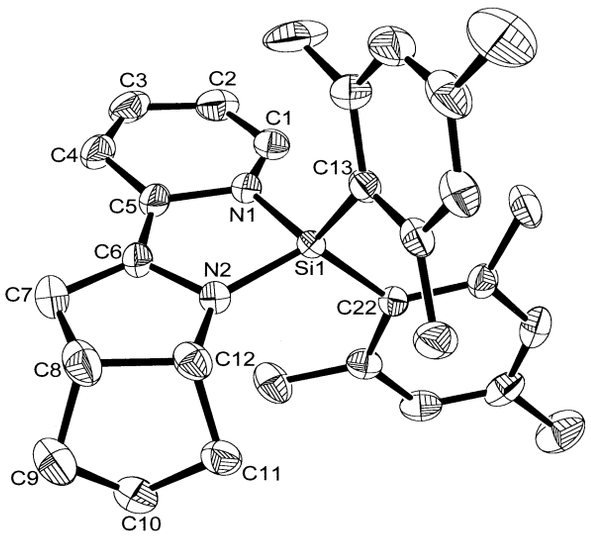
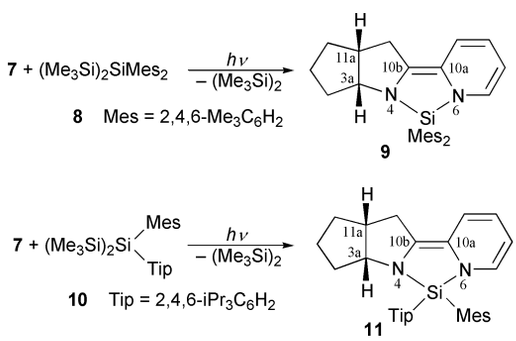


Fig. 1 Molecular structure of **9** (50% probability, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.340(3), C(2)–C(3) 1.451(4), C(3)–C(4) 1.342(4), C(4)–C(5) 1.440(3), C(5)–C(6) 1.347(3), C(5)–N(1) 1.445(2), C(6)–N(2) 1.406(3), N(1)–Si 1.7559(16), N(2)–Si 1.7404(17), N(1)–Si–N(2) 90.09(8), Si–N(1)–C(5) 110.90(14), N(1)–C(5)–C(6) 111.73(16), C(5)–C(6)–N(2) 114.89(19), C(6)–N(2)–Si 113.36(14).



Scheme 2 Reactions of **7** with two diarylsilylenes.

conjugated system. The arrangements of the substituents about the two nitrogen atoms in **9** are almost planar so that these atoms do not constitute additional stereogenic centres.

Thus, in order to generate a new stereogenic centre, compound **7** was irradiated in the presence of the trisilane **10**;[17] under these conditions the latter compound dissociates to give the heteroleptic mesityl(2,4,6-triisopropylphenyl)silylene. Dark red, highly air- and moisture-sensitive crystals of **11** were isolated from the reaction mixture in 43% yield. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the product each exhibit a double set of signals, demonstrating that the [4+1] cycloaddition of the heteroleptic silylene to **7** has resulted in a 1 : 1 mixture of diastereomers.

An X-ray crystallographic analysis of **11** (Fig. 2) again revealed that the heteroaromatic ring of **7** has been transformed into a system of conjugated double bonds by addition of the silylene. Compound **11** crystallises in space group *P*1 with two independent molecules in the unit cell. Similarly to the situation in **8**, the nitrogen atom N(2) shows only minimal pyramidalisation (angular sum: 353°). In view of the small barriers to inversion at the nitrogen atom in ring systems of this type, it is however unlikely that this nitrogen atom constitutes a further stereogenic centre.[18]

The high sensitivities of compounds **9** and **11** towards air and moisture are indicative of an increased reactivity of the conjugated double bonds. In order to test this hypothesis, **7** was allowed to react with the cyclotrisilane **12** which, upon photolysis, generates the silylene **13** together with the disilene

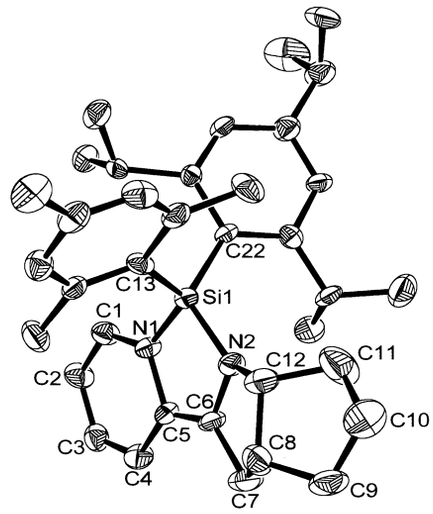
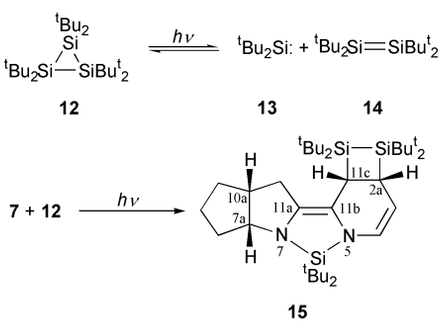


Fig. 2 Molecular structure of **11** (50% probability, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.366(9), C(2)–C(3) 1.430(11), C(3)–C(4) 1.358(10), C(4)–C(5) 1.440(9), C(5)–C(6) 1.337(9), C(5)–N(1) 1.455(9), C(6)–N(2) 1.412(8), N(1)–Si 1.747(5), N(2)–Si 1.736(6), N(1)–Si–N(2) 89.8(3), Si–N(1)–C(5) 112.6(4), N(1)–C(5)–C(6) 109.9(6), C(5)–C(6)–N(2) 116.3(6), C(6)–N(2)–Si 111.3(4).



Scheme 3 Silylene and disilene additions to the imine **7**.

14 (Scheme 3).[19] Although disilenes like **14** undergo a wide variety of [2+2] cycloaddition reactions, they only exceptionally react with C=C double bonds.[20]

Irradiation of **7** in the presence of **12** resulted in the formation of colourless crystals isolated in 41% yield, the analytical and spectral data of which were indicative of the polycyclic system **15**. In this case also it would appear that the reaction sequence involves an initial [4+1] cycloaddition of the dialkylsilylene **13** to the nitrogen atoms of **7** and a subsequent [2+2] cycloaddition of the disilene **14** to the activated double bond.

The constitution of **15** was confirmed by an X-ray crystallographic analysis (Fig. 3), which also revealed some interesting features. The cycloaddition of **14** is a regio- and diastereoselective process. As a consequence of the presence of bulky *tert*-butyl groups all bond lengths within the 3,4-disilacyclobutane ring are elongated. With angular sums of about 355° both nitrogen atoms show slight pyramidalisations which—similarly to the case of compound **11**—are of little stereochemical relevance on account of the presumably low barrier to inversion.

Experimental

General remarks

All reactions involving air- and moisture-sensitive materials were performed in oven dried glassware under an inert gas atmosphere of dry argon. Photolyses were carried out at room temperature by using a high-pressure mercury immersion lamp (Heraeus TQ 150). Thin layer chromatography (TLC) analyses

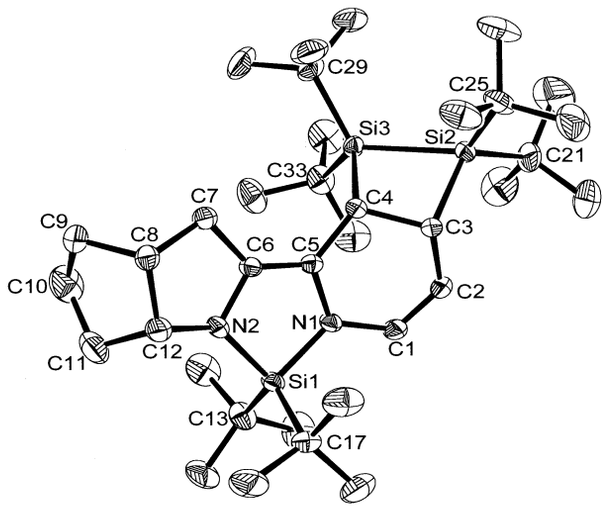


Fig. 3 Molecular structure of **15** (50% probability, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.327(3), C(2)–C(3) 1.501(3), C(3)–C(4) 1.586(3), C(4)–C(5) 1.497(3), C(5)–C(6) 1.341(3), C(5)–N(1) 1.436(2), C(6)–N(2) 1.426(2), N(1)–Si(1) 1.7661(16), N(2)–Si(1) 1.7474(19), C(3)–Si(2) 1.936(2), C(4)–Si(3) 1.951(2), Si(2)–Si(3) 2.4145(9), N(1)–Si(1)–N(2) 91.59(8), Si(1)–N(1)–C(5) 110.10(13), N(1)–C(5)–C(6) 112.10(17), C(5)–C(6)–N(2) 116.52(19), C(6)–N(2)–Si(1) 108.83(13), C(3)–Si(2)–Si(3) 77.78(7), Si(2)–Si(3)–C(4) 74.74(7), Si(3)–C(4)–C(3) 101.94(12), C(4)–C(3)–Si(2) 98.37(13).

were performed on silica gel Polygram® plates using a fluorescence indicator from Macherey Nagel & Co., Düren. TLC spots were detected with either UV light or iodine. For preparative chromatography Merck silica gel 60, 230–400 mesh was used. Melting points were determined in open capillaries (in the case of air- and moisture-sensitive materials in closed capillaries) in a Dr Lindström or a MelTemp Laboratory Devices, Cambridge (USA) instrument and are uncorrected. Optical rotations were measured on a Perkin-Elmer automatic polarimeter 241 MC; values are given in 10^{-1} deg cm^2 g^{-1}. Infrared spectra were recorded on a Beckmann IR 4220 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 300 or a Bruker AMX 500 spectrometer (300.1 MHz/75 MHz and 500.1 MHz/125.8 MHz, respectively). Chemical shifts are reported on the δ-scale [ppm] relative to residual nondeuterated solvent or tetramethylsilane (TMS) in $CDCl_3$ or C_6D_6. Coupling constants, *J*, are given in hertz (Hz). Mass spectra were taken on a Finnigan-MAT 212 instrument in a CI mode with isobutane as reactant gas. Elemental analyses were performed with a C, H, N-Analyser EA 1108 from Fisons Instruments at the University of Oldenburg or by Analytische Laboratorien, D-51789 Lindlar, Germany.

(all-*R*)-*N*-(*tert*-Butyloxycarbonyl)-2-azabicyclo[3.3.0]octane 4[13]

Under an atmosphere of dry argon the bicyclic amine **3** (5.50 g, 50 mmol) was dissolved in anhydrous THF (50 mL). At room temp. triethylamine (11.10 g, 110 mmol) was added over 15 minutes. After cooling to 0 °C $(Boc)_2O$ (10.90 g, 49 mmol) in anhydrous THF (50 mL) was slowly dropped into the reaction mixture. After complete addition the cooling bath was removed and stirring was continued for 18 h at room temp. THF was removed *in vacuo* and the residue was dissolved in Et_2O (50 mL). The ethereal solution was washed with H_2O, 2 M HCl, saturated $NaHCO_3$ solution and brine (2 × 25 mL each). The organic layer was dried ($MgSO_4$) and was concentrated *in vacuo* to give the protected amine **4** (8.49 g, 80% yield) as a slightly yellow oil, which was used without further purification (Found: C, 68.04; H, 10.23; N, 6.72. $C_{12}H_{21}NO_2$ (211.2) requires C, 68.20; H, 10.02; N, 6.63%); $[\alpha]_D^{20}$ −110.9 (*c* 1.90, CH_2Cl_2); ν_{max} (NaCl)/cm^{-1} 1740; δ_H ($CDCl_3$, 300.1 MHz) 1.25–1.91 (8H, m, 4-H, 5-H, 6-H$_2$, 7-H$_2$, 8-H$_2$), 1.46 (9H, s, $C(CH_3)_3$), 2.49–2.65 (1H, m, 4-H), 3.13–3.39 (1H, m, 3-H), 3.43–3.51 (1H, m, 3-H), 3.90–4.09 (1H, m, 1-H); δ_C ($CDCl_3$, 75 MHz, rotamers) 28.46 ($C(CH_3)_3$), 25.10, 30.10, 31.12, 31.89, 34.01, 34.56 (C-4, C-6, C-7, C-8), 42.41, 43.18 (C-3), 45.79, 46.46 (C-3), 62.49 (C-1), 78.60 ($C(CH_3)_3$), 154.51 (C=O); *m*/*z* (CI-isobutane) 156 (100%) [$MH^+ - C_4H_8$], 212 (35%) [MH^+].

(all-*R*)-*N*-(*tert*-Butyloxycarbonyl)-2-azabicyclo[3.3.0]octan-3-one 5

In a 1000 mL, three-necked, round-bottomed flask, equipped with a reflux condenser and 250 mL dropping funnel, ruthenium dioxide hydrate (0.28 g) was dissolved in aqueous $NaIO_4$ solution (330 mL, 10% aqueous solution). To the bright yellow solution the *N*-protected bicyclic amine **4** (7.00 g, 33 mmol), dissolved in ethyl acetate (110 mL), was added dropwise at room temp. with vigorous stirring over a period of 1 h. After the addition the stirring was continued for 3 h until TLC showed no more starting material. The phases were separated and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were treated with propan-2-ol (8 mL) with stirring for 2 h. The black precipitate was filtered off and the organic phase was washed with H_2O (50 mL). After drying ($MgSO_4$) the ethyl acetate was removed *in vacuo*. The resulting dark red oil was purified by column chromatography on silica gel 60, eluent: *n*-hexane–ethyl acetate 2 : 1, R_f 0.50. Crystallisation of the yellow oil from Et_2O at −20 °C is possible, but for the next step the oil obtained after column chromatography was used; yield 5.65 g (76%) as a colourless solid, mp 79–82 °C (Found: C, 63.86; H, 8.47; N, 6.21. $C_{12}H_{19}NO_3$ (225.1) requires C, 63.98; H, 8.50; N, 6.22%); $[\alpha]_D^{20}$ −11.7 (*c* 1.00, CH_2Cl_2); ν_{max} (KBr)/cm^{-1} 1690; δ_H ($CDCl_3$, 300.1 MHz) 1.51 (9H, s, $C(CH_3)_3$), 1.55–2.05 (6H, m, 6-H$_2$, 7-H$_2$, 8-H$_2$), 2.23 (1H, dd, ^2J = 17.5 and ^3J = 4.4, H-4), 2.62 (1H, m, H-5), 2.75 (1H, dd, ^2J = 17.5 and ^3J = 10.4, H-4), 4.41 (1H, m, H-1); δ_C ($CDCl_3$, 75 MHz) 27.96 ($C(CH_3)_3$), 23.96, 32.88, 33.71, 34.47 (C-4, C-6, C-7, C-8), 39.02 (C-5), 63.09 (C-1), 82.52 ($C(CH_3)_3$), 149.99 (C=O), 174.57 (C-3); *m*/*z* (CI-isobutane) 170 (100%) [$MH^+ - C_4H_8$], 226 (50%) [MH^+], 126 (30) [$MH^+ - C_4H_8 - CO_2$].

(all-*R*)-2-[*N*-(*tert*-Butyloxycarbonyl)-2′-amino-1′-cyclopentyl]-1-(pyridin-2-yl)ethanone 6

Under an atmosphere of dry argon *n*-butyllithium (19.3 mL of a 1.6 M solution in *n*-hexane, 30.9 mmol) was introduced into a dry 250 mL, three-necked, round-bottomed flask, equipped with a thermometer, a dropping funnel and a septum. The reaction flask was cooled down to −78 °C, at which temperature a solution of 2-bromopyridine (4.30 g, 27.5 mmol) in anhydrous Et_2O (50 mL) was slowly added. After complete addition the reaction mixture was stirred at −78 °C for an additional 30 minutes. To the dark red solution the *N*-protected lactam **5**, dissolved in anhydrous Et_2O (25 mL), was added dropwise over a period of 15 minutes. The reaction mixture was stirred for another 4 h and then slowly allowed to warm to −40 °C. At this temperature, the mixture was hydrolysed with saturated NH_4Cl solution (40 mL). The cooling bath was removed and the reaction flask was allowed to warm to room temp. The phases were separated and the aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with brine (30 mL) and dried ($MgSO_4$). Evaporation of the solvent gave the crude γ-aminoketone **6** as a dark red oil, which was submitted to column chromatography, eluent: *n*-hexane–ethyl acetate 2 : 1, addition of 1% triethylamine, R_f 0.33; yield 3.80 g (50%), yellow oil with impurities; the oily product was used without characterisation in the next step.

(all-*R*)-3-(Pyridin-2-yl)-2-azabicyclo[3.3.0]oct-2-ene 7

The crude Boc-protected γ-aminoketone **6** (3.39 g, 11.5 mmol) was dissolved in anhydrous CH_2Cl_2 (50 mL) and cooled down

to 0 °C. At this temperature trifluoroacetic acid (44 mL) was added dropwise over a period of 30 minutes. After complete addition the cooling bath was removed and the reaction mixture was allowed to reach room temp. Stirring was continued for 3 h. For work-up the reaction flask was cooled again to 0 °C and NaOH (35% aqueous solution, 70 mL) was added dropwise. During the addition the temperature should not exceed 10 °C. The alkaline solution was extracted with Et_2O (3 × 50 mL) and the combined organic extracts were washed with brine. After drying ($MgSO_4$) the solvent was removed *in vacuo*. The resulting brown oil was purified by column chromatography, eluent: *n*-hexane–ethyl acetate 4 : 1, addition of 2% triethylamine, R_f 0.50; yield 1.65 g (79%), yellow oil which solidified on standing, mp 39–40 °C (Found: C, 77.33; H, 7.61; N, 15.00. $C_{12}H_{14}N_2$ (186.1) requires C, 77.38; H, 7.58; N, 15.04%); $[\alpha]_D^{20}$ +51.3 (*c* 1.00, CH_2Cl_2); ν_{max} (KBr)/cm^{-1} 2940, 1670, 1570, 1500; δ_H ($CDCl_3$, 500.1 MHz) 1.40, 1.54, 1.77, 1.93 (6H, 4 m, 6-H_2, 7-H_2, 8-H_2), 2.82 (1H, m, 5-H), 2.93 (1H, dd, ^2J = 18.1 and ^3J = 3.3, 4-H), 3.33 (1H, dd, ^2J = 18.1 and ^3J = 9.9, 4-H), 4.73 (1H, m, 1-H), 7.30 (1H, ddd, ^3J = 7.1, ^3J = 4.9 and ^4J = 1.1, pyridine-H), 7.72 (1H, m, pyridine-H), 8.10 (1H, d, ^3J = 7.1, pyridine-H), 8.63 (1H, d, ^3J = 4.9, pyridine-H); δ_C (125.8 MHz, $CDCl_3$) 24.04, 33.09, 34.78 (C-6, C-7, C-8), 38.84 (C-5), 43.84 (C-4), 80.01 (C-1), 121.99, 124.39, 136.19, 148.94, 153.21 (pyridine-C), 173.13 (C-3); *m*/*z* (CI-isobutane) 187 (100%) [MH^+].

(all-*R*)-1,2,3,3a,11,11a-Hexahydro-5,5-bis(2,4,6-trimethylphenyl)cyclopenta[4′,5′]pyrrolo[1′,2′ : 3,4][1,3,2]diazasilolo-[1,5-*a*]pyridine 9

A solution of the acyclic trisilane **8** (1 g, 2.4 mmol) and imine **7** (0.45 g, 2.4 mmol) in *n*-hexane (80 mL) was irradiated for 6 h at room temperature. The red solution was concentrated *in vacuo* to a volume of 10 mL and kept at −50 °C for several days. The product (0.4 g, 38%) was obtained as dark red crystals, mp 148 °C (Found: C, 79.40; H, 8.20; N, 6.00. $C_{30}H_{36}N_2Si$ (452.7) requires C, 79.59; H, 8.02; N, 6.19%); $[\alpha]_D^{20}$ −476.7 (*c* = 0.03, *n*-hexane); ν_{max} (KBr)/cm^{-1} 1527, 1547, 1570, 1604, 1632; λ_{max}(ε/dm^3 mol^{-1} cm^{-1}) (*n*-hexane)/nm 456 (1520); δ_H (C_6D_6, 500.1 MHz) 1.19–1.45 (6H, m, 1-H_2, 2-H_2, 3-H_2), 2.03 (1H, dd, 11-H, ^2J 15.4, ^3J 6.0), 2.07 (3H, s, *p*-CH_3), 2.09 (3H, s, *p*-CH_3), 2.34 (6H, s, *o*-CH_3), 2.43 (6H, s, *o*-CH_3), 2.53 (1H, dd, 11-H, ^2J 15.4, ^3J 9.5), 2.61 (1H, m, 11a-H), 3.81 (1H, ddd, 3a-H, $^3J_{3a,3}$ 3.7, $^3J_{3a,3}$ 7.0, $^3J_{3a,11a}$ 14.1), 4.88 (1H, ddd, 8-H, $^3J_{8,7}$ 7.2, $^3J_{8,9}$ 5.5, $^5J_{8,10}$ 0.9), 5.44 (1H, dd, 9-H, $^3J_{9,10}$ 10.0, $^3J_{9,8}$ 5.5), 5.94 (1H, dd, 10-H, $^3J_{10,9}$ 10.0, $^4J_{10,8}$ 0.9), 6.13 (1H, dd, 7-H, $^3J_{7,8}$ 7.2, $^4J_{7,9}$ 0.9), 6.69 (4H, s, aryl-H); δ_C (C_6D_6, 125.0 MHz) 21.06 (C_p, *p*-CH_3), 21.10 (C_p, *p*-CH_3), 23.94 (C_p, *o*-CH_3), 24.06 (C_p, *o*-CH_3), 25.01, 32.63, 34.20 (C_s, 1-C, 2-C, 3-C), 30.68 (C_s, 11-C), 46.84 (C_t, 11a-C), 63.75 (C_t, 3a-C), 103.11 (C_t, 8-C), 116.64 (C_t, 9-C), 118.06 (C_q, 10b-C), 119.96 (C_t, 10-C), 122.42 (C_q, 10a-C), 129.70 (C_t, aryl-C), 132.60 (C_t, 7-C), 133.45, 139.23, 139.47, 142.55, 142.94 (C_q, aryl-C) (C_p, C_s, C_t and C_q refer to primary, secondary, tertiary and quaternary carbon atoms); δ_{Si} (C_6D_6) −17.71; *m*/*z* (CI-isobutane) 452 (100%) [M^+].

(3a*R*,11a*R*,*RS*$_{Si}$)-1,2,3,3a,11,11a-Hexahydro-5-(2,4,6-trimethylphenyl)-5-(2,4,6-triisopropylphenyl)cyclopenta[4′,5′]pyrrolo-[1′,2′ : 3,4][1,3,2]diazasilolo[1,5-*a*]pyridine 11

A solution of the acyclic trisilane **10** (1.3 g, 2.6 mmol) and imine **7** (0.49 g, 2.6 mmol) in *n*-hexane (80 mL) was irradiated for 6 h at room temperature. The red solution was concentrated *in vacuo* to a volume of 10 mL and kept at −50 °C for several days. The dark red crystals (0.6 g, 43%) contained a 1 : 1 mixture of the diastereomers with respect to the stereogenic centre at the silicon atom, mp 128 °C (Found: C, 80.32; H, 9.18; N, 5.17. $C_{36}H_{48}N_2Si$ (452.7) requires C, 80.54; H, 9.01; N, 5.22%); $[\alpha]_D^{20}$ −638 (*c* = 0.03, *n*-hexane); ν_{max} (KBr)/cm^{-1} 1531, 1549, 1602, 1638; λ_{max}(ε/dm^3 mol^{-1} cm^{-1}) (*n*-hexane)/nm 466 (1223); δ_H (C_6D_6, 500.1 MHz) 1.14 (6H, d, CH(CH_3)$_2$, ^3J 6.5), 1.19 (6H, d, CH(CH_3)$_2$, ^3J 7.1), 1.21 (6H, d, CH(CH_3)$_2$, ^3J 7.2), 1.22 (12H, d, CH(CH_3)$_2$, ^3J 7.2), 1.24 (6H, d, CH(CH_3)$_2$, ^3J 6.6), 1.26–1.29, 1.30–1.34, 1.40–1.45, 1.49–1.59 (12H, m, 1-H_2, 2-H_2, 3-H_2), 2.02–2.07 (2H, m, 11-H), 2.05 (3H, s, *p*-CH_3), 2.07 (3H, s, *p*-CH_3), 2.38 (12H, s, *o*-CH_3), 2.52–2.63 (3H, m, 11a-H, 11-H), 2.69 (1H, m, 11a-H), 2.77 (2H, sept, C*H*(CH$_3$)$_2$, ^3J 6.7), 3.47 (4H, sept, C*H*(CH$_3$)$_2$, ^3J 6.6), 3.76 (1H, ddd, 3a-H, $^3J_{3a,3}$ 3.8, $^3J_{3a,3}$ 7.2, $^3J_{3a,11a}$ 14.2), 3.93 (1H, ddd, 3a-H, $^3J_{3a,3}$ 5.0, $^3J_{3a,3}$ 7.0, $^3J_{3a,11a}$ 14.1), 4.90 (1H, ddd, 8-H, $^3J_{8,7}$ 7.5, $^3J_{8,9}$ 5.5, $^4J_{8,10}$ 0.9), 4.95 (1H, ddd, 8-H, $^3J_{8,7}$ 7.5, $^3J_{8,9}$ 5.5, $^4J_{8,10}$ 0.9), 5.42 (1H, dd, 9-H, $^3J_{9,10}$ 9.5, $^3J_{9,8}$ 5.2), 5.45 (1H, dd, 9-H, $^3J_{9,10}$ 9.2, $^3J_{9,8}$ 5.4), 5.90 (1H, dd, 10-H, $^3J_{10,9}$ 9.6, $^4J_{10,8}$ not resolved), 5.94 (1H, dd, 10-H, $^3J_{10,9}$ 9.7, $^4J_{10,8}$ not resolved), 6.32 (1H, dd, 7-H, $^3J_{7,8}$ 7.5, $^5J_{7,9}$ 0.8), 6.35 (1H, dd, 7-H, $^3J_{7,8}$ 7.4, $^5J_{7,9}$ 0.8), 6.65 (2H, s, aryl-H), 6.66 (2H, s, aryl-H), 7.15 (4H, s, aryl-H); δ_C (C_6D_6, 125.0 MHz) 21.04 (C_p, *p*-CH_3), 21.08 (C_p, *p*-CH_3), 24.03 (C_p, CH(*C*H$_3$)$_2$), 24.15 (C_p, *o*-CH_3), 24.83, 24.88, 25.15, 25.25 (C_p, CH(*C*H$_3$)$_2$), 30.88, 31.17 (C_s, 11-C), 32.07, 32.61, 33.88, 34.04, 34.12, 35.25 (C_s, CH_2), 34.61, 34.62 (C_t, *p*-*C*H(CH$_3$)$_2$), 46.50, 46.90 (C_t, 11a-C), 63.31, 64.08 (C_t, 3a-C), 103.17, 103.27 (C_t, 8-C), 116.54, 116.71 (C_t, 9-C), 118.28 (C_q, 10b-C), 119.93, 119.99 (C_t, 10-C), 121.66, 121.75 (C_t, aryl-C), 122.66, 122.72 (C_q, 10a-C), 129.46, 129.51 (C_t, aryl-C), 132.84 (C_t, 7-C), 131.63, 133.39, 134.17, 138.65, 139.00, 141.58, 142.16, 150.96, 151.27, 154.17, 154.68 (C_q, aryl-C); δ_{Si} (C_6D_6) −17.77, −16.85; *m*/*z* (CI-isobutane) 536 (20%) [M^+].

(11c*S*,2a*R*,7a*R*,10a*R*)-1,1,2,2,6,6-Hexa-*tert*-butyl-1,2,2a,7a,8,9,10,10a,11,11c-decahydrocyclopenta[4′,5′]pyrrolo[1′,2′ : 3,4]-[1,3,2]diazasilolo[1,5-*a*][1,2]disileto[3,4-*c*]pyridine 15

A solution of cyclotrisilane **12** (1.0 g, 2.3 mmol) and imine **7** (0.43 g, 2.3 mmol) in *n*-hexane (80 mL) was irradiated for 6 h at room temperature. The solution was concentrated *in vacuo* to a volume of 10 mL and kept at −30 °C for several days. The product (0.58 g, 41%) was obtained as colourless crystals, mp 273 °C (Found: C, 70.67; H, 11.02; N, 4.52. $C_{36}H_{68}N_2Si_3$ (613.2) requires C, 70.51; H, 11.17; N, 4.56%); $[\alpha]_D^{20}$ −328.1 (*c* = 0.53, *n*-hexane); ν_{max} (KBr)/cm^{-1} 1618, 1653, 1677; λ_{max}(ε/dm^3 mol^{-1} cm^{-1}) (*n*-hexane)/nm 275 (8005); δ_H (C_6D_6, 500.1 MHz) 1.11 (9H, s), 1.19 (9H, s), 1.24 (9H, s), 1.31 (9H, s), 1.34 (9H, s), 1.42 (9H, s), 1.36–1.46 (2H, m, 9H, 10-H), 1.51–1.62 (3H, m, 8-H, 10-H), 1.69–1.76 (1H, m, 9H), 2.10 (1H, ddd, 11-H, ^3J 18.7, ^3J 11.0, *J* 1.4), 2.58–2.66 (2H, m, 10a-H, 11-H), 2.86 (1H, ddd, 2a-H, $^3J_{2a,11c}$ 10.4, $^3J_{2a,3}$ 2.2, $^5J_{2a,4}$ 3.3), 2.94 (1H, d, 11c-H, *J* 10.4), 3.93 (1H, m, 7a-H), 4.85 (1H, dd, 3-H, $^3J_{3,4}$ 7.7, $^3J_{3,2a}$ 2.2), 6.23 (1H, dd, 4-H, $^3J_{4,3}$ 7.7, $^5J_{4,2a}$ 3.3); δ_C (C_6D_6, 125.0 MHz) 22.37, 22.41, 22.63, 23.57, 25.22, 25.44, 26.75, 27.13, 35.62 (C_q, *C*(CH$_3$)$_3$; C_s, CH_2), 27.74, 28.55, 31.40, 31.56, 32.29, 32.78 (C_p, C(*C*H$_3$)$_3$), 32.91 (C_p, C(*C*H$_3$)$_3$), 32.99 (C_p, C(*C*H$_3$)$_3$), 46.56 (C_t, 10a-C), 63.77 (C_t, 7a-C), 97.52 (C_t, 3-C), 116.59 (C_q), 128.28 (C_t, 4-C); δ_{Si} (C_6D_6) 3.19, 26.76, 43.77; *m*/*z* (CI-isobutane) 612 (100%) [M − H^+].

Crystallographic analyses of 9, 11 and 15†

Crystal and numerical data for the structure determinations are given in Table 1. In each case, the crystal was mounted in an inert oil. Data collection was performed at 193(2) K with a Stoe IPDS area-detector using graphite-monochromated Mo-Kα radiation (0.71073 Å). The structures were solved by direct phase determinations and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system.[21] Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically.

† CCDC reference numbers 152446, 152447 and 152448. See http://www.rsc.org/suppdata/p1/b0/b008708o/ for crystallographic data in CIF or other electronic format.

Table 1 Crystallographic data for compounds **9**, **11** and **15**

	9	**11**	**15**
Empirical formula	$C_{30}H_{36}N_2Si$	$C_{36}H_{48}N_2Si$	$C_{36}H_{68}N_2Si_3$
Formula weight	452.70	536.85	613.19
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$C2$
a/Å	7.5318(2)	9.7011(5)	26.2381(15)
b/Å	13.3032(5)	11.7040(8)	9.2920(3)
c/Å	25.6712(5)	14.5996(10)	16.1808(10)
α/°	90	96.862(8)	90
β/°	90	100.249(7)	105.905(7)
γ/°	90	100.163(7)	90
Volume/Å^3	2572.18(13)	1585.37(17)	3793.9(3)
Z	4	2	4
Calculated density/g cm^{-3}	1.169	1.125	1.074
Absorption coefficient/mm^{-1}	0.111	0.100	0.150
Reflections collected	18649	19376	14144
Unique reflections	4806	11412	6894
Parameters	298	703	370
Final R indices $R1$ [$I > 2\sigma(I)$]	0.0414	0.0486	0.0351
$wR2$ (all data)	0.1161	0.1025	0.0762

Acknowledgements

Financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

1 Part 19. H. Pennemann, S. Wassmann, J. Wilken, H. Gröger, S. Wallbaum, M. Kossenjans, D. Haase, W. Saak, S. Pohl and J. Martens, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 2467.

2 F. Fache, E. Schulz, M. L. Tommasino and M. Lemaire, *Chem. Rev.*, 2000, **100**, 2159.

3 R. Bhushan and J. Martens, *Biomed. Chromatogr.*, 1997, **11**, 280.

4 J. Reedijk, *Comprehensive Coordination Chemistry*, vol. 2, ed. G. Wilkinson, Pergamon Press, Oxford, 1987, p. 73.

5 (*a*) C. Botteghi, A. Schinato, G. Chelucci, H. Brunner, A. Kürzinger and U. Obermann, *J. Organomet. Chem.*, 1989, **370**, 17; (*b*) G. Chelucci, M. Falorni and G. Giacomelli, *Tetrahedron: Asymmetry*, 1990, **1**, 843; (*c*) G. Chelucci, G. Falorni and G. Giacomelli, *Synthesis*, 1990, 1121; (*d*) G. Chelucci, S. Conti, M. Falorni and G. Giacomelli, *Tetrahedron*, 1991, **47**, 8251; (*e*) M. Falorni, G. Chelucci, S. Conti and G. Giacomelli, *Synthesis*, 1992, 972; (*f*) H. Brunner and S. Altmann, *Chem. Ber.*, 1994, **127**, 2285; (*g*) P. Scrimin, P. Tecilla and U. Tonellato, *J. Org. Chem.*, 1994, **59**, 4194; (*h*) G. Chelucci, *Tetrahedron: Asymmetry*, 1995, **6**, 811; (*i*) G. Chelucci, S. Medici and A. Saba, *Tetrahedron: Asymmetry*, 1997, **8**, 3183; (*j*) K. Nordström, E. Macedo and C. Moberg, *J. Org. Chem.*, 1997, **62**, 1604; (*k*) U. Bremberg, F. Rahm and C. Moberg, *Tetrahedron: Asymmetry*, 1998, **9**, 3437.

6 (*a*) H. Brunner and G. Riepl, *Angew. Chem.*, 1982, **94**, 369; H. Brunner and G. Riepl, *Angew. Chem.*, *Int. Ed. Engl.*, 1982, **21**, 377; (*b*) H. Brunner, B. Reiter and G. Riepl, *Chem. Ber.*, 1984, **117**, 1330; (*c*) C. Botteghi, A. Schionato, G. Chelucci, H. Brunner, A. Kürzinger and U. Obermann, *J. Organomet. Chem.*, 1989, **370**, 17; (*d*) S. De Martin, G. Zassinovich and G. Mestroni, *Inorg. Chim. Acta*, 1990, **174**, 9.

7 (*a*) H. Brunner and U. Obermann, *Chem. Ber.*, 1989, **122**, 499; (*b*) H. Nishiyama, H. Sakaguchi, T. Nakamura, M. Horihata, M. Kondo and K. Itoh, *Organometallics*, 1989, **8**, 846; (*c*) H. Brunner and P. Brandl, *Tetrahedron: Asymmetry*, 1991, **2**, 919; (*d*) G. Chelucci, S. Gladiali and A. Saba, *Tetrahedron: Asymmetry*, 1999, **10**, 1393.

8 (*a*) M. Weidenbruch, H. Piel, K. Peters and H. G. von Schnering, *Organometallics*, 1993, **12**, 2881; (*b*) M. Weidenbruch, H. Piel, K. Peters and H. G. von Schnering, *Organometallics*, 1994, **13**, 3990.

9 S. Wallbaum, T. Mehler and J. Martens, *Synth. Commun.*, 1994, **24**, 1381.

10 (*a*) V. Teetz, R. Geiger and H. Gaul, *Tetrahedron Lett.*, 1984, **25**, 4479; (*b*) H. Urbach and R. Henning, *Heterocycles*, 1989, **28**, 957.

11 J. Courtney, *Organic Synthesis by Oxidation with Metal Compounds*, ed. W. Mijs and C. de Jonge, Plenum Press, New York, London, 1986, p. 445.

12 (*a*) J. Street, M. Harris, D. I. Bishop, F. Heatley, R. C. Beddoes, O. S. Mills and J. A. Joule, *J. Chem. Soc.*, *Perkin Trans. 1*, 1987, 1599; (*b*) T. Ohta, A. Hsoi, T. Kimura and S. Nozoe, *Chem. Lett.*, 1987, 2091; (*c*) A. Giovannini, D. Savoia and A. Umani-Ronchi, *J. Org. Chem.*, 1989, **54**, 228; (*d*) J. Ezquerra, C. Pedregal, A. Rubio, J. Valenciano, J. Garcia Navio, J. Alvarez-Builla and J. Vaquero, *Tetrahedron Lett.*, 1993, **34**, 6317; (*e*) J. van Betsbrugge, W. van den Nest, P. Verbujden and D. Tourwé, *Tetrahedron Lett.*, 1998, **54**, 1753; (*f*) Y. Xu, J. Choi, M. I. Calaza, S. Turner and H. Rapoport, *J. Org. Chem.*, 1999, **64**, 4069; (*g*) S. C. Turner, H. Zhai and H. Rapoport, *J. Org. Chem.*, 2000, **65**, 861.

13 J. Wilken, PhD thesis, Universität Oldenburg, 1996.

14 S. Yochifuji, K. Tanaka, T. Kawai and Y. Nitta, *Chem. Pharm. Bull.*, 1986, **34**, 3873.

15 H. Gilmann and S. M. Spatz, *J. Org. Chem.*, 1951, **16**, 1485.

16 M. J. Fink, M. J. Michalczyk, K. J. Haller, R. West and J. Michl, *Organometallics*, 1984, **3**, 793.

17 R. S. Archibald, Y. van den Winkel, D. R. Powell and R. West, *J. Organomet. Chem.*, 1993, **446**, 67.

18 E. L. Eliel, S. H. Wilen and L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley-Interscience, New York, 1994.

19 A. Schäfer, M. Weidenbruch, K. Peters and H. G. von Schnering, *Angew. Chem.*, 1984, **96**, 311; A. Schäfer, M. Weidenbruch, K. Peters and H. G. von Schnering, *Angew. Chem.*, *Int. Ed. Engl.*, 1984, **23**, 302.

20 Review: R. Okazaki and R. West, *Adv. Organomet. Chem.*, 1996, **39**, 231.

21 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, Göttingen, Germany, 1997.