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# Head-to-head versus head-to-tail dimerizations of transient silenes—the synthesis and reactivity of 2-(8-dimethylamino-1-naphthyl)- and 2-(4-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene

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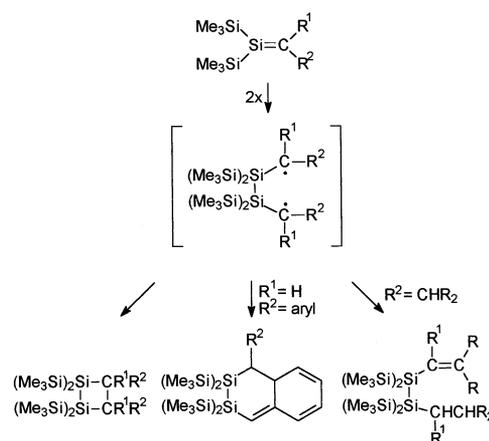
## Abstract

In the absence of scavenger reagents, the transient 2-(8-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**4**), generated by a base-initiated elimination of trimethylsilanol from (8-dimethylamino-1-naphthyl)-tris(trimethylsilyl)silyl-methanol (**3**), undergoes a spontaneous formal [2 + 2] head-to-tail cyclodimerization to give a substituted 1,3-disilacyclobutane **5**. In contrast, the similarly produced 2-(4-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**10**) dimerizes in a head-to-head mode, finally affording the hexahydro-2,3-disilaphenanthren-9-on (**12**). The ketone **12** is the result of a formal [2 + 4] cycloaddition of the silene **10** producing an intermediate with an enamine unit (**11**), which is hydrolysed during the aqueous workup to give **12**. A model, explaining the different dimerization regioselectivity of the two isomeric silenes is proposed. In the presence of  $\text{BH}_3 \cdot \text{THF}$  the generated silene **4** is trapped to afford 3-[bis(trimethylsilyl)silyl]-1,1-dimethyl-1-aza-2-bora-2,3-dihydrophenalene (**6**). All the compounds isolated, were fully characterised by IR, NMR and MS data. The compounds *Z*-**5**, **8** and *E*-**12** were also examined by X-ray crystal structure analyses. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Silenes; Silaethenes; 1,3-Disilacyclobutanes; 2,3-Disilaphenanthren-9-on, hexahydro; Peterson reaction

## 1. Introduction

Sterically congested transient silenes are known to undergo rapid dimerizations, and depending on their substitution pattern head-to-head as well as head-to-tail dimers were observed as the reaction products [1]. 1,1-Bis(trimethylsilyl)silenes generally dimerize in a head-to-head mode under formation of 1,2-disilacyclobutanes [2]; in the case of 2-arylsilenes, tetrahydro-2,3-disilaphthalenes were produced as the result of a formal [2 + 4] reaction [3], and silenes possessing an  $\alpha$ -hydrogen atom in the substituent at the silene C-atom ('allylic' hydrogen) preferentially stabilise under hydrogen transfer giving linear dimers [4,5] (Scheme 1). The reason for this peculiar dimerization regioselectivity is



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Scheme 1. The different modes of head-to-head dimerizations of transient 1,1-bis(trimethylsilyl)silenes.

not clear, but, obviously, decreasing polarity of the Si=C bond favours a head-to-head coupling [2].

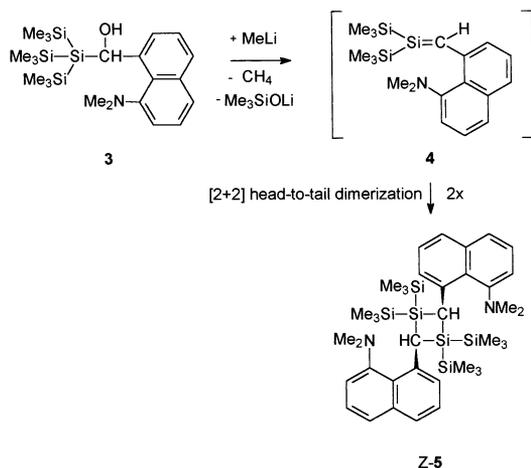
Deviating from this general dimerization pattern of 1,1-bis(trimethylsilyl)silenes, 2-(2-dimethylaminophenyl)-1,1-bis(trimethylsilyl)silene (**1**), as we found recently [6], dimerizes exclusively under formation of the [2 + 2] head-to-tail product, the respective 1,3-disilacyclobutane, and, interestingly, the dimerization regioselectivity of 2-(2-methoxyphenyl)-1,1-bis(trimethylsilyl)silene (**2**) is controlled by the donor capacity of the solvent and can be reversed by changing the reaction medium [7]. Obviously, the unusual dimerization behaviour of **1** and **2** is a consequence of the donating properties of the dimethylaminophenyl and methoxyphenyl substituents at the silene C atoms of these two silaethenes. Supplementing these observations, in this paper we describe the synthesis and behaviour of 2-(8-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**4**) and the isomeric 2-(4-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**10**), whose dimerization regioselectivity agrees with and confirms the mechanism, proposed for the cyclodimerization of **1** and **2** [6,7].

## 2. Results and discussion

### 2.1. The generation and formal [2 + 2] head-to-tail dimerization of 2-(8-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**4**)

2-(8-Dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**4**) was generated by deprotonation of (8-dimethylamino-1-naphthyl)-tris(trimethylsilyl)silyl-methanol (**3**) with methyllithium in ether following the well-established procedure for the modified Peterson reaction (Scheme 2) [5]. The alcohol **3** was obtained by our standard method from tris(trimethylsilyl)silylmagnesium bromide and 8-dimethylamino-1-naphthaldehyde.

Expectedly, the silene **4** proved to be unstable and underwent rapid dimerization to give a colourless solid, the structure of which was elucidated by comprehensive spectroscopic studies as 2,4-bis(8-dimethylamino-1-naphthyl)-1,1,3,3-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**5**) (see Section 3.2.). An X-ray structural analysis of **5** was also performed, which revealed the obtained product in a yield of 82%, to be the pure *Z*-isomer of the 1,3-disilacyclobutane system. This is illustrated in Fig. 1. The four-membered ring is slightly folded, the dihedral angle formed by the planes Si1–C1–Si2 and Si1–C2–Si2 is 19.9°. Apart from slightly elongated ring Si–C distances, which are considered as being due to steric congestion, the bond parameters are



Scheme 2. The generation and head-to-tail dimerization of the transient 2-(8-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**4**).

comparable with those found for other 1,3-disilacyclobutanes [6,7].

Compound **5** is the formal [2 + 2] head-to-tail cyclodimer of the silene **4**. As outlined above, this regioselectivity is untypical for 1,1-bis(trimethylsilyl)silenes but in full consistency with the behaviour of 2-(2-dimethylaminophenyl)-1,1-bis(trimethylsilyl)silene (**1**), which gives the head-to-tail cyclodimer as well. In agreement with the model proposed for the dimerization of **1** [6], the deviation of **4** from the usual dimerization pattern is interpreted as the consequence of a strong intermolecular donor–acceptor interaction of the dimethylamino group and the electrophilic silene silicon atom. As model studies show, an effective intramolecular donor–acceptor interaction, which actu-

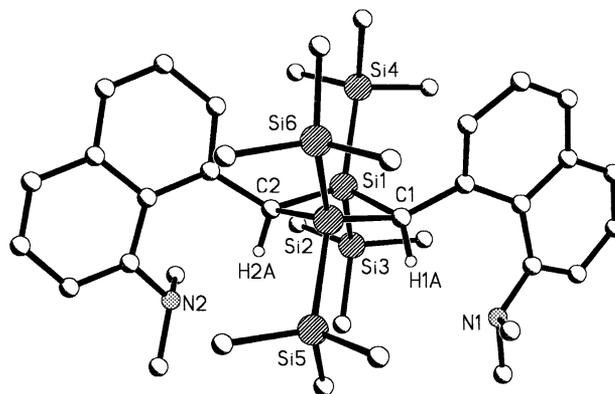
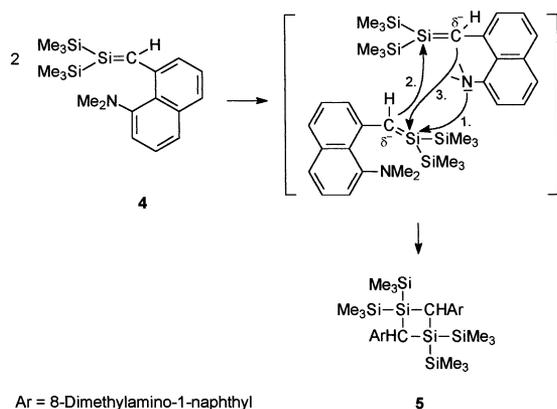


Fig. 1. Molecular structure of *Z*-**5** in the crystal; hydrogen atoms, except C1H and C2H, omitted for clarity. Selected bond distances (Å) and angles (°): C1–Si1 1.933(4), C1–Si2 1.930(4), C2–Si1 1.930(4), C2–Si2 1.931(4), C1–C3 1.500(5), C2–C15 1.514(5), Si1–Si3 2.3695(15), Si1–Si4 2.3803(15), Si2–Si5 2.3707(16), Si2–Si6 2.3773(16); C1–Si1–C2 90.15(15), C1–Si2–C2 90.20(15), Si1–C1–Si2 88.11(15), Si1–C2–Si2 88.14(15), Si3–Si1–Si4 105.35(6), Si5–Si2–Si6 106.02(6).

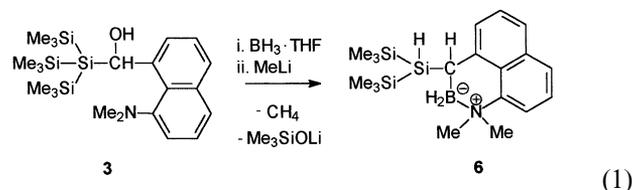


Scheme 3. Proposed mechanism of the dimerization of 2-(8-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**4**).

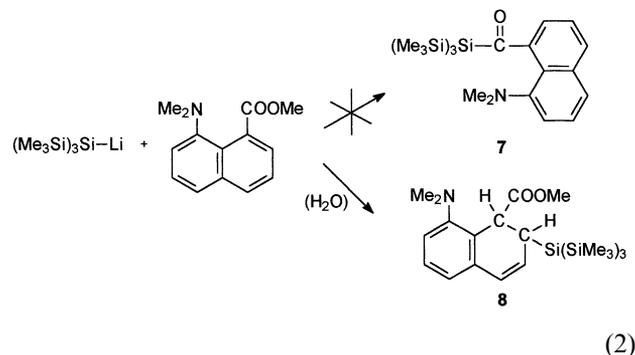
ally is expected to increase the polarity of the silene double bond, thus facilitating a head-to-tail dimerization, is rather unlikely for steric reasons. Therefore we discuss an intermolecular process, in which the dialkylamino group is acting as some kind of an anchor. Its interaction with the electrophilic silene silicon atom of a neighbouring molecule and the attack of the activated silene carbon atom at the Si=C group of the first silene molecule initiates a head-to-tail dimerization through a cyclic eight-membered transition state (Scheme 3). A plausible explanation of the exclusive formation of the *Z*-isomer of **3** can not be given, but it is worth mentioning that also in case of the dimerization of **1** the *Z*-1,3-disilacyclobutane derivative dominates.

As demonstrated, the uncommon dimerization mode of the silene **4** is effected by the 8-dimethylamino group of the *C*-naphthyl substituent. With the intention to rule out the function of this group in the cyclodimerization process and probably inverse the silene dimerization regioselectivity, we tried to block the donor ability of the group by formation of a respective triethylborane adduct. But addition of the triethylborane THF complex to an ethereal solution of **3** and subsequent deprotonation with methyllithium gave a complex mixture of products from which a pure compound could not be separated. But the comparable reaction of **3** with  $\text{BH}_3 \cdot \text{THF}$ , followed by the base initiated elimination of lithium trimethylsilanolate according to the modified Peterson mechanism led to a product, which was identified by IR, NMR and MS studies as the 1-aza-2-boradihydrophenalene (**6**). The cyclic structure of **6** as a result of an intramolecular boron–nitrogen donor–acceptor interaction is confirmed by two separate *N*-methyl signals in the  $^1\text{H}$ -NMR spectra of the compound. The revealed structure of **6** confirms a clean formation of the silene **4**, which is trapped by insertion of the Si=C unit into the boron hydrogen bond, i.e. under these conditions the silene cyclodimerization is a slow process compared with the borane addition (Eq.

(1)). Whether the BH-addition to the Si=C bond is an intramolecular reaction of the borane amine complex or takes place with free borane formed in the reaction equilibrium, remains an open question.



In this context we would like to mention that attempts of a slight variation of the structure of **4** failed. We intended to generate and study the dimerization of 2-methyl-2-(8-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene, which should be the outcome of the reaction of 8-dimethylamino-1-naphthoyl-tris(trimethylsilyl)silane (**7**) with methyllithium. But we failed in synthesising the acylsilane **7**. Generally, the reaction of tris(trimethylsilyl)silyllithium with carboxylic acid esters was found to be an easy route to acyl-tris(trimethylsilyl)silanes [8]. But, as demonstrated in Eq. (2), tris(trimethylsilyl)silyllithium and methyl 8-dimethylamino-1-naphthoate gave compound **7** but an addition of the silanide at the 2-position of the naphthalene system affording the substituted dihydronaphthalene **8** in a yield of 70%. The structure of **8** was proved by IR, NMR and MS studies. Also an X-ray structural analysis was performed, which unambiguously revealed the position, at which the attack of the silicon nucleophile at the aromatic system occurred and the *E*-configuration of the compound (Fig. 2). Bond distances and angles were found to meet standard values.



## 2.2. The generation and formal [2 + 4] head-to-head dimerization of 2-(4-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**10**)

Of course, the discussed head-to-tail dimerization of **4** is related to a suitable position of the dimethylamino group at the naphthyl substituent. To confirm the

proposed course of the reaction, we were interested in studying the behaviour of 2-(4-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**10**), which, for steric reasons, cannot follow the dimerization mechanism described above for **1**, **2** and **4**. Actually, after generation of **10** by a base initiated trimethylsilylanolate elimination from 4-dimethylamino-1-naphthyl-tris(trimethylsilyl)-silylmethanol (**9**) according to the modified Peterson process, we obtained, almost expectedly, a silene head-to-head dimer exclusively. The structure of the final product, which was revealed as 1-(4-dimethylamino-1-naphthyl)-2,2,3,3-tetrakis(trimethylsilyl)-1,2,3,9,10,10a-hexahydro-2,3-disilaphenanthren-9-one (**12**) appears to be rather complex, but the generation of the compound can easily be interpreted. As outlined in Scheme 4, the transient silene **10** undergoes a rapid formal [2 + 4] cyclodimerization, in which the compound simultaneously acts as the Si=C monoene and involving the naphthyl substituent also as the diene. The resulting enamine **11** could not be isolated but was hydrolysed during the aqueous workup to give **12** as a mixture of the *E/Z*-isomers. Repeated recrystallization from ethanol led to pure *E*-**12** in a yield of almost 70%. The structure of *E*-**12** was elucidated on the basis of IR, NMR and MS studies (see Section 3) and was confirmed also by an X-ray structural analysis (Fig. 3). Most bond distances and angles are in agreement with standard values; worth mentioning is the elongation of the Si2–C12 bond (1.93 Å), which is undoubtedly due to steric congestion at these two atoms.

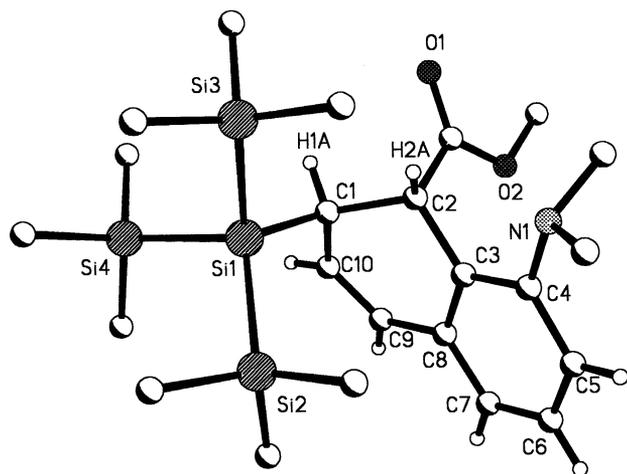
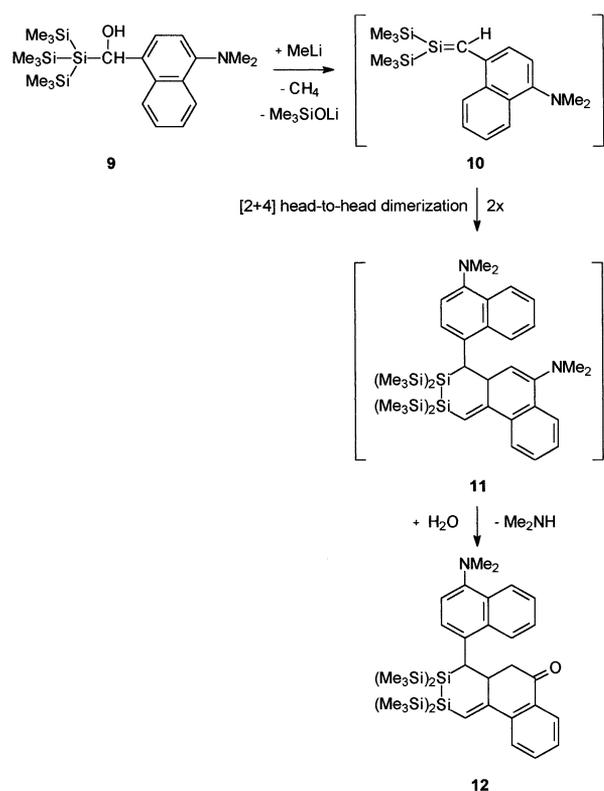


Fig. 2. Molecular structure of *E*-**8** in the crystal; hydrogen atoms, except C1H, C2H, C9H and C10H, omitted for clarity. Selected bond distances (Å) and angles (°): C1–C2 1.562(4), C2–C3 1.508(4), C3–C8 1.409(5), C8–C9 1.461(6), C9–C10 1.315(6), C1–C10 1.489(5), C1–Si1 1.932(4), Si1–Si2 2.3614(14), Si1–Si3 2.3664(14), Si1–Si5 2.3674(15); C2–C1–C10 110.5(3), C2–C1–Si1 115.8(2), C10–C1–Si1 113.1(2), C1–Si1–Si2 117.35(11), C1–Si1–Si3 105.89(11), C1–Si1–Si4 105.01(11).

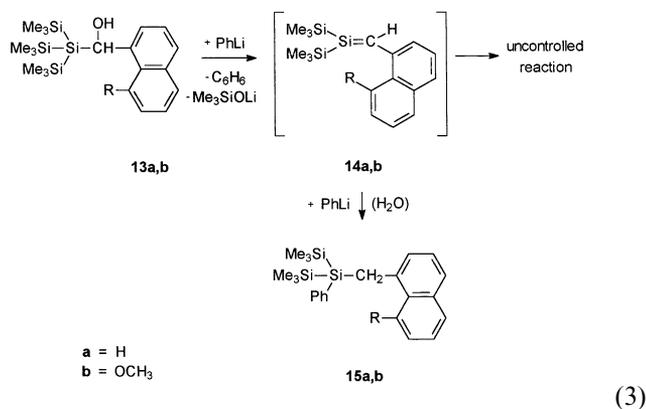


Scheme 4. The generation and head-to-head dimerization of the transient 2-(4-dimethylamino-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**10**).

As mentioned already, attempts of the isolation of the intermediate **11** by a non-aqueous workup of the product mixture obtained after the reaction of **9** with methyllithium failed. Compound **11** is the result of a formal [2 + 4] cyclodimerization of the silene **10**. This mode of dimerization is not uncommon for 2-aryl-1,1-bis(trimethylsilyl)silenes [3], and the [2 + 4] cyclodimers were generally found to be the kinetically preferred products of the reaction, which on thermal treatment isomerize to give the thermodynamically stable [2 + 2] dimers, the 1,2-disilacyclobutanes [3b,9]. Unfortunately, in the course of the generation of the silene **10** we did not succeed in isolating a respective [2 + 2] dimer either, after heating of the crude product mixture of the reaction of **9** with methyllithium before workup or after thermal treatment of isolated **12**. After heating of the product mixture in boiling toluene we always obtained the [2 + 4] cyclodimer **12**; prolonged heating of **12** to 220°C led to uncontrolled decomposition.

Finally we want to communicate that we were unsuccessful in preparing the dimerization products of 2-(1-naphthyl)-1,1-bis(trimethylsilyl)silene (**14a**) and of 2-(8-methoxy-1-naphthyl)-1,1-bis(trimethylsilyl)silene (**14b**). Treatment of 1-naphthyl-tris(trimethylsilyl)silylmethanol (**13a**) and (8-methoxy-1-naphthyl)-tris(trimethylsilyl)silylmethanol (**13b**), respectively, with equimolar quan-

tities of methylolithium or phenyllithium, following the same procedure used for the synthesis of **5** and **12**, gave complex mixtures of products, which could not be separated. The reaction of **13a** and **13b** with excess phenyllithium afforded the trisilanes **15a** and **15b** in yields of 65 and 83%, respectively, indicating a clean formation of the silenes **14a** and **14b**, which were trapped by the excess organolithium compound. In absence of the scavenger reagent the transient silenes undergo uncontrolled oligomerization or polymerisation processes (Eq. (3)).



### 3. Experimental

All reactions involving organometallic reagents were carried out under purified argon. NMR: Bruker AC

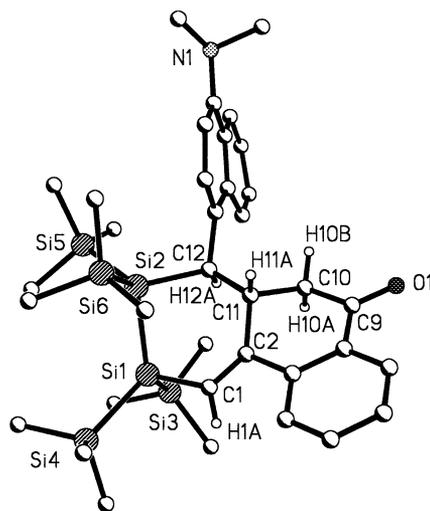


Fig. 3. Molecular structure of *E*-**12** in the crystal; hydrogen atoms, except C1H, C10H, C11H and C12H, omitted for clarity. Selected bond distances (Å) and angles (°): Si1–Si2 2.3511(19), C1–Si1 1.880(5), C1–C2 1.331(6), C2–C11 1.524(5), C11–C12 1.545(5), C12–Si2 1.930(4), Si1–Si3 2.369(2), Si1–Si4 2.368(2), Si2–Si5 2.3633(18), Si2–Si6 2.3711(19); C1–Si1–Si2 97.63(16), C12–Si2–Si1 94.59(13), C2–C1–Si1 131.2(3), C1–C2–C11 127.4(4).

250 or Bruker ARX 300, TMS as internal standard. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402 (70 eV).  $(\text{Me}_3\text{Si})_3\text{SiLi}\cdot 3\text{THF}$  was prepared as reported in the literature [10]. All yields given refer to amounts obtained after chromatographic separation and purification or recrystallization.

#### 3.1. (8-Dimethylamino-1-naphthyl)-tris-(trimethylsilyl)silylmethanol (**3**)

A 2.12 g (10.6 mmol) sample of 8-dimethylamino-1-naphthaldehyde was added to a solution of tris(trimethylsilyl)silylmagnesium bromide, made by dissolving 5.00 g (10.6 mmol) of  $(\text{Me}_3\text{Si})_3\text{SiLi}\cdot 3\text{THF}$  in 30 ml of ether and subsequent addition of the equimolar quantity of  $\text{MgBr}_2\cdot \text{OEt}_2$  (2.75 g). After stirring of the mixture for 24 h at room temperature (r.t.), water was added and the product was extracted with ether. Evaporation of the dried ethereal solution and chromatographic separation of the residue (silica gel, 20:1 heptane–ethyl acetate) afforded 3.23 g (68%) of **3**, m.p. 108–110°C. IR (Nujol):  $\tilde{\nu} = 3597\text{ cm}^{-1}$  ( $\text{OH}_{\text{free}}$ ),  $3417\text{ cm}^{-1}$  ( $\text{OH}_{\text{ass}}$ ).  $^1\text{H-NMR}$  (benzene- $d_6$ ):  $\delta = 0.26$  (s,  $\text{SiCH}_3$ , 27H), 2.34 and 2.59 (2s,  $\text{NCH}_3$ ,  $2 \times 3\text{H}$ ), 3.02 (d,  $^3J = 4.6\text{ Hz}$ , OH, 1H), 6.81 (d,  $^3J = 4.3\text{ Hz}$ , HCO, 1H), 6.91–7.96 (m, arom. H, 6H).  $^{13}\text{C-NMR}$  (benzene- $d_6$ ):  $\delta = 1.8$  ( $\text{SiCH}_3$ ), 44.9 and 46.4 ( $\text{NCH}_3$ ), 65.4 (COH), 116.4, 125.2, 125.3, 125.5, 125.8, 128.6, 129.1, 137.2, 143.9 and 151.1 (arom. C).  $^{29}\text{Si-NMR}$  (benzene- $d_6$ ):  $\delta = -67.8$  ( $\text{SiSiMe}_3$ ),  $-13.0$  ( $\text{SiMe}_3$ ). MS  $m/z$  (%): 447 (2) [ $\text{M}^+$ ], 432 (7) [ $\text{M}^+ - \text{CH}_3$ ], 374 (14) [ $\text{M}^+ - \text{SiMe}_3$ ], 200 (100) [ $\text{M}^+ - \text{Si}(\text{SiMe}_3)_3$ ]. Anal. Calc. for  $\text{C}_{22}\text{H}_{41}\text{ONSi}_4$  (447.92): C, 58.99; H, 9.23; N, 3.13. Found: C, 57.60; H, 8.84; N, 3.22%.

#### 3.2. 2,4-Bis-(8-dimethylamino-1-naphthyl)-1,1,3,3-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**5**)

To a solution of 0.50 g (1.12 mmol) of **3** in 20 ml of ether an equimolar quantity of methylolithium was added at  $-78^\circ\text{C}$ . The mixture was allowed to warm up to r.t. within 2 h. At about  $-20^\circ\text{C}$  the dark green colour disappeared and crystals of **5** gradually precipitated. The reaction was quenched with water, and THF was added until all of **5** had dissolved. After separation of the organic layer, the aqueous phase was extracted with ether. The combined and dried organic solutions were evaporated and the residue was recrystallized from heptane to give 0.36 g of pure *Z*-**5**, yield (89%), m.p.  $> 235^\circ\text{C}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = -0.19$  and  $-0.02$  (2s,  $\text{SiCH}_3$ ,  $2 \times 18\text{H}$ ), 2.62 (s,  $\text{NCH}_3$ , 12H), 5.47 (s, ring CH, 2H), 6.88–7.84 (m, arom. CH, 12H).  $^{13}\text{C-NMR}$  (benzene- $d_6$ ):  $\delta = 0.5$  and  $1.8$  ( $\text{SiCH}_3$ ), 12.6 (ring CH), 45.7 ( $\text{NCH}_3$ ), 113.7, 124.7, 124.8, 125.0, 125.2, 126.6, 130.5, 137.4, 144.3 and 152.0 (arom. C).  $^{29}\text{Si-NMR}$  (benzene- $d_6$ ):  $\delta = -16.6$  and  $-14.2$  ( $\text{SiMe}_3$ ), 2.3 (ring

Si). MS  $m/z$  (%): 714 (19) [ $M^+$ ], 699 (6) [ $M^+ - CH_3$ ], 641 (18) [ $M^+ - SiMe_3$ ], 357 (90) [( $Me_3Si_2Si=CH-(Me_2NC_{10}H_6)^+$ ), 284 (100) [( $Me_3Si_2Si=CH(Me_2NC_{10}H_6)^+ SiMe_3$ ]. Anal. Calc. for  $C_{38}H_{62}N_2Si_6$  (715.44): C, 63.80; H, 8.73; N, 3.92. Found: C, 63.58; H, 8.73; N, 4.00%.

### 3.3. 3-[Bis(trimethylsilyl)silyl]-1,1-dimethyl-1-aza-2-bora-2,3-dihydrophenalene (6)

To a solution of 0.5 g (1.12 mmol) of **3** in 20 ml of ether an equimolar quantity of the  $BH_3 \cdot THF$  complex was given at  $-78^\circ C$ , and subsequently 1.12 mmol of ethereal methyllithium was added at the same temperature. After gradual warming up to r.t., water was added and the product was extracted with ether. Evaporation of the dried extracts gave a colourless oil, which was separated by chromatography (silica gel, 30:1 heptane–ethyl acetate). The resulting oil crystallized after addition of some ml of acetone to afford 0.18 g (46%) of **6**, m.p.  $58-59^\circ C$ . IR (Nujol):  $\tilde{\nu} = 2025\text{ cm}^{-1}$  (SiH).  $^1H$ -NMR (benzene- $d_6$ ):  $\delta = 0.09$  and  $0.51$  (2s,  $SiCH_3$ ,  $2 \times 9H$ ), 2.14 and 2.59 (2s,  $NCH_3$ ,  $2 \times 3H$ ), 2.61 (s, SiH, 1H), 2.63–2.71 (br. m,  $BH_2$ , 2H), 4.24 (s, CH, 1H), 6.70–8.09 (m, arom. CH, 6H).  $^{13}C$ -NMR (benzene- $d_6$ ):  $\delta = 1.1$  and  $1.4$  ( $SiCH_3$ ), 51.4 and 53.7 ( $NCH_3$ ), 65.4 (BCH), 113.9, 123.7, 124.4, 126.8, 128.8 and 130.0 (arom. CH), 125.3, 135.8, 143.2, 146.1 (quart. arom. C).  $^{29}Si$ -NMR (benzene- $d_6$ ):  $\delta = -59.6$  ( $SiSiMe_3$ ),  $-14.9$  and  $-14.6$  ( $SiMe_3$ ).  $^{11}B$ -NMR (benzene- $d_6$ ):  $\delta = -3.31$  ( $BH_2$ ). MS  $m/z$  (%): 371 (2) [ $M^+$ ], 356 (9) [ $M^+ - CH_3$ ], 298 (16) [ $M^+ - SiMe_3$ ], 195 (100) [ $M^+ - SiH(SiMe_3)_2 - H$ ]. Anal. Calc. for  $C_{19}H_{34}BNSi_3$  (371.55): C, 61.42; H, 9.22; N, 3.77. Found: C, 60.83; H, 8.95; N, 3.93%.

### 3.4. 8-Dimethylamino-2-[tris(trimethylsilyl)silyl]-2,3-dihydronaphthalene-1-carboxylic acid methylester (8)

At  $-78^\circ C$ , 11.00 g (23.3 mmol) of  $(Me_3Si)_3SiLi \cdot 3THF$ , dissolved in 30 ml of ether, were given gradually to a solution of 5.00 g (21.8 mmol) in 20 ml of ether. After warming up to r.t., water was added, the organic phase was separated and the aqueous solution was extracted with ether. The dried extracts were evaporated and the residue was recrystallized from *n*-heptane. Colourless crystals, yield 7.8 g (70%), m.p.  $144-147^\circ C$ . IR (KBr):  $\tilde{\nu} = 1720\text{ cm}^{-1}$  (CO).  $^1H$ -NMR (benzene- $d_6$ ):  $\delta = 0.21$  (s,  $SiCH_3$ , 27H), 2.50 (s,  $NCH_3$ , 6H), 3.26 (s,  $OCH_3$ , 3H), 3.29 (2 pseudo-t,  $^3J = 6.1$ ,  $^3J = 1.2$ ,  $^4J = 1.2$  Hz, C2–H, 1H), 4.64 (br. s, C1–H, 1H), 6.03 (dd,  $^3J = 6.1$ ,  $^3J = 9.7$  Hz, C3–H, 1H), 6.26 (dd,  $^3J = 9.7$ ,  $^4J = 1.2$  Hz, C4–H), 6.77 (dd,  $^3J = 7.3$ ,  $^4J = 1.2$  Hz, C5–H, 1H), 6.95 (dd,  $^3J = 7.9$ ,  $^4J = 1.2$  Hz, C7–H, 1H), 7.10 (dd,  $^3J = 7.3$ ,

$^3J = 7.9$  Hz, C6–H, 1H).  $^{13}C$ -NMR (benzene- $d_6$ ):  $\delta = 1.8$  ( $SiCH_3$ ), 28.2 ( $SiCH$ ), 42.2 (CH), 45.3 ( $NCH_3$ ), 51.5 ( $OCH_3$ ), 120.8, 122.8, 125.1, 128.4 and 130.8 (olef. and arom. CH), 135.9, 148.6 and 153.2 (quart. arom. C), 175.3 (CO).  $^{29}Si$ -NMR (benzene- $d_6$ ):  $\delta = -73.2$  ( $SiSiMe_3$ ),  $-12.8$  ( $SiMe_3$ ). MS  $m/z$  (%): 477 (11) [ $M^+$ ], 462 (9) [ $M^+ - CH_3$ ], 418 (17) [ $M^+ - COOMe$ ], 404 (24) [ $M^+ - SiMe_3$ ], 247 (42) [ $Si(SiMe_3)_3^+$ ], 171 (92) [ $Me_2NC_{10}H_9^+$ ]. Anal. Calc. for  $C_{23}H_{43}NO_2Si_4$  (477.94): C, 57.80; H, 9.07; N, 2.93. Found: C, 58.00; H, 8.97; N, 2.95%.

### 3.5. (4-Dimethylamino-1-naphthyl)-tris(trimethylsilyl)silylmethanol (9)

As described for the synthesis of **3**, 5.00 g (10.6 mmol) of  $(Me_3Si)_3SiLi \cdot 3THF$ , 2.75 g (10.6 mmol) of  $MgBr_2 \cdot OEt_2$  and 2.10 g (10.6 mmol) of 4-dimethylamino-1-naphthaldehyde gave 3.45 g (73%) **7**, pale yellow crystals, m.p.  $104-106^\circ C$ . IR (Nujol):  $\tilde{\nu} = 3265\text{ cm}^{-1}$  ( $OH_{ass}$ ).  $^1H$ -NMR (benzene- $d_6$ ):  $\delta = 0.22$  (s,  $SiCH_3$ , 27H), 1.18 (d,  $^3J = 3.1$  Hz, OH, 1H), 2.64 (s,  $NCH_3$ , 6H), 5.71 (d,  $^3J = 2.8$  Hz, HCO, 1H), 6.98–8.51 (m, arom. CH, 6H).  $^{13}C$ -NMR (benzene- $d_6$ ):  $\delta = 1.85$  ( $SiCH_3$ ), 45.2 ( $NCH_3$ ), 65.0 (COH), 114.2, 123.9, 124.4, 125.2, 125.5 and 125.7 (arom. CH), 129.7, 131.2, 138.6 and 150.1 (quart. arom. C).  $^{29}Si$ -NMR (benzene- $d_6$ ):  $\delta = -66.5$  ( $SiSiMe_3$ ),  $-12.9$  ( $SiMe_3$ ). MS  $m/z$  (%): 447 (2) [ $M^+$ ], 432 (1) [ $M^+ - CH_3$ ], 374 (1) [ $M^+ - SiMe_3$ ], 200 (100) [ $M^+ - Si(SiMe_3)_3$ ]. Anal. Calc. for  $C_{22}H_{41}NOSi_4$  (447.92): C, 58.99; H, 9.23; N, 3.13. Found: C, 58.78; H, 9.21; N, 3.15%.

### 3.6. E-1-(4-Dimethylamino-1-naphthyl)-2,2,3,3-tetrakis(trimethylsilyl)-1,2,3,9,10,10a-hexahydro-2,3-disilaphenanthren-9-one (E-12)

To 0.50 g (1.12 mmol) of **9** in 20 ml of ether, the equimolar quantity of methyllithium was added at  $-78^\circ C$ . The stirred mixture was allowed to warm up to r.t. within 2 h. After addition of water the product was extracted with ether and the dried extracts were evaporated. Chromatographic separation of the yellow viscous residue (silica gel, 20:1 heptane–ethyl acetate) and recrystallization from ethanol gave 0.27 g (69%) almost colourless crystalline *E*-**12**, m.p.  $204-207^\circ C$ . IR (KBr):  $\tilde{\nu} = 1687\text{ cm}^{-1}$  (CO).  $^1H$ -NMR (benzene- $d_6$ ):  $\delta = -0.27$ , 0.35, 0.42 and 0.47 (4s,  $SiCH_3$ ,  $4 \times 9H$ ), 2.45 (dd,  $^2J = 16.5$ ,  $^3J = 12.5$  Hz,  $CH_2$ , 1H), 2.64 (s,  $NCH_3$ , 6H), 3.08 (dd,  $^2J = 16.5$ ,  $^3J = 3.4$  Hz,  $CH_2$ , 1H), 3.65 (ddd, broadened,  $^3J = 12.5$ ,  $^3J = 3.4$ ,  $^3J = 10.8$  Hz, C10a–H, 1H), 3.78 (d,  $^3J = 10.9$  Hz, C1–H, 1H), 6.84 (s, olef. H, 1H), 6.88–8.53 (m, arom. CH, 10H).  $^{13}C$ -NMR (benzene- $d_6$ ):  $\delta = 1.4$ , 1.9 (2 signals unseparated), 3.5

(SiCH<sub>3</sub>), 31.1 (CH), 45.2 (NCH<sub>3</sub>), 47.3 (CH<sub>2</sub>), 49.4 (CH), 114.3, 122.6, 124.7, 125.3, 125.6, 125.7, 126.0, 126.7, 126.8, 127.9, 130.1, 131.6, 133.5, 133.7, 137.0, 146.4, 149.5, 156.1 (olef. and arom. C), 196.1 (CO). <sup>29</sup>Si-NMR (benzene-*d*<sub>6</sub>):  $\delta = -86.7$  and  $-74.2$  (ring Si),  $-13.8$ ,  $-13.3$ ,  $-12.2$  and  $-11.1$  (SiMe<sub>3</sub>). MS *m/z* (%): 687 (100) [M<sup>+</sup>], 672 (8), [M<sup>+</sup> - CH<sub>3</sub>], 614 (30) [M<sup>+</sup> - SiMe<sub>3</sub>], 357 (11) [(Me<sub>3</sub>Si<sub>2</sub>Si=CH-(Me<sub>2</sub>NC<sub>10</sub>H<sub>6</sub>)<sup>+</sup>]. Anal. Calc. for C<sub>36</sub>H<sub>57</sub>NOSi<sub>6</sub> (688.37): C, 62.81; H, 8.35; N, 2.04. Found: C, 62.81; H, 8.44; N, 2.26%.

### 3.7. (1-Naphthyl)-tris(trimethylsilyl)silylmethanol (**13a**)

As described for **3**, 5.00 g (10.6 mmol) of (Me<sub>3</sub>Si)<sub>3</sub>SiLi·3THF, 2.75 g MgBr<sub>2</sub>·OEt<sub>2</sub> and 1.66 g (10.6 mmol) 1-naphthaldehyde gave 3.05 g (71%) of **13a**, m.p. 90–93°C. IR (Nujol):  $\tilde{\nu} = 3525$  cm<sup>-1</sup> (OH<sub>free</sub>). <sup>1</sup>H-NMR (benzene-*d*<sub>6</sub>):  $\delta = 0.19$  (s, SiCH<sub>3</sub>, 27H), 1.17 (br. s, OH, 1H), 5.69 (s, HCO, 1H), 7.23–8.07 (arom. H). <sup>13</sup>C-NMR (benzene-*d*<sub>6</sub>):  $\delta = 1.8$  (SiCH<sub>3</sub>), 65.3 (COH), 123.7, 123.9, 125.7, 125.8, 125.9, 126.7 and 129.3 (arom. CH, 7H), 129.8, 134.3 and 144.2 (quart. arom. C). <sup>29</sup>Si-NMR (benzene-*d*<sub>6</sub>):  $\delta = -65.5$  (SiSiMe<sub>3</sub>),  $-12.9$  (SiMe<sub>3</sub>). MS *m/z* (%): 404 (3) [M<sup>+</sup>], 387 (1) [M<sup>+</sup> - OH], 247 (26) [Si(SiMe<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, 173 (100) [Si(SiMe<sub>3</sub>)<sub>2</sub><sup>+</sup> - H]. Anal. Calc. for C<sub>20</sub>H<sub>36</sub>OSi<sub>4</sub> (404.85): C, 59.34; H, 8.96. Found: C, 59.78; H, 8.84%.

### 3.8. (8-Methoxy-1-naphthyl)-tris(trimethylsilyl)silylmethanol (**13b**)

Following the procedure given for the synthesis of **3**, 5.00 g (10.6 mmol) of (Me<sub>3</sub>Si)<sub>3</sub>Si·3THF, 2.57 g of MgBr<sub>2</sub>·OEt<sub>2</sub> and 1.98 g (10.1 mmol) of 8-methoxy-1-naphthaldehyde afforded 3.56 g (75%) of **13b**, m.p. 136–138°C. IR (Nujol):  $\tilde{\nu} = 3498$  cm<sup>-1</sup> (OH<sub>free</sub>). <sup>1</sup>H-NMR (benzene-*d*<sub>6</sub>):  $\delta = 0.25$  (s, SiCH<sub>3</sub>, 27H), 1.68 (d, <sup>3</sup>J = 3.7 Hz, OH, 1H), 3.42 (s, OCH<sub>3</sub>, 3H), 6.66 (d, <sup>3</sup>J = 3.7 Hz, CHO, 1H), 6.44–7.98 (m, arom. CH). <sup>13</sup>C-NMR (benzene-*d*<sub>6</sub>):  $\delta = 1.9$  (SiCH<sub>3</sub>), 55.1 (OCH<sub>3</sub>), 66.8 (OCH), 106.1, 122.6, 125.3, 126.1, 126.7 and 127.1 (arom. CH), 128.3, 136.8, 145.6 and 157.6 (quart. arom. C). <sup>29</sup>Si-NMR (benzene-*d*<sub>6</sub>):  $\delta = -65.7$  (SiSiMe<sub>3</sub>),  $-13.0$  (SiMe<sub>3</sub>). MS *m/z* (%): 434 (6) [M<sup>+</sup>], 417 (2) [M<sup>+</sup> - OH], 361 (25) [M<sup>+</sup> - SiMe<sub>3</sub>], 187 (100) [M<sup>+</sup> - Si(SiMe<sub>3</sub>)<sub>3</sub>]. Anal. Calc. for C<sub>21</sub>H<sub>38</sub>O<sub>2</sub>Si<sub>4</sub> (434.87): C, 58.00; H, 8.81. Found: C, 57.48; H, 8.96%.

### 3.9. (1-Naphthylmethyl)-phenyl-bis(trimethylsilyl)silane (**15a**)

A 0.50 g (1.25 mmol) sample of **13a**, dissolved in

20 ml of ether, was added at r.t. within 1 h to a five-fold molar excess of phenyllithium. After stirring for 0.5 h, water was added. Evaporation of the dried ethereal extracts gave a colourless solid, which was recrystallized from ethanol, yield 0.31 g (65%). <sup>1</sup>H-NMR (benzene-*d*<sub>6</sub>):  $\delta = 0.05$  (s, SiCH<sub>3</sub>, 18H), 3.05 (s, CH<sub>2</sub>, 2H), 7.18–7.98 (m, arom. CH, 12H). <sup>13</sup>C-NMR (benzene-*d*<sub>6</sub>):  $\delta = -0.1$  (SiCH<sub>3</sub>), 17.2 (CH<sub>2</sub>), 125.1, 125.5, 125.6, 125.7, 125.8, 126.2, 128.6, 129.0, 129.1, 132.3, 133.4, 135.7, 137.8 and 138.2 (arom. C). <sup>29</sup>Si-NMR (benzene-*d*<sub>6</sub>):  $\delta = -39.2$  (SiSiMe<sub>3</sub>),  $-16.6$  (SiMe<sub>3</sub>). MS *m/z* (%): 392 (8) [M<sup>+</sup>], 377 (4) [M<sup>+</sup> - CH<sub>3</sub>], 319 (6) [M<sup>+</sup> - SiMe<sub>3</sub>], 251 (35) [Si(SiMe<sub>3</sub>)<sub>2</sub>Ph<sup>+</sup>]. Anal. Calc. for C<sub>23</sub>H<sub>32</sub>Si<sub>3</sub> (392.76): C, 70.34; H, 8.21. Found: C, 70.87; H, 8.18%.

### 3.10. (8-Methoxy-1-naphthylmethyl)phenyl-bis(trimethylsilyl)silane (**15b**)

As described for **15a**, 0.50 g (1.15 mmol) of **13b** and excess phenyllithium afforded 0.41 g (83%) of **15b**, m.p. 109–111°C. <sup>1</sup>H-NMR (benzene-*d*<sub>6</sub>):  $\delta = 0.09$  (s, SiCH<sub>3</sub>, 18H), 3.08 (s, OCH<sub>3</sub>, 3H), 3.68 (s, CH<sub>2</sub>, 2H), 6.31–7.50 (m, arom. CH). <sup>13</sup>C-NMR (benzene-*d*<sub>6</sub>):  $\delta = 0.0$  (SiCH<sub>3</sub>), 22.2 (OCH<sub>3</sub>), 54.4 (CH<sub>2</sub>), 105.10, 122.04, 124.94, 125.57, 125.63, 126.12, 127.91, 128.09, 135.72 (2 signals), 137.31, 138.51, 139.11 and 158.13 (arom. C). <sup>29</sup>Si-NMR (benzene-*d*<sub>6</sub>):  $\delta = -39.3$  (SiSiMe<sub>3</sub>),  $-15.8$  (SiMe<sub>3</sub>). MS *m/z* (%): 407 (5) [M<sup>+</sup> - CH<sub>3</sub>], 349 (100) [M<sup>+</sup> - SiMe<sub>3</sub>]. Anal. Calc. for C<sub>24</sub>H<sub>34</sub>OSi<sub>3</sub> (422.79): C, 68.18; H, 8.11. Found: C, 68.15; H, 8.06%.

### 3.11. Crystal structure determination of *Z*-**5**, *E*-**8** and *E*-**10**

The crystal structure determinations were performed on a Siemens P4 four-circle diffractometer with graphite monochromator. The data were collected in routine  $\omega$ -scan. The structures were solved by direct methods (Siemens SHELXTL, 1990, Siemens Analytical X-ray Inst. Inc.) and refined by the full-matrix least-squares method of Bruker SHELXTL, Version 5.03 (1997). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into theoretical positions and refined using the riding model. The weighting schemes were calculated according to:  $w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 0.6651P]$  for *Z*-**5**,  $w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.1488P]$  for *E*-**8** and  $w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 1.9582P]$  for *E*-**12** with  $P = (F_o^2 + 2F_c^2)/3$  in all three cases (for full crystallographic data see Table 1).

Table 1  
Crystal and structure solution data for compounds **Z-5**, **E-8** and **E-12**

Compound	<b>Z-5</b>	<b>E-8</b>	<b>E-12</b>
Formula	C <sub>38</sub> H <sub>62</sub> N <sub>2</sub> Si <sub>6</sub>	C <sub>23</sub> H <sub>43</sub> NO <sub>2</sub> Si <sub>4</sub>	C <sub>36</sub> H <sub>57</sub> NOSi <sub>6</sub>
<i>M<sub>r</sub></i> (g mol <sup>-1</sup> )	715.44	477.94	688.37
Temperature (K)	293(2)	293(2)	293(2)
Radiation (Mo–K <sub>α</sub> ), graphite monochromator (Å)	λ = 0.71073	λ = 0.71073	λ = 0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	11.8000(10)	8.9310(10)	20.282(4)
<i>b</i> (Å)	36.017(4)	10.575(2)	10.348(2)
<i>c</i> (Å)	11.0290(10)	15.894(3)	20.575(3)
α (°)	90	85.130(10)	90
β (°)	112.25	83.860(10)	90.820(10)
γ (°)	90	81.210(10)	90
<i>V</i> (Å <sup>3</sup> )	4338.3(7)	1471.4(4)	4255.0(4)
<i>Z</i>	4	2	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.095	1.079	1.075
μ (Mo–K <sub>α</sub> ) (mm <sup>-1</sup> )	0.219	0.220	0.222
<i>F</i> (000)	1552	520	1488
Crystal size (mm <sup>3</sup> )	0.44 × 0.32 × 0.32	0.5 × 0.32 × 0.3	0.55 × 0.46 × 0.58
θ Scan range (°)	1.86–22.00	1.95–21.99	2.01–21.99
Index ranges	–12 ≤ <i>h</i> ≤ 11, –1 ≤ <i>k</i> ≤ 37, –1 ≤ <i>l</i> ≤ 11	–1 ≤ <i>h</i> ≤ 9, –11 ≤ <i>k</i> ≤ 11, –16 ≤ <i>l</i> ≤ 16	–1 ≤ <i>h</i> ≤ 21, –10 ≤ <i>k</i> ≤ 1, –21 ≤ <i>l</i> ≤ 21
Data collection mode	ω-scan	ω-scan	ω-scan
Reflections collected	6571	4761	6530
Independent reflections ( <i>R</i> <sub>int</sub> )	5328 = 0.0419	3618 = 0.0385	5216 = 0.0393
Reflections observed	3718	2619	3371
Complies to θ = 21.99° (%)	100.0	100.0	100.0
Reference method on <i>F</i> <sup>2</sup>	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares
Data/restraints/parameters	5314/0/415	3618/0/271	5216/0/397
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.011	1.018	1.019
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	0.0540	0.0518	0.0580
<i>wR</i> <sub>2</sub>	0.1277	0.1287	0.1315
<i>R</i> <sub>1</sub> for all data	0.0865	0.0777	0.1005
<i>wR</i> <sub>2</sub> for all data	0.1474	0.1432	0.1568
Δρ (max./min.) (e Å <sup>-3</sup> )	0.276/–0.208	0.232/–0.162	0.190/–0.174

#### 4. Supplementary material

Crystallographic data (excluding structural factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CSD-115671, CSD-115672 and CSD-115673. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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