Novel, strained 10b,10c-dihydropyrenes bearing bulky TMSCH$_2$ groups at the internal positions

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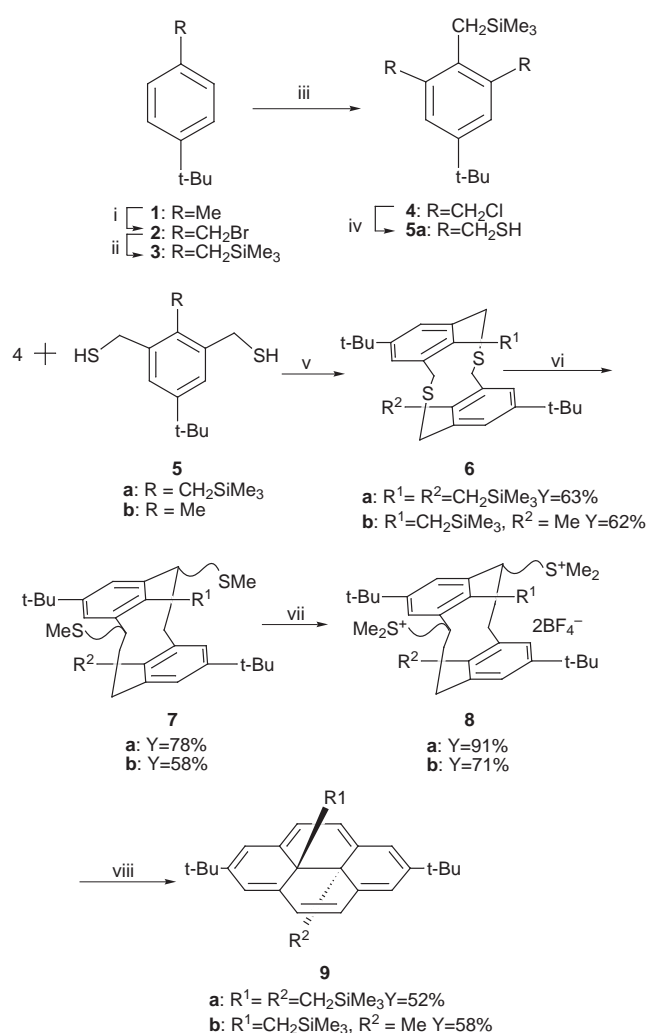Two novel, strained *trans*-10b,10c-dihydropyrenes, **9a–b**, with internal, bulky trimethylsilylmethyl substituent(s) were synthesized. Their 14π-electron annulene systems were found to be distorted, as shown by X-ray crystallographic analyses and ^{1}H-NMR and UV spectroscopy.

The functional groups at the internal positions in 10b,10c-substituted *trans*-10b,10c-dihydropyrenes are influenced by the magnetic anisotropy due to the 14π-electron annulene system. They can be used to probe the aromaticity of these compounds.[1–3] On the other hand, introduction of bulky substituents into the 10b,10c-positions of dihydropyrenes[4,5] may alter the aromatic character of the annulene system. One such substituent, in which the authors have been interested, is the trimethylsilylmethyl group, as it is bulky and it can also serve both as a protective group and as an activating group for further functional conversions.[6,7] Here, the preparation of the two novel, strained dihydropyrenes 2,7-di-*tert*-butyl-*trans*-10b,10c-bis(trimethylsilylmethyl)-10b,10c-dihydropyrene **9a** and 2,7-di-*tert*-butyl-*trans*-10b-trimethylsilylmethyl-10c-methyl-10b,10c-dihydropyrene **9b** is described and their spectral properties are discussed.

From *p-tert*-butyltoluene **1**, *trans*-10b,10c-dihydropyrenes **9a** and **9b** have been prepared in eight steps (Scheme 1). Wittig rearrangement of dithia[3.3]metacyclophanes **6a** and **6b**, followed by Hoffmann elimination using potassium *tert*-butoxide in THF, gave **9a** (37%) and **9b** (24%), respectively.

The structures of **9a** and **9b** were analyzed by X-ray crystallography (Fig. 1 and 2). One measure of the distortion from planarity of the dihydropyrene periphery is the distance of the two carbons C2 and C7 from the plane containing the four carbon atoms (C3a, C5a, C8a, C10a) which are bonded to the internal position (Fig. 3).

In the case of non-symmetrical dihydropyrene **9b**, the average distance† of the C2 carbon atoms (A: C02 and B: C33 in X-ray) neighboring the TMSCH$_2$ group from the plane C3a–C5a–C8a–C10a is 0.319 Å. The distance between C7 carbon atoms (A: C07 and B: C37 in X-ray) neighboring the methyl group and the plane is only 0.011 Å. The corresponding distance of the C2 carbon atom in **9a** (C02) is 0.265 Å. For comparison, the distance in the *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene is 0.117 Å.[8] From this result, it can be seen that the dihydropyrene periphery is more distorted in the vicinity of the TMSCH$_2$ group. The dihedral angle of **9b** on the TMSCH$_2$ side (C09–

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† The X-ray crystallographic structure of **9b** showed two independent positions for **9b** in the crystal lattice. Perhaps due to a crystal packing effect, **9b** in these two positions shows slightly different structural parameters, which the author deemed not to be significant. Thus, forthwith in the discussion of the structural features of **9b**, the average value **9b-A/9b-B** is used.

Scheme 1 *Reagents and Conditions*: i, NBS, benzoyl peroxide, 79%; ii, Me$_3$SiCl, Mg, 70%; iii, ClCH$_2$OCH$_3$, ZnCl$_2$, 63%; iv, (1) (NH$_2$)$_2$CS–KOH, (2) HCl, 74%; v, KOH–NaBH$_4$; vi, (1) *n*-BuLi, (2) MeI; vii, (MeO)$_3$CH, BF$_3$–Et$_2$O; viii, KOBu^t.

C10–C10a–C01) is 8° and that on the methyl side (C04–C05–C05a–C06) is only 1°. The corresponding angle in the symmetrical dihydropyrene **9a** (C09–C10–C10a–C01) is 6°. These

" Step "

Fig. 1 ORTEP View of **9a**.

" Bow "

9b-A

B

A

Fig. 2 ORTEP View of **9b**.

9a: R^1, R^2 = CH$_2$SiMe$_3$

9b: R^1 = CH$_2$SiMe$_3$, R^2 = Me

	9a (Å)	**9b** (Å)		
		A	B	Average
C1–C2	1.396	1.38	1.39	1.385
C2–C3	1.409	1.41	1.40	1.405
C3–C3a	1.383	1.36	1.42	1.390
C3a–C4	1.404 (C03a–C09)	1.43	1.41	1.420
C4–C5	1.390 (C09–C10)	1.39	1.36	1.375
C5–C5a	1.396 (C10–C10a)	1.37	1.39	1.380
C5a–C6	1.386 (C10a–C1)	1.38	1.37	1.375
C6–C7	1.396 (C01–C02)	1.39	1.42	1.405
C7–C8	1.409 (C02–C03)	1.39	1.37	1.380
C8–C8a	1.383 (C03–C03a)	1.43	1.41	1.420
C8a–C9	1.404 (C03a–C09)	1.36	1.37	1.365
C9–C10	1.390	1.41	1.41	1.410
C10–C10a	1.396	1.40	1.37	1.385
C10A–C01	1.386	1.42	1.43	1.425

Fig. 3 Distortion of dihydropyrene periphery of **9a**.

angle within the periphery of the *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene is 4°.[2] Thus, the dihydropyrenes **9a** and **9b**, which have bulky TMSCH$_2$ groups at the internal position(s), are clearly more distorted than the 10b,10c-dimethyl-10b,10c-dihydropyrene.[2,8] It is interesting to note that, while **9a** has the larger mean deviation from planarity of its periphery, **9b** exhibits the largest single deviation. The bond angles (C10b–C19–Si01) in **9a** and **9b** are 126° and 125°, and the distance from the methylene carbon in TMSCH$_2$ to the nearest carbon in the periphery is 3.39 Å (C21–C01) in **9a** and 3.41 Å (average of C51–C31, C21–C01) in **9b**, respectively. These results indicate the existence of a steric repulsion between the TMSCH$_2$ groups and the dihydropyrene periphery.

The bond lengths within the dihydropyrene periphery of **9a** and **9b** are given in Table 1. In the case of *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene,[9] bond alternation is almost absent around the perimeter, with bond lengths running between 1.388 and 1.398 Å. In the case of **9a**, the bond lengths of the dihydropyrene periphery run between 1.383 and 1.409 Å and bond alternation is also almost absent. The same can be observed for **9b** (1.38–1.42 Å). These results indicate that the aromaticities of the dihydropyrene peripheries of **9a** and **9b** are intact, although the peripheries are distorted due to the steric repulsion of the TMSCH$_2$ group.

The ¹H-NMR chemical shifts of **9a**, **9b**, and of 2,7-di-*tert*-
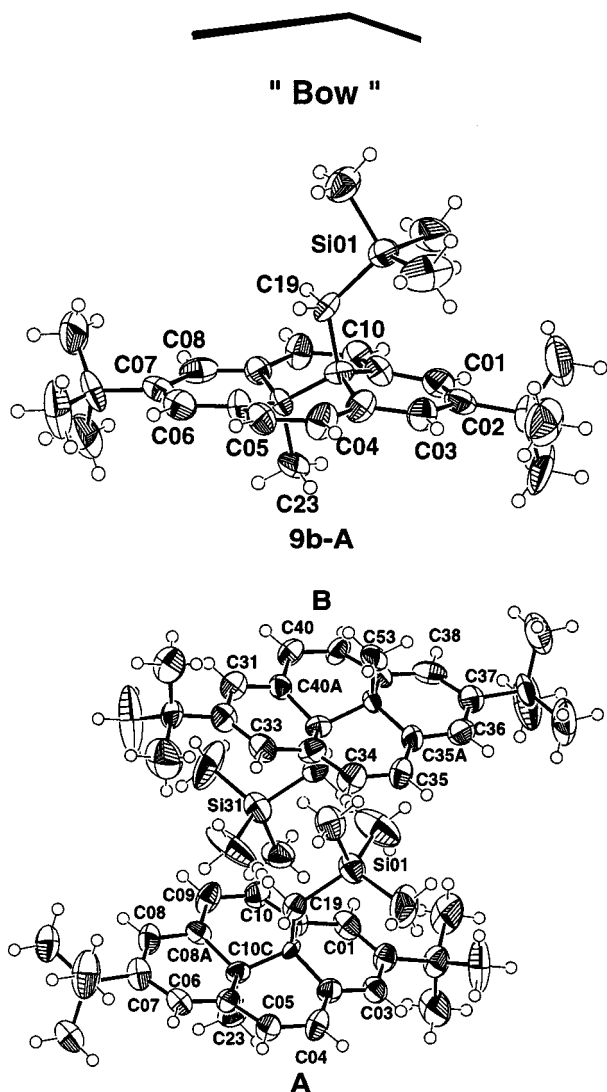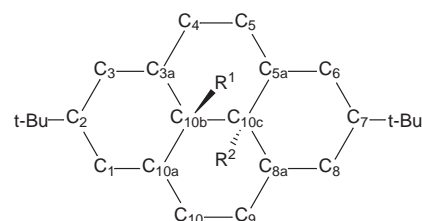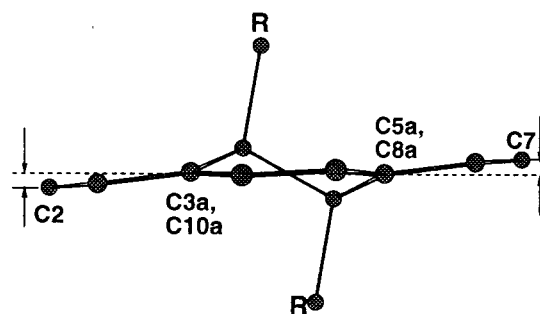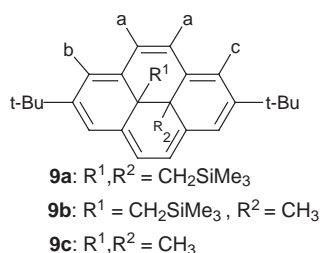
results show that the dihydropyrene periphery of **9a** has a distorted structure, which looks like a step. The periphery of **9b** has the slightly curved structure of a bow. The largest dihedral

Table 2 ^{1}H-NMR spectra of dihydropyrenes **9a**, **9b** and **9c** in CDCl$_3$ at 23 °C

9a: R^1,R^2 = CH$_2$SiMe$_3$

9b: R^1 = CH$_2$SiMe$_3$, R^2 = CH$_3$

9c: R^1,R^2 = CH$_3$

Compound	Ar H			Me$_3$Si	SiCH$_2$	CH$_3$
	a	b	c			
9a	8.32	8.47	8.47	−0.98	−4.28	—
9b	8.39	8.47	8.53	−0.95	−4.22	−4.08
9c	8.46	8.54	8.54	—	—	−4.06

Table 3 Maximal absorptions in the UV spectra of **9a**, **9b** and **9c** in cyclohexane

Compound	λ_{max}/nm (log ε)
9a	670(2.3) 505(3.5) 395(4.1) 351(4.5)
9b	657(2.8) 490(3.9) 388(4.5) 346(4.8)
9c	644(2.8) 478(3.7) 383(4.1) 340(4.5)

butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**9c**) [10] are given in Table 2. The aromatic protons were assigned by NOE techniques. The aromatic protons H$_a$ of **9a** and **9b** show an up-field shift of 0.14 and 0.07 ppm, respectively, when compared to H$_a$ of **9c**. The chemical shifts of H$_a$ can be correlated with the number of TMSCH$_2$ groups. It is expected that the distortion of the dihydropyrene periphery caused by TMSCH$_2$ groups, influences the electron density at the H$_a$ position. It must be noted that the electron donor capability of the TMSCH$_2$ group to carbons C10b and C10c may have an added effect on the electron density.

In the UV spectra, λ_{max} of **9a**, **9b** and **9c** are observed at 670, 657, and 644 nm, respectively. The bis-TMSCH$_2$ substituted dihydropyrene **9a** is distorted and looks like a step and the mono substituted dihydropyrene **9b** is distorted like a bow. Thus, it is expected that the red shift of λ_{max} seems to correlate with the degree of distortion of the periphery (**9a** > **9b** > **9c**). Again, an added effect may stem from the electron donor capability of the TMSCH$_2$ groups.

The study of the reactivity of **9a** and **9b** is underway.

Experimental

All melting points are uncorrected. IR spectra were measured as KBr pellets. ^{1}H-NMR spectra were determined in CDCl$_3$ at 270 MHz with a JEOL EX-270 instrument. UV spectra were measured on a HITACHI 220A spectrophotometer using cyclo-hexane as solvent. Mass spectra were measured on a JEOL JMS-01-SG-2 machine at 75 eV using a direct inlet system. Elemental analysis was performed on a YANAKO MT-5 instrument.

1-*tert*-Butyl-4-trimethylsilylmethylbenzene 3

A solution of 4-*tert*-butylbenzyl bromide **2** (150 g, 0.7 mol) in dry THF (200 mL) was added to a stirred suspension of chlorotrimethylsilane (109 g, 1 mol) and Mg (20 g, 0.8 mol) in dry THF (100 mL) under an argon atmosphere at room tem-perature. After the reaction mixture was stirred under reflux for 3 h, it was poured into ice–water, and extracted with dichloro-methane (300 mL). The combined extracts were washed with water, dried over anhydrous MgSO$_4$, and concentrated. The residue was distilled under reduced pressure to give **3** (99.8 g, 0.45 mol, 70%), bp 63–66 °C/0.9 Torr (Found: C, 76.41; H, 11.10. C$_{14}$H$_{24}$Si required C, 76.28; H, 10.97%); δ_H (270 MHz, CDCl$_3$) −0.01 (9 H, s, (CH$_3$)$_3$Si), 1.31 (9 H, s, *t*-Bu), 2.04 (2 H, s, TMSCH$_2$), 6.92 (2 H, d, ^3J = 8.2 Hz, arom. H), 7.24 (2 H, d, ^3J = 8.2 Hz, arom. H); *m/z*: 220 (M$^+$).

1-*tert*-Butyl-3,5-bis(chloromethyl)-4-trimethylsilylmethyl-benzene 4

A mixture of 1-*tert*-butyl-4-trimethylsilylmethylbenzene **3** (2.2 g, 10 mmol) and chloromethyl methyl ether (10.5 g, 130 mmol) was added to activated zinc chloride (1.8 g, 13 mmol) under an argon atmosphere. After the reaction mixture was stirred under reflux for 2 h, it was poured into ice–water, and stirred for 30 min. The reaction mixture was extracted with dichloromethane (300 mL). The organic phase was washed with water, dried over anhydrous MgSO$_4$, and concentrated. The residue was distilled under reduced pressure to give **4** (2.0 g, 6.3 mmol, 63%), bp 138–140 °C/0.9 Torr (Found: C, 60.95; H, 8.42. C$_{16}$H$_{26}$Cl$_2$Si required C, 60.55; H, 8.26%); δ_H (270 MHz, CDCl$_3$) 0.04 (9 H, s, (CH$_3$)$_3$Si), 1.25 (9 H, s, *t*-Bu), 2.37 (2 H, s, TMSCH$_2$), 4.52 (4 H, s, CH$_2$Cl), 7.25 (2 H, s, arom. H); *m/z*: 320 (^{37}Cl$_2$ M$^+$), 318 (^{37}Cl ^{35}Cl M$^+$), 316 (^{35}Cl$_2$ M$^+$).

1-*tert*-Butyl-3,5-bis(mercaptomethyl)-4-trimethylsilylmethyl-benzene 5a

A solution of thiourea (500 mg, 6.6 mmol) and 1-*tert*-butyl-3,5-bis(chloromethyl)-4-trimethylsilylmethyl-benzene **4** (950 mg, 3.0 mmol) in ethanol (15 mL) was stirred under reflux for 1 h. A 10% aq. NaOH solution (5 mL) and NaBH$_4$ (20 mg, 0.6 mmol) were added to the reaction mixture. Then, the mixture was stirred under reflux for another 1 h. The reaction mixture was cooled, neutralized with a 5% aq. HCl solution, and extracted with dichloromethane (100 mL). The organic layer was washed with water, dried over anhydrous MgSO$_4$, and concentrated. The residue was distilled under reduced pressure to give **5a** (700 mg, 2.2 mmol, 74%) as colorless needles (hexane); bp 117 °C/0.5 Torr, mp 48–51 °C (Found: C, 61.57; H, 9.09. C$_{16}$H$_{28}$S$_2$Si required C, 61.48; H, 9.03%); δ_H (270 MHz, CDCl$_3$) 0.39 (9 H, s, (CH$_3$)$_3$Si), 1.29 (9 H, s, *t*-Bu), 1.55 (2H, t, ^3J = 6.9 Hz, SH), 2.35 (2 H, s, TMSCH$_2$), 3.69 (4 H, d, ^3J = 6.9 Hz, CH$_2$S), 7.16 (2 H, s, arom. H); *m/z*: 312 (M$^+$).

6,15-Di-*tert*-butyl-9,18-bis(trimethylsilylmethyl)-2,11-dithia-[3.3]metacyclophanes 6a, 6,15-di-*tert*-butyl-9-methyl-18-tri-methylsilylmethyl-2,11-dithia[3.3]metacyclophanes 6b

A solution of **4** (3.17 g, 10 mmol) and **5a** (3.13 g, 10 mmol) in EtOH (200 mL) was added slowly to a refluxing suspension of KOH (2.10 g, 32 mmol) and NaBH$_4$ (0.56 g, 14.9 mmol) in EtOH (2 L). After the reaction mixture was stirred under reflux for another 2 h, the solvent was evaporated. The residue was neutralized with 10% aq. HCl solution, and extracted with dichloromethane (300 mL). Then the organic layer was washed with water, dried over anhydrous MgSO$_4$, and concentrated. The residue was recrystallized from hexane to give **6a** (3.50 g, 6.3 mmol, 63%), mp 222–224 °C (Found: C, 69.18; H, 9.62. C$_{32}$H$_{52}$S$_2$Si$_2$ required C, 69.00; H, 9.41%); δ_H (270 MHz, CDCl$_3$) −0.26 (18 H, s, (CH$_3$)$_3$Si), 1.29 (4 H, s, TMSCH$_2$), 1.32 (18 H, s, *t*-Bu), 3.53 (4 H, d, ^2J = 14 Hz, bridge), 3.60 (4 H, d, ^2J = 14 Hz, bridge), 7.24 (4 H, s, arom. H); *m/z*: 556 (M$^+$).

The same procedure was used for **6b**; **4** (4.76 g, 15 mmol) and **5b** (3.61 g, 15 mmol) afforded **6b** (4.5 g, 9.3 mmol, 62%), mp 204–206 °C (hexane) (Found: C, 71.85; H, 9.14. C$_{29}$H$_{44}$S$_2$Si required C, 71.84; H, 9.15%); δ_H (270 MHz, CDCl$_3$) −0.27 (9 H, s, (CH$_3$)$_3$Si), 1.27 (2 H, m, TMSCH$_2$), 1.29 (3H, s, CH$_3$), 1.32 (9 H, m, *t*-Bu), 1.34 (9 H, m, *t*-Bu), 3.57–3.67 (8 H, m, bridge), 7.23 (2 H, s, arom. H), 7.30 (2 H, s, arom. H); *m/z*: 484 (M$^+$).

[2.2]Metacyclophanes 7 by Wittig rearrangement of dithia-[3.3]metacyclophanes 6

Using a syringe, *n*-BuLi (1.6 M in hexane, 9.5 mL, 15 mmol) was added to a stirred solution of dithia[3.3]metacyclophane **6a** (1.67 g, 3 mmol) in dry THF (16.5 mL) under an argon atmosphere at 0 °C. After the reaction mixture was stirred at room temperature for 2 h, methyl iodide (0.93 mL, 15 mmol) was added and the reaction mixture was stirred for 30 min. Then the mixture was poured into ice–water, and extracted with dichloromethane (100 mL). The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluant. The product was recrystallized from hexane to give mixed isomers of **7a** (1.35 g, 2.3 mmol, 78%), mp 220–224 °C (Found: C, 69.71; H, 9.69. $C_{34}H_{56}S_2Si_2$ required C, 69.77; H, 9.65%); δ_H (270 MHz, $CDCl_3$) −0.46 to −0.38 (18 H, m, $(CH_3)_3$-Si), 0.72–0.88 (4 H, m, $TMSCH_2$), 1.26–1.43 (18 H, m, *t*-Bu), 2.19–2.23 (6 H, m, SCH_3), 2.53–2.66 (4 H, m, bridge), 4.04–4.19 (2 H, m, bridge), 7.04–7.19 (2 H, m, arom. H), 7.66–7.68 (2 H, m, arom. H); *m/z*: 584 (M⁺).

The same procedure was used for **7b**; **6a** (1.45 g, 3.0 mmol) gave **7b** (890 mg, 1.7 mmol, 58%), as colorless prisms (hexane), mp 199–204 °C (Found: C, 72.90; H, 9.61. $C_{31}H_{48}S_2Si_1$ required C, 72.59; H, 9.43%); δ_H (270 MHz, $CDCl_3$) −0.46 to −0.43 (9 H, m, $(CH_3)_3Si$), 0.65–0.67 (3 H, m, CH_3), 0.86–0.91 (2 H, m, $TMSCH_2$), 1.25–1.43 (18 H, m, *t*-Bu), 2.14–2.23 (6 H, m, SCH_3), 2.56–2.71 (2 H, m, bridge), 3.04–3.21 (2 H, m, bridge), 4.00–4.19 (2 H, m, bridge), 7.04–7.19 (2 H, m, arom. H), 7.68–7.81 (2 H, m, arom. H); *m/z*: 512 (M⁺).

2,7-Di-*tert*-butyl-*trans*-10b,10c-bis(trimethylsilylmethyl)-10b,10c-dihydropyrene 9a, 2,7-di-*tert*-butyl-*trans*-10b-trimethyl-silylmethyl-10c-methyl-10b,10c-dihydropyrene 9b

A solution of boron trifluoride diethyl ether complex (7.3 mL, 56 mmol) in dichloromethane (6 mL) was added to trimethyl orthoformate (5.5 mL, 50 mmol) at −30 °C under an argon atmosphere. After the reaction mixture was stirred for 15 min at 0 °C, it was cooled to −30 °C, and the mixed isomers **7a** (700 mg, 1.2 mmol) in dichloromethane (5 mL) were added under stirring at −30 °C. After the mixture was stirred for another 3 h at −30 °C, ethyl acetate (5 mL) was added to dissolve excess methylating agent, and the mixture was stirred for a further 3 h. Then the white precipitate was collected and dried to give **8a** (0.86 g, 1.1 mmol, 91%), mp 285–287 °C decomp (Found: C, 54.59; H, 7.72. $C_{36}H_{62}B_2F_8S_2Si_2$ required C, 54.82; H, 7.92%); δ_H (270 MHz, DMSO-d_6) −0.37 (18 H, s, $(CH_3)_3Si$), 0.60–1.06 (4 H, m, $TMSCH_2$), 1.29–1.32 (18 H, m, *t*-Bu), 2.92–3.00 (12 H, m, $S(CH_3)_2^+$), 3.28–3.37 (4 H, m, bridge), 4.89–4.99 (2 H, m, bridge), 7.28–7.51 (4 H, m, arom. H).

The same procedure was used for **8b**; **7b** (850 mg, 1.7 mmol) gave **8b** (860 mg, 1.2 mmol, 71%) as colorless prisms (hexane), mp 231–234 °C decomp. δ_H (270 MHz, DMSO-d_6) −0.44 to −0.39 (9 H, m, $(CH_3)_3Si$), 0.73–0.79 (5 H, m, $TMSCH_2$, CH_3), 1.28–1.32 (18 H, m, *t*-Bu), 2.92 (12 H, s, $S(CH_3)_2^+$), 3.26–3.35 (4 H, m, bridge), 4.01–4.04 (2 H, m, bridge), 7.29–7.60 (4 H, m, arom. H).

This material was used without further purification to prepare **9**. Potassium *tert*-butoxide (270 mg, 2.4 mmol) was added to a stirred solution of salt **8a** (370 mg, 0.47 mmol) in dry THF (36 mL) under an argon atmosphere. The reaction mixture was stirred for 15 min. Then benzene (20 mL) was added and the mixture was acidified with dilute aq. HCl solution. The layers were separated and the aqueous layer was further extracted with benzene. The combined extracts were washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residue was chromatographed over silica gel using hexane as eluant to give **9a** (120 mg, 0.25 mmol, 52%) as deep brown prisms (hexane), mp 156–157 °C (Found: C, 78.27; H, 9.85. $C_{32}H_{48}Si_2$ required C, 78.62; H, 9.90%); δ_H (270 MHz, $CDCl_3$) −4.18

(4 H, s, $TMSCH_2$), −0.98 (18 H, s, $(CH_3)_3Si$), 1.68 (18 H, s, *t*-Bu), 8.32 (4 H, br s, arom. H), 8.47 (4 H, br s, arom. H); *m/z*: 488 (M⁺).

The same procedure was used for **9b**; **8b** (200 mg, 0.28 mmol) gave **9b** (68 mg, 0.16 mmol, 58%) as deep brown prisms (hexane), mp 142–146 °C (Found: C, 83.52; H, 9.86. $C_{29}H_{40}Si$ required C, 83.59; H, 9.67%); δ_H (270 MHz, $CDCl_3$) −4.22 (2 H, s, $TMSCH_2$), −4.08 (3 H, s, CH_3), −0.95 (9 H, s, $(CH_3)_3$-Si), 1.69 (18 H, s, *t*-Bu), 8.39 (4 H, br s, arom. H), 8.47 (2 H, br s, arom. H), 8.53 (2 H, br s, arom. H); *m/z*: 416 (M⁺).

X-Ray crystal structure determination of 9a ‡

Crystal data. $C_{32}H_{48}Si_2$, $M = 488.88$, triclinic, $a = 9.537(1)$ Å, $b = 9.828(2)$ Å, $c = 9.090(1)$ Å, $\alpha = 115.50(1)°$, $\beta = 97.54(1)°$, $\gamma = 89.19(1)°$, $V = 761.5(2)$ Å³, (by least-squares refinement on diffractometer angles for 25 automatically centered reflections, $\lambda = 1.54184$ Å), space group $P\bar{1}$ (No. 2), $Z = 1$ (special position), $D_x = 1.066$ g cm⁻³, deep brown prism, crystal size $0.20 \times 0.15 \times 0.10$ mm, μ(Cu-Kα) = 1.162 mm⁻¹.

Data collection and processing. Intensity data were measured on a CAD4 FR590 diffractometer, ω-2θ mode with ω scan width = 0.6 + 0.410 tan θ, scan speed 2 to 20 deg min⁻¹ and graphite-monochromated Cu-Kα radiation; 2760 reflections were measured (4.68 ≤ θ ≤ 64.94°, ±h, −k, ±l). 2592 unique reflections [merging $R = 0.0753$ after absorption correction (max, min transmission factor = 0.9681, 0.9455)], linear and approximate isotopic crystal decay, *ca.* −1.0% corrected during procedure.

Structure analysis and refinement. The structure was solved by the direct method (SIR92).[11] Full-matrix least-squares refinement on F^2 was performed with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with $U_{iso} = 1.3$ $U_{(bonded\ atoms)}$. The weighting scheme is $w = 1/[\sigma^2(F_o^2) + (0.1687P)^2 + 26.0206P]$ where $P = (F_o^2 + 2F_c^2)/3$. Final R and R_w values are 0.0454, 0.1171 (refined on F^2). All calculations were performed on a MicroVAX3100 and IBM RISC System/6000 3100 using MolEN[12] and SHELXL-93.[13]

X-Ray crystal structure determination of 9b

Crystal data. $C_{29}H_{40}Si_1$, $M = 426.70$, monoclinic, $a = 20.586(18)$ Å, $b = 13.153(6)$ Å, $c = 19.186(8)$ Å, $\beta = 93.23(5)°$, $V = 5186.7(56)$ Å³, (by least-squares refinement on diffractometer angles for 25 automatically centered reflections, $\lambda = 1.54184$ Å), space group $P2_1/n$ (No. 14), $Z = 8$, $D_x = 1.067$ g cm⁻³, deep brown prism, crystal size $0.20 \times 0.20 \times 0.03$ mm, μ(Cu-Kα) = 0.864 mm⁻¹.

Data collection and processing. Intensity data were measured on a CAD4 FR590 diffractometer, ω-2θ mode with ω scan width = 1.4 + 0.270 tan θ, scan speed 4 to 20 deg min⁻¹ and graphite-monochromated Cu-Kα radiation; 6077 reflections were measured (3.99 ≤ θ ≤ 52.38°, +h, +k, ±l). 5876 unique reflections [merging $R = 0.1637$ after absorption correction (max, min transmission factor = 0.9990, 0.6407)], linear and approximate isotopic crystal decay, *ca.* −0.01% corrected during procedure.

Structure analysis and refinement. The structure was solved by the direct method (SIR92).[11] Full-matrix least-squares

refinement on F^2 was performed with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with $U_{iso} = 1.3\ U_{(bonded\ atoms)}$. The weighting scheme is $w = 1/[\sigma^2(F_o^2) + (0.1687P)^2 + 26.0206P]$ where $P = (F_o^2 + 2F_c^2)/3$. Final R and R_w values are 0.0917, 0.2042 (refined on F^2). The large R value seems to be due to the rotation of the *tert*-butyl groups. All calculations were performed on a MicroVAX3100 and IBM RISC System/6000 3100 using MolEN[12] and SHELXL-93.[13]

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