Synthesis and Structure of a 2,4-Unsubstituted *cis*/*trans*-1,3-Disilacyclobutane by Dehydrofluorination of a Highly Hindered Fluorosilane

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The preparation, molecular structure, and metalation behavior of a sterically highly congested fluorosilane (*t*BuTipMeSiF) are described. This silane is subjected to dehydrofluorination under thermally mild conditions. A *C*-unsubstituted transient intermediate – either the silene or the corresponding silenoid – is generated in a metalation/elimination sequence at low temperatures, and this intermediate dimerizes to give the corresponding 1,3-disilacyclobutane exclusively, even in the presence of a trapping agent. The significant steric hindrance in the starting fluorosilane and the final 1,3-disilacyclobutane is corroborated by their crystal structures.

Introduction

Since the preparation of the first stable silenes a broad variety of methods to synthesize such compounds has been developed.[1,2] *C*-Substituted transient and stable silenes can be prepared under especially mild conditions by a metalation/elimination sequence. For this approach, all so-far-known examples carry activating silyl groups at the carbon atom designated for metalation. Besides steric protection of the resulting silene, these substituents also provide an increase of the acidity of the neighboring C–H unit due to the α-silyl effect.[3] Alternatively, α-lithiohalosilanes have also been prepared by conjugate addition of organolithium reagents to halovinylsilanes. Since the first reaction of this type, described by Jones and Lim in 1977,[4,5] many other transient silenes have been synthesized by this route, particularly by Auner and coworkers,[6] but also by some other authors.[7] Despite the use of more and more bulky substituents, all these silenes are unstable at room temperature and lead to dimeric 1,3-disilacyclobutanes (head-to-tail dimerization), except for the stable dimesitylneopentylsilene.[8] Since in these silenes the multiply bonded carbon atom also carries at least one substituent, we were interested in whether the scope of the metalation/elimination technique could be extended to silenes without any activating or protecting groups at the carbon end of the silene unit. In this contribution, we describe the preparation and structure of a sterically crowded fluorosilane which should be a suitable precursor for a *C*-unsubstituted α-lithiofluorosilane. Upon metalation, the corresponding transient silenoid is formed, which subsequently eliminates LiF. The resulting silene is unstable and dimerizes to the corresponding 1,3-disilacyclobutane. The precursor for metalation as well as the resulting *cis*-1,3-disilacyclobutane have been characterized spectroscopically and by X-ray diffraction on single crystals.

Results and Discussion

In the reaction of sterically encumbered halosilanes with organolithium compounds direct nucleophilic halide displacement competes with lithiation of activated sites such as the α-position. Therefore, the steric protection of the silicon center in fluorosilanes is crucial to favor metalation over nucleophilic displacement. To accomplish the formation of a silenoid by direct deprotonation of a methyl group adjacent to a fluorosilyl, we synthesized a suitable precursor starting from *t*BuTipSiF$_2$ (**1**, Tip = 2,4,6-triisopropylphenyl).[9,10] Since no C–H bonds are available in the α-position to the silicon atom in this fluorosilane, we selectively introduced a methyl group as the designated site for further metalation. The methyl group can be introduced in a straightforward manner by treating **1** with methyllithium at low temperature to cleanly afford **2** (Scheme 1). The NMR spectra of **2** show a ^{19}F resonance at $\delta = -160.5$ ppm, and the ^{29}Si signal at $\delta = 25.0$ ppm is split into a doublet with a $^{1}J_{\mathrm{Si,F}}$ coupling constant of 287 Hz (Figure 1). We were able to obtain a crystal structure of **2** which illustrates the steric situation within the molecule (Table 1).

Even though **1** and **2** are isoelectronic, the steric situation around the silicon center appears to be even more congested in **2**. Accordingly, the Si(1)–F(1) bond length increases from 1.595(2) Å in **1**[9] to 1.625(2) Å in **2** and is even longer than in the closely related compound *i*Pr$_2$TipSiF.[11] Also, the silicon–carbon distances for the *tert*-butyl and the

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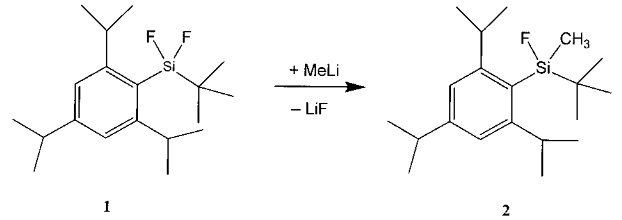


Scheme 1. Synthesis of **2**.

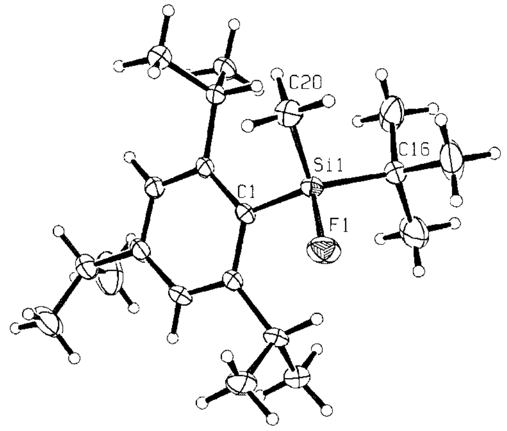


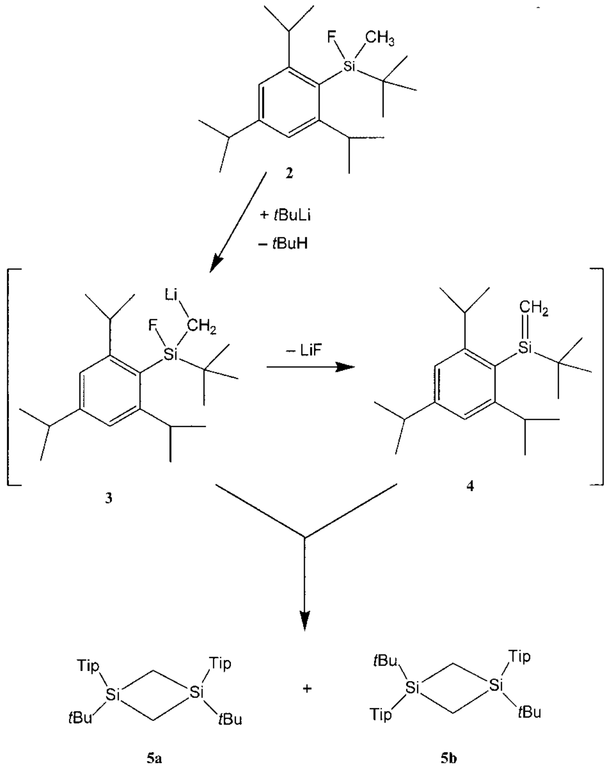
Figure 1. Molecular structure of **2** in the solid state.

Table 1. Selected bond lengths [Å] and angles [°] for **2**.

Si(1)–F(1)	1.625(2)	F(1)–Si(1)–C(20)	101.17(14)
Si(1)–C(20)	1.866(4)	F(1)–Si(1)–C(16)	106.18(14)
Si(1)–C(16)	1.883(3)	F(1)–Si(1)–C(1)	107.42(12)
Si(1)–C(1)	1.892(4)	C(20)–Si(1)–C(16)	111.27(16)
C(16)–Si(1)–C(1)	114.09(15)	C(20)–Si(1)–C(1)	115.36(16)

2,4,6-triisopropylphenyl group in **2** are, at 1.883(3) and 1.892(4) Å, respectively, longer than in **1**, while the bond to the methyl carbon atom is slightly shorter [1.866(4) Å]. Surprisingly, the bond between Si(1) and the aryl carbon atom C(1) is longer than the corresponding Si–C_{alkyl} distances of the molecule. The steric repulsion of the substituents at silicon is also obvious from the angles between the groups adjacent to this atom. Hence, the C–Si–C angles are, at 111.27(16)°, 114.09(15)°, and 115.36(16)°, larger than the corresponding F–Si–C angles [101.17(14)°, 106.18(14)°, and 107.42(12)°].

The sterically congested situation in **2** combined with the absence of activated C–H bonds other than in the methyl group makes this fluorosilane an ideal starting material for the generation of a Li–F silenoid without further substituents on carbon. To achieve metalation of the methyl group, we treated **2** with *tert*-butyllithium at low temperature (–100 °C). No reaction could be detected in apolar solvents such as pentane, even when the mixture was warmed to room temperature. In contrast, the onset of a reaction can be observed by the formation of a precipitate along with a color change on addition of stoichiometric amounts of coordinating reagents such as TMEDA or THF, even at –100 °C. After warming to room temperature, the corresponding 1,3-disilacyclobutane (**5**) was obtained as the final product (Scheme 2).



Scheme 2. Metalation of **2** and formation of **5** (Tip = 2,4,6-triisopropylphenyl).

In the ^{29}Si NMR spectrum **5** shows a resonance for each of the two isomers [*cis* (**5a**)/*trans* (**5b**)] which appear very close to each other at $\delta = 9.2$ and 9.3 ppm. The ratio of the isomers is approximately 1:1, which in related cases has been found to be indicative of the formation of the 1,3-disilacyclobutane from intermediate silenes rather than silenoids.[12,13] Upon recrystallization we were able to obtain crystalline samples of the *cis*-isomer of **5** that were suitable for analytical purposes and X-ray diffraction.

The molecular structure of **5** proves the presence of a central 1,3-disilacyclobutane system, where the ring carbon atoms are unsubstituted while the silicon atoms carry sterically demanding 2,4,6-triisopropylphenyl and *tert*-butyl groups (Figure 2). The internal angles of the 1,3-disilacyclobutane ring are all approximately 90°, with smaller values found at the silicon atoms [88.31(10)°, 88.37(10)°, 90.86(10)°, and 91.28(11)°] (Table 2).

The ring-puckering angle [11.79(11)°], which is defined by the dihedral angle of the two Si–Si–C planes of the ring, falls well within the range of such angles in other structurally characterized 1,3-disilacyclobutanes (0–25.5°).[14–17] As a consequence of the steric repulsion of the substituents at the silicon atoms, the Si–C distances within the ring [1.901(2)–1.909(2) Å] are the longest observed so far for 1,3-disilacyclobutanes without substituents at the ring carbon atoms. According to previous studies long Si–C bond lengths in the ring correspond to reduced puckering angles.[18] The steric pressure at the silicon atoms is also obvious from the exocyclic Si–C distances, which are significantly longer than standard Si–C bond lengths.[19] Therefore, as expected, the Si–C_{aryl} distances [1.907(2) and 1.909(2) Å] are slightly shorter than the Si–C_{alkyl} distances [1.932(3) and 1.933(3) Å]. The solution NMR spectra corroborate the steric pressure within **5** derived from the static picture of the crystal structure. Hence, in the ^{13}C NMR spectra the CH_3 units of the isopropyl groups in the *ortho* position of the Tip substituent are not equivalent at room temperature. Obviously, the rotation by which they would become equivalent is prevented by the proximity of the *tert*-butyl group. As a consequence of the puckered structure of the disilacyclobutane ring, the dihedral angles between the methylene carbon atoms and the transannular methylene hydrogen atoms differ significantly [C(1)–Si(1)–C(2)–H(21) = 124.6°; C(1)–Si(1)–C(2)–H(22) = –108.1°]. Therefore, in the proton-coupled ^{13}C NMR spectra the coupling of only one of these protons with the carbon atom is observed ($^{3}J_{C,H}$ = 4.9 Hz) apart from the coupling with the directly bonded chemically inequivalent methylene protons ($^{1}J_{C,Ha}$ = 117.9, $^{1}J_{C,Hb}$ = 121.7 Hz).

Although we were unable to directly observe any of the intermediates discussed in the formation of **5**, this process is likely to proceed by the initial formation of silenoid **3**, which could either dimerize to yield **5** directly, or eliminate LiF to form silene **4** which, on dimerization, would yield the same product (**5**). As is known from the literature, the ratio of the *cis*/*trans* isomers of the resulting 1,3-disilacyclobutane can be used as an indicator of which of the above mechanisms is dominant.[12,13] According to these findings, the 1:1 ratio of the isomers found in our experiments should be indicative of the formation of **5** from transient silene **4**. In contrast, the occurrence of a precipitate, along with the color change observed on addition of stoichiometric amounts of THF at low temperature, could be interpreted as a hint for the formation of silenoid **3**. The identity of this precipitate was elucidated with a trapping experiment with a reactive chlorophosphane. On addition of the latter at low temperature the precipitate disappears. However, in the ^{31}P NMR spectra the resonance of the resulting product indicates that the initially formed precipitate is not silenoid **3** but rather an etherate of butyllithium.[20]

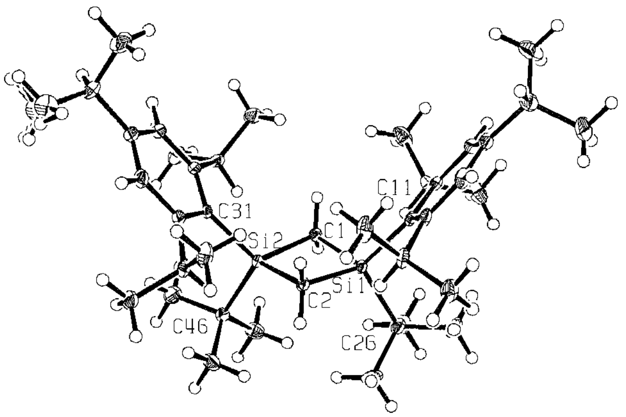


Figure 2. Molecular structure of **5a** in the solid state.

Conclusions

Compound **2** is a sterically hindered fluorosilane that can be metalated selectively in the α-position despite of the absence of activating groups. The resulting Li–F silenoid carries no further substituents at the carbon end of the metalated unit and spontaneously eliminates LiF below room temperature. Due to insufficient steric protection, transient silenoid **3** or silene **4** dimerize to the corresponding 1,3-disilacyclobutane. The ratio of the *cis* and *trans* isomers indicates formation from the silene rather than from the silenoid, although no direct evidence for the silene could be found. The sterically highly congested silenoid precursor **2** and the final product **5** have been fully characterized and their crystal structures determined. From their geometric parameters, as well as from spectroscopic data, the steric hindrance within both molecules is evident. However, to accomplish the stabilization of a C-unsubstituted silene a further increase of the steric congestion at the silicon end of the unsaturated unit will be necessary.

Experimental Section

All chemical experiments were performed under argon using standard Schlenk techniques or a glovebox. Solvents other than $CDCl_3$ were dried with sodium/potassium alloy and stored under argon.

Table 2. Selected bond lengths [Å] and angles [°] for the central Si_2C_2 ring of **5a**.

Si(1)–C(2)	1.903(2)	Si(2)–C(1)	1.909(2)
Si(1)–C(1)	1.909(2)	Si(2)–C(2)	1.901(2)
Si(1)–C(11)	1.909(3)	Si(2)–C(31)	1.907(2)
Si(1)–C(26)	1.933(3)	Si(2)–C(46)	1.932(3)
C(2)–Si(1)–C(1)	88.31(10)	C(2)–Si(2)–C(31)	112.99(11)
C(2)–Si(1)–C(11)	115.51(11)	C(2)–Si(2)–C(1)	88.37(10)
C(1)–Si(1)–C(11)	113.11(11)	C(31)–Si(2)–C(1)	116.95(11)
C(2)–Si(1)–C(26)	113.37(11)	C(2)–Si(2)–C(46)	115.41(11)
C(1)–Si(1)–C(26)	117.28(11)	C(31)–Si(2)–C(46)	108.63(10)
C(11)–Si(1)–C(26)	108.41(11)	C(1)–Si(2)–C(46)	113.58(11)
Si(1)–C(1)–Si(2)	90.86(10)	Si(2)–C(2)–Si(1)	91.28(11)
Si(1)–C(1)–Si(2)–C(2)	8.22(11)	C(2)–Si(1)–C(26)–C(28)	4.0(2)
C(2)–Si(1)–C(11)–C(12)	35.6(2)	C(1)–Si(2)–C(46)–C(48)	11.0(2)
C(1)–Si(2)–C(31)–C(32)	37.9(2)	Si(1)···Si(2)	2.270(2)

^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded on Bruker AMX 360 or Bruker Avance DRX 500 instrument. Mass spectra were measured on a Masslab VG 12-250 by the electron impact ionization technique. Melting points were determined on a Mettler FP 61 in glass capillaries. *tert*-Butyldifluoro(2,4,6-triisopropylphenyl) silane [tBu(2,4,6-iPrC$_6$H$_2$)SiF$_2$] was prepared according to literature procedures.[9,10] Other chemicals were obtained from different chemical suppliers and used as received.

Synthesis of *tert*-Butylfluoro(methyl)(2,4,6-triisopropylphenyl)silane (2): A solution of MeLi (1.6 M in diethyl ether; 8.8 mL, 14 mmol) was added, at –100 °C, to a solution of tBu(2,4,6-iPrC$_6$H$_2$)SiF$_2$ (4.17 g, 12.8 mmol) in diethyl ether (40 mL), while stirring. The mixture was warmed to room temperature; the precipitate that formed at –80 °C redissolved at higher temperatures. Stirring was continued for 16 h, after which the solvent was removed in vacuo. The residue was extracted with hexanes (2 × 30 mL) and the insoluble precipitate (LiF) was separated by filtration. The filtrate was recovered and removal of the solvent in vacuo and recrystallization from chloroform yielded **2** as colorless, deliquescent crystals (4.09 g, 98.9 %); m.p. 49.4 °C. ^{1}H NMR (CDCl$_3$, 360 MHz, 25 °C): δ = 7.08 (s, 2 H), 3.23 (sept, $^{3}J_{H,H}$ = 6.6 Hz, 1 H), 2.90 (sept, $^{3}J_{H,H}$ = 7.0 Hz, 2 H), 1.29 (d, $^{3}J_{H,H}$ = 7.0 Hz, 12 H), 1.26 (d, $^{3}J_{H,H}$ = 6.6 Hz, 6 H), 1.08 (s, 9 H), 0.57 (d, $^{3}J_{H,F}$ = 10.3 Hz, 3 H) ppm. ^{13}C NMR (CDCl$_3$, 91 MHz, 25 °C): δ = 156.58 (s), 150.54 (s), 127.04 (d, $^{2}J_{C,F}$ = 11.1 Hz), 121.70 (s), 34.12 (s), 33.84 (s), 26.63 (s), 25.61 (s), 23.74 (s), 20.12 (d, $^{2}J_{C,F}$ = 12.5 Hz), 0.16 (d, $^{2}J_{C,F}$ = 18.7 Hz) ppm. ^{19}F NMR (CDCl$_3$, 471 MHz, 25 °C): δ = –160.5 (q, $^{3}J_{F,H}$ = 9.9 Hz) ppm. ^{29}Si NMR (CDCl$_3$, 72 MHz, 25 °C): δ = 25.0 (d, $^{1}J_{Si,F}$ = 287 Hz) ppm. MS: m/z (%) = 322.2494 (high resolution: Δ = 0.89 ppm) (8) [M$^+$], 265.1 (100) [M$^+$ – tBu], 245.1 (12) [M$^+$ – tBu– HF], 187.1 (10), 77.0 (19). C$_{20}$H$_{35}$FSi (322.58): calcd. C 74.47, H 10.94; found C 74.41, H 11.25.

Synthesis of *cis*/*trans*-1,3-Di-*tert*-butyl-1,3-bis(2,4,6-triisopropylphenyl)-1,3-disilacyclobutane (5): A solution of **2** (0.85 g, 2.6 mmol) in pentane (10 mL) was cooled to –100 °C and 1.7 mL (2.9 mmol) of a solution of tBuLi (1.7 M in pentane) was added while stirring. Upon addition of THF (0.74 mL, 9 mmol) the mixture turned yellow and a precipitate was observed. The temperature was maintained for 2 h and the mixture was then slowly warmed to room temperature. Stirring was continued for 12 h, after which the solution was concentrated under reduced pressure to obtain a sample suitable for the recording of ^{29}Si NMR spectra [^{29}Si NMR (THF/CDCl$_3$, 72 MHz, 25 °C): δ = 9.3, 9.2 ppm]. After complete removal of the solvent in vacuo, the residue was extracted with hexanes (2 × 30 mL) and the insoluble precipitate (LiF) was separated by filtration. The filtrate was recovered and removal of the solvent in vacuo and recrystallization from acetone yielded *cis*-**5** as colorless crystals (0.7 g, 44.0 %); m.p. 243 °C (dec.). ^{1}H NMR (CDCl$_3$, 360 MHz, 25 °C): δ = 6.94 (s, 4 H), 3.26 (sept, $^{3}J_{H,H}$ = 7.0 Hz, 4 H), 2.84 (sept, $^{3}J_{H,H}$ = 7.0 Hz, 2 H), 1.25 (d, $^{3}J_{H,H}$ = 7.0 Hz, 24 H), 1.19 (d, $^{3}J_{H,H}$ = 7.0 Hz, 12 H), 1.15 (s, 18 H), 0.44 (s, 4 H) ppm. ^{13}C NMR (CDCl$_3$, 91 MHz, 25 °C): δ = 154.75, 149.18, 133.82 ($^{1}J_{C,Si}$ = 45.8 Hz), 121.57, 34.00, 33.79, 30.59, 25.84, 25.45, 23.75, 17.94 ($^{1}J_{C,Si}$ = 32.6 Hz), 8.12 ($^{1}J_{C,Si}$ = 36.8 Hz) ppm. ^{29}Si NMR (CDCl$_3$, 72 MHz, 25 °C): δ = 9.3 ppm. MS: m/z (%) = 604.5 (3) [M$^+$], 547.5 (100) [M$^+$ – tBu], 302, (25) [M$^+$/2], 245.1 (15) [M$^+$/2 – tBu], 57.1 (8) [tBu$^+$]. C$_{40}$H$_{68}$Si$_2$ (605.14): calcd. C 79.39, H 11.33; found C 78.85, H 11.70.

Trapping Experiments: The procedure for the synthesis of **5** was followed to the point where a precipitate occurred on addition of the lithiating reagent. After addition of chlorobis(diethylamino)phosphane as trapping reagent, at –70 °C, we observed no conversion of the starting fluorosilane **2** in the NMR spectra. The trapping reagent, in contrast, was completely converted into *tert*-butylbis(diethylamino)phosphane under these conditions, as is evident from its ^{31}P NMR chemical shift.

Crystallographic Details for 2: A colorless crystal of **2** with dimensions 0.1 × 0.2 × 0.1 mm^3 was coated in paraffin oil, mounted on a glass fiber, and placed under a cold stream of nitrogen. All the measurements were performed using graphite-monochromated Mo-K_α radiation at 213 K. A total of 3201 reflections were collected (θ_{max} = 23°), of which 2238 were unique (R_{int} = 0.0162). Additional experimental details are given in Table 3. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[21,22] The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. For 199 parameters final R indices of R = 0.0539 and $wR2$ = 0.1553 (GOF = 1.102) were obtained.

Table 3. Crystal data and structure refinement for **2** and **5a**.

	2	**5a**
Formula	C$_{20}$H$_{35}$FSi	C$_{40}$H$_{68}$Si$_2$
Formula mass	322.58	605.12
Temperature [K]	213	100
Wavelength	0.71073	0.71069
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a [Å]	9.495(5)	9.771(3)
b [Å]	9.933(5)	18.957(4)
c [Å]	11.976(6)	21.025(4)
α [°]	68.236(15)	90
β [°]	86.175(13)	94.64 (2)
γ [°]	83.452(18)	90
V [Å^3]	1041.8(9)	3882.2(16)
Z	3	4
Density (calcd.) [Mg m^{-3}]	1.028	1.035
μ [mm^{-1}]	0.118	0.116
θ Range for data collection [°]	1.83–22.47	2.61–26.00
Goodness-of-fit on F^2	1.102	1.042
$R1$ (obsd. data)	0.0539	0.0600
wR_2 (all data)	0.1553	0.1401

Crystallographic Details for 5a: A colorless crystal of **5a** with dimensions 0.15 × 0.10 × 0.10 mm^3 was coated in paraffin oil, mounted on a glass fiber, and placed under a cold stream of nitrogen. All the measurements were performed with graphite-monochromated Mo-K_α radiation at 100 K. A total of 8923 reflections were collected (θ_{max} = 26.0°), of which 7606 were unique (R_{int} = 0.0472), with 5689 having $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[21,22] One methyl group was disordered over two positions (C41 and C51). The atoms C41 and C51 have site occupation factors of 0.454(18) and 0.546(18), respectively, and were isotropically refined with the constraint of equal bond lengths to C40. All other non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH$_2$ groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99 Å. The C atoms of the phenyl rings were refined without any constraints. The H atoms were put at the external bisector of the C–C–C angle at a C–H distance of 0.95 Å and common isotropic displacement parameters were used for the H atoms of the same phenyl group. The H atoms of the tertiary C–H groups were refined with all X–C–H angles equal at a C–H distance of 1.00 Å and with common isotropic displacement parameters for the H atoms of the tertiary C–H groups bonded to the same phenyl ring. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with tetrahedral angles, enabling rotation around the X–C bond, and C–H distances of 0.98 Å. For 419 parameters final R indices of $R = 0.0600$ and $wR_2 = 0.1401$ (GOF = 1.042) were obtained. The largest peak in the difference Fourier map was 0.479 e Å^{-3}. CCDC-254269 (for **2**) and -254270 (for **5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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