

Synthesis and reactivity of a novel oligosilyl anion

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Abstract

A highly efficient route for the preparation of the sterically overcrowded oligosilyl anion TBTS–Li(THF)₄ (**3**) {TBTS = Si[Si(SiMe₃)₂Me]₃} in a large scale is reported. The reactions of HSiCl₃ and SiCl₄ with **3** do not give coupling products, instead they produce TBTS–H and TBTS–Cl, probably as a result of steric interactions. On the contrary, PhSiF₃ and SiF₄ can be reacted with **3** to give TBTS–SiF₃ (**5**) and TBTS–SiF₂Ph (**6**), respectively, in excellent yields. The X-ray analysis revealed **6** to be a sterically overcrowded molecule, in which the SiF₂Ph group is strongly shielded by the TBTS substituent. Despite the extensive space demand of the TBTS group, **5** and **6** can be transformed into TBTS–SiH₃ (**7**) and TBTS–SiH₂Ph (**8**) by treatment with LiAlH₄. The controlled hydrolysis of **5** leads to the selective formation of TBTS–SiF₂OH (**9**), the first isolated difluorosilanol, which is stable towards condensation.

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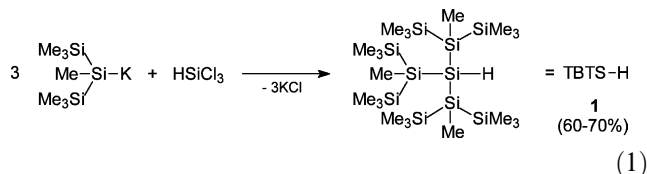
Keywords: Silicon; Silanes; Fluorosilanes; Silyl anions

1. Introduction

In recent years, the chemistry of silyl anions [1] has attracted great interest not only from the structural point of view, but also due to the fact that these highly reactive reagents could be used as anionic ligands for the kinetic stabilization of low-valent intermediates [2]. For example, the large steric requirements and the electron releasing properties of the (Me₃Si)₃Si group cause alkaline metal compounds containing the (Me₃Si)₃Si substituent [3] to be useful precursors in the chemistry of main group [4] and transition metals [5]. However, even considering all the advantages of this substituent, the possibility of steric and electronic control is highly desirable [6].

Recently, we reported the X-ray structures of several oligosilanes of the general formula [Me(Me₃Si)₂Si]₃Si–X

(X = F, Cl, Br, OH, H) [7] of which the oligosilyl group is called TBTS [8]. The key step in the synthesis of such derivatives was the reaction of 3 equiv. of Me(Me₃Si)₂Si–K with HSiCl₃, which gave the desired hydridosilane TBTS–H (**1**) in good yields (Eq. (1)).



Structurally, the TBTS substituent can be described as a ligand in which three Me(Me₃Si)₂Si groups and the central silicon atom form an extended hemispherical shield providing a center with exceptional steric protection. The extraordinary spatial demand of this ligand compared to that of the (Me₃Si)₃Si substituent probably makes the TBTS group attractive for conversions into reactive species such as silyl anions, cations or radicals [9]. In this context, we report the synthesis of the novel sterically overcrowded silyl anion TBTS–Li, and we

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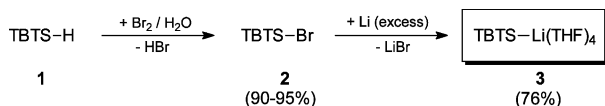
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describe its reaction behaviour towards several chloro- and fluorosilanes.

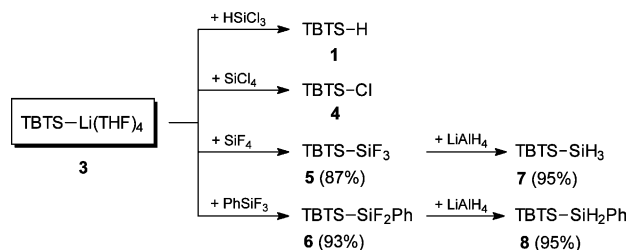
2. Results and discussion

A suitable entry into the chemistry of silicon–metal derivatives is the use of organosilicon compounds possessing good leaving groups such as bromine or chlorine which can easily be exchanged by elemental lithium. Unfortunately, attempts to synthesize the precursor compound TBTS–Br (**2**) on a large scale by the reaction of TBTS–H (**1**) with excess of tribromomethane failed and only small amounts of TBTS–Br (**2**) were obtained. Also, the reaction with elemental bromine in CCl_4 led mainly to decomposition products. Surprisingly, at low temperatures and in the presence of water as an HBr acceptor TBTS–Br (**2**) could be isolated in nearly quantitative yields (Scheme 1). The reaction behaviour of **2** is relatively unusual insofar as sterically less encumbered bromosilanes [10] rapidly hydrolyse to silanols or siloxanes. However, under the condition applied, only traces of substitution products were observed, probably due to the remarkably steric protection of the bromine by the TBTS group.

Finally, treatment of **2** with an excess of lithium in THF at 0°C leads to the formation of TBTS–Li (**3**) which can be isolated by crystallization from hot pentane in a yield of 76%. Compound **3** is soluble in common organic solvents (heptane, pentane, THF and ether) and forms reddish-orange crystals, which are stable for months under an atmosphere of argon. Although attempts to obtain single crystals of **3** suitable for an X-ray structure analysis failed, the structure proposed was in full agreement with the NMR data indicating that TBTS–Li (**3**) contains four molecules of THF. The ^{29}Si -NMR spectrum of **3** is straightforward and shows only three signals for the silicon atoms. The observed value of -170 ppm for the anionic silicon atom in **3** is slightly shifted to lower field in comparison to those in $(\text{Me}_3\text{SiMe}_2\text{Si})_3\text{Si-Li(THF)}_3$ with -177 ppm and in $(\text{Me}_3\text{Si})_3\text{Si-Li(THF)}_3$ with -189 ppm [6b,6c]. This order in the chemical shift is in agreement with the observation that additional replacement of methyl groups by trimethylsilyl groups in the β -position in compounds of the general formula $\text{Me}_n(\text{Me}_3\text{Si})_{3-n}\text{Si-X}$ ($n = 1$ and 2) typically leads to a low field shift of the signal for the central silicon nucleus [11]. This effect of β -substitution in oligosilyl anions can be attributed



Scheme 1. Synthesis of TBTS–Li(THF)₄ (**3**).



Scheme 2. Reaction behaviour of TBTS–Li(THF)₄ (**3**).

mainly to a distribution of the anionic charge along the oligosilane backbone by charge polarization [6b,6c].

In order to check the synthetic potential of TBTS–Li(THF)₄, we have investigated silylation reactions using easily available electrophilic silicon compounds (Scheme 2). But in view of the extreme bulkiness of **3** the fixation of one TBTS group at a silicon atom by salt elimination reaction appears to be difficult. Thus, we obtained no coupling products after treatment of **3** with SiCl_4 or HSiCl_3 . On the contrary, mainly metal–halogen exchange yielding TBTS–Cl (**4**) and deprotonation by the strong base **3** giving TBTS–H (**1**) could be observed. Even the reaction of less acidic hydrosilanes such as MeSiHCl_2 , Me_2SiHCl , PhSiHCl_2 , PhSiH_2Cl with **3** at -78°C yields only mixtures of **1** and the desired coupling products [12]. However, when SiF_4 and PhSiF_3 were allowed to react with TBTS–Li (**3**), the respective fluorosilanes TBTS– SiF_3 (**5**) and TBTS– SiF_2Ph (**6**) could be isolated in nearly quantitative yields. The colourless crystalline compounds **5** and **6** are stable towards air and moisture, and the structures proposed

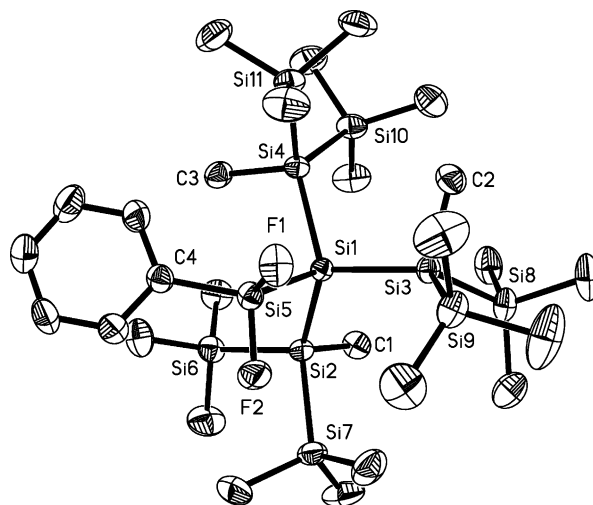


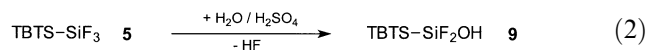
Fig. 1. Molecular structure of TBTS– SiF_2Ph (**6**) in the crystal (ORTEP, 30% probability level, H-atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): F1–Si5, 1.595(2); F2–Si5, 1.596(2); Si1–Si(5), 2.3535(13); Si1–Si2, 2.4000(13); Si1–Si4, 2.4099(13); Si1–Si3, 2.4143(13); Si5–C4, 1.859(4); Si5–Si1–Si2, 101.85(5); Si5–Si1–Si4, 108.64(5); Si2–Si1–Si4, 114.98(5); Si5–Si1–Si3, 104.03(5); Si2–Si1–Si3, 116.09(5); Si4–Si1–Si3, 110.06(5); C4–Si5–Si1, 123.21(12); F1–Si5–F2, 103.27(15).

were in full agreement with the elemental analysis and the NMR data (see Section 4).

In addition, the molecular structure of **6** (Fig. 1) has been confirmed by X-ray diffraction data, which verify an approximately spherical shape with the silicon atom Si1 at the center of the sphere. The geometry around the central silicon atom Si1 is described best as distorted tetrahedral, with a Si2–Si1–Si3 angle of 116.09° and a Si5–Si1–Si2 angle of 101.85°. Furthermore, the results confirm the expected extensive shielding of the SiF₂Ph group by the hemispherical TBTS substituent, which forces a remarkable widening of the C4–Si5–Si1 angle (123.21°) of the PhF₂Si–Si tetrahedron. In contrast to the Si1–Si5 bond (2.3535(13) Å) which is somewhat shortened, probably due to the electronegative fluorine substituents, most of the Si–Si bonds are elongated within the range 2.37–2.41 Å, as expected.

Despite the extensive shielding of the fluorosilyl functions by the TBTS group, both compounds **5** and **6** are proven to be reactive towards nucleophilic attack. Thus, simple treatment with an excess of LiAlH₄ in ether at room temperature led to a full exchange of the fluorine atoms by hydrogen under formation of the corresponding hydridosilanes **7** and **8**, respectively, in excellent yields (Scheme 2).

Furthermore, we have investigated the hydrolytic stability of TBTS–SiF₃. Surprisingly, the hydrolysis of **5** in a two-phase mixture of ether and 10% sulfuric acid at room temperature leads to the formation of TBTS–SiF₂OH (**9**) in almost quantitative yields after 10 days (Eq. (2)). The incomplete exchange of fluorine is unusual insofar as sterically less congested trifluorosilanes commonly hydrolyse to silanetriols or siloxanes. However, neither the formation of condensation products nor of the corresponding silanediols or silanetriols were observed even under hydrolytic conditions with extended reaction times.



Although we were not able to obtain single crystals of **9** suitable for X-ray diffraction studies, the structure proposed was unambiguously evidenced by means of elemental analysis, IR and NMR spectroscopic data. As expected, the ¹H, ¹³C and ²⁹Si resonances of the TBTS group are in the typical range. Additionally, the ¹⁹F-NMR spectrum shows a fluorine resonance at –98 ppm and in the ²⁹Si-NMR spectrum a triplet signal characteristic of a SiF₂ group was observed at –37 ppm (¹J_{Si-F} = 370.1 Hz). Finally, in the IR spectrum of **9** a stretching mode for the free hydroxy group was found to appear at 3649 cm^{–1} clearly indicating the presence of a SiF₂OH group in the molecule. To the best of our knowledge, compound **9** is the first isolated and stable example of a difluorosilanol which shows neither tendency to undergo condensation reaction nor further

nucleophilic substitution of the remaining fluorine by hydroxy groups.

3. Conclusion

We have described an efficient high yielding route for the large-scale synthesis of TBTS–Li (**3**), a novel sterically overcrowded oligosilyl anion. The reaction behaviour of **3** towards electrophilic silicon compounds strongly depends on the size and nature of the leaving group. Thus, **3** could be reacted very easily with PhSiF₃ and SiF₄ to give the coupling products TBTS–SiF₃ (**5**) and TBTS–SiF₂Ph (**6**) selectively. In contrast, treatment with simple chlorosilanes such as HSiCl₃ and SiCl₄ did not give the desired coupling products, instead TBTS–H and TBTS–Cl were obtained. These differences in reactivity can be attributed to the fact that chlorine which is significantly larger than fluorine hampers the nucleophilic attack of TBTS–Li at the electrophilic silicon due to steric reasons. Consequently, only deprotonation and metal–halogen exchange reactions were observed.

Although the X-ray analysis proved **6** to be a sterically overcrowded molecule, in which the SiF₂Ph group is strongly shielded by the TBTS substituent, compounds **5** and **6** are reactive compounds. Thus, simple treatment with LiAlH₄ led to a full exchange of fluorine by hydrogen in **5** and **6**. Finally, the reaction of **5** with water yields the first incompletely hydrolyzed stable silanol TBTS–SiF₂OH (**9**). The fluorosilanes TBTS–SiF₃ (**5**) and TBTS–SiF₂OH (**9**) might be very attractive as precursors for low-valent silicon species [13]. Further investigations concerning the synthesis, isolation and structurally characterization of such species are in progress.

4. Experimental

4.1. General procedures and materials

All reactions involving organometallic reagents were carried out under an atmosphere of argon using standard Schlenk techniques. TBTS–H (**1**) was prepared as previously described [7]. NMR: Bruker AC 250, Bruker ARX 300, Bruker ARX 400 (250, 62.9, 79.5 and 235.3 MHz for ¹H, ¹³C, ²⁹Si and ¹⁹F, respectively). For ¹H-, ¹³C- and ²⁹Si-NMR, [D₆]benzene as solvent and TMS as internal standard; for ¹⁹F-NMR, [D₆]benzene as solvent and CFC₃ as internal standard. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas.

4.2. TBTS–Br (2)

To an ice-cooled and vigorously stirred suspension of 65.05 g TBTS–H (1) (108.9 mmol), 200 ml CCl₄ and 200 ml water, a solution of 6 ml bromine (117.1 mmol) in 350 ml CCl₄ was added dropwise over a period of 5–6 h. After stirring the suspension for 1 h at room temperature, the organic phase was separated, dried with MgSO₄ and evaporated. The solid residue was suspended in acetonitrile, filtered off and dried under vacuum to give 69.98 g of 2 (95%). The spectroscopic data obtained were in full agreement with those reported [7].

4.3. TBTS–Li(THF)₄ (3)

A suspension of 1.5 g (220 mmol) lithium, 15.14 g (22.4 mmol) 2 and ca. 50 ml THF was stirred at 0 °C for 3 h. After removal of the solvent, the residue was extracted with hot pentane and the combined extracts were slowly cooled to –40 °C. Reddish-orange crystals of 3 started to precipitate. 11.6 g of 3 could be isolated by filtration, washing with cold pentane, and drying under vacuum. Crystallization from the mother liqueur gave another 3.57 g of 3. Yield: 15.17 g (76%). ¹H-NMR: δ = 3.49 (t, THF, ³J = 6.3 Hz, 16H), 1.36 (t, THF, ³J = 6.3 Hz, 16H), 0.60 (s, SiMe, 9H), 0.45 (s, SiMe₃, 54H) ppm. ¹³C-NMR: δ = 68.2 (THF), 25.5 (THF), 2.3 (SiMe₃), –1.6 (SiMe₃) ppm. ²⁹Si-NMR: δ = –12.3 (SiMe₃), –75.6 (SiMe), –170.2 (SiLi) ppm.

4.4. Silylation of TBTS–Li(THF)₄ (3)

4.4.1. General procedure

To a suspension of 3 in pentane, the appropriate silane was added at –78 °C. Stirring was continued for 1 h, and the mixture was allowed to warm up to room temperature within 2 h. After filtration and removal of the solvent under reduced pressure, the solid residue was purified as described below.

4.4.2. TBTS–SiF₃ (5)

Excess of gaseous SiF₄ and 5.11 g of 3 were used. The residue was suspended with cold acetone, filtered off and dried under vacuum. Yield: 3.25 g (87%); m.p.: 101 °C. ¹H-NMR: δ = 0.47 (s, SiMe, 9H), 0.33 (s, SiMe₃, 54H) ppm. ¹³C-NMR: δ = –4.4 (SiMe), 1.6 (SiMe₃) ppm. ²⁹Si-NMR: δ = –9.7 (SiMe₃), –75.4 (SiMe), –44.5 (q, ¹J_{Si–F} = 389.5 Hz, SiF₃), –135.2 (SiSi₄) ppm. F-NMR: δ = –100.4 (SiF₃) ppm. Anal. Calc. for C₂₁H₆₃F₃Si₁₁ (680.23): C, 37.00; H, 9.32. Found: C, 36.65; H, 9.04%.

4.4.3. TBTS–SiF₂Ph (6)

1.29 g (7.95 mmol) PhSiF₃ and 7.03 g of 3 were used. Purification was achieved by crystallization from ace-

tone. Yield: 5.41 g (93%); m.p.: 205 °C. ¹H-NMR: δ = 7.83–7.79, 7.16–7.13 (2m, phenyl, 5H), 0.54 (s, SiMe, 9H), 0.34 (s, SiMe₃, 54H) ppm. ¹³C-NMR: δ = 136.0 (t, ²J_{C–F} = 14.3 Hz, C-*ipso*) 134.4 (t, ³J_{C–F} = 2.9 Hz, CH-*ortho*), 131.7, 128.3 (CH), –3.4 (SiMe), 2.2 (SiMe₃) ppm. ²⁹Si-NMR: δ = –9.5 (SiMe₃), –74.6 (SiMe), 5.3 (t, ¹J_{Si–F} = 357.7 Hz, SiF₂), –119.0 (SiSi₄) ppm. ¹⁹F-NMR: δ = –111.6 (SiF₂) ppm. Anal. Calc. for C₂₇H₆₈F₂Si₁₁ (738.28): C, 43.84; H, 9.27. Found: C, 43.41; H, 9.45%.

4.5. TBTS–SiH₃ (7)

A suspension of TBTS–SiF₃ (5) (0.42 g, 0.617 mmol), excess LiAlH₄ (0.2 g) and 20 ml ether was vigorously stirred for 20 h at room temperature. After changing the solvent from ether to pentane, the reaction mixture was filtered and the solvent was removed. Drying under vacuum afforded analytically pure 7 as a white solid. Yield: 0.37 g (95%); m.p.: 111 °C. IR (nujol) $\tilde{\nu}$ = 2140 cm^{–1} (SiH). ¹H-NMR: δ = 3.82 (s, SiH₃, 3H), 0.46 (s, SiMe, 9H), 0.34 (s, SiMe₃, 54H) ppm. ¹³C-NMR: δ = –4.7 (SiMe), 2.2 (SiMe₃) ppm. ²⁹Si-NMR: δ = –9.4 (SiMe₃), –74.0 (SiMe), –85.0 (q, ¹J_{Si–H} = 187.7 Hz, SiH₃), –122.5 (SiSi₄) ppm. Anal. Calc. for C₂₁H₆₆Si₁₁ (627.69): C, 40.18; H, 10.60. Found: C, 39.82; H, 10.51%.

4.6. TBTS–SiH₂Ph (8)

A suspension of TBTS–SiF₂Ph (6) (0.4 g, 0.542 mmol), excess LiAlH₄ (0.2 g) and 20 ml ether was vigorously stirred for 7 days at room temperature. After changing the solvent from ether to pentane, the reaction mixture was filtered and the solvent was removed. Drying in the vacuum afforded analytically pure 8 as a white solid. Yield: 36 g (95%). m.p.: 168 °C. IR (nujol) $\tilde{\nu}$ = 2125 cm^{–1} (SiH). ¹H-NMR: δ = 7.77–7.74, 7.18–7.14 (2 m, phenyl, 5H), 4.95 (s, SiH₂, 2H), 0.51 (s, SiMe, 9H), 0.33 (s, SiMe₃, 54H) ppm. ¹³C-NMR: δ = 137.3 (C-*ipso*), 133.8, 129.6, 128.2 (C-aromatic), –3.7 (SiMe), 2.5 (SiMe₃) ppm. ²⁹Si-NMR: δ = –9.1 (SiMe₃), –73.1 (SiMe), –45.2 (t, ¹J_{Si–H} = 186.2 Hz, SiH₂), –109.9 (SiSi₄) ppm. Anal. Calc. for C₂₇H₇₀Si₁₁ (703.79): C, 46.08; H, 10.03. Found: C, 45.81; H, 9.98%.

4.7. TBTS–SiF₂OH (9)

To a stirred solution of TBTS–SiF₃ (5) (0.635 g, 0.934 mmol) in 20 ml of ether 20 ml of 0.1 M sulfuric acid were added. The resulting mixture was stirred for 10 days at room temperature. The organic phase was separated, dried with MgSO₄, and evaporated. The remaining white solid can be further purified by crystallization from heptane at –40 °C to give an analytically pure

sample of **9**. Yield: 0.42 g (66%). m.p.: 185 °C. IR (nujol) $\tilde{\nu} = 3649 \text{ cm}^{-1}$ (OH). $^1\text{H-NMR}$: $\delta = 2.24$ (s, OH, 1H), 0.49 (s, SiMe, 9H), 0.36 (s, SiMe₃, 54H) ppm. $^{13}\text{C-NMR}$: $\delta = -4.3$ (SiMe), 1.9 (SiMe₃) ppm. $^{29}\text{Si-NMR}$: $\delta = -9.3$ (SiMe₃), -74.6 (SiMe), -37.4 (t, $^1J_{\text{Si-F}} = 370.1 \text{ Hz}$, SiF₂), -129.8 (SiSi₄) ppm. F-NMR: $\delta = -98.0$ (SiF₂) ppm. Anal. Calc. for C₂₁H₆₄F₂O Si₁₁ (679.67): C, 37.11; H, 9.49. Found: C, 36.88; H, 9.35%.

4.8. Crystal structure determination of **6**

The data collection was performed in routine ω -scan on a Bruker P4 four circle diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a graphite monochromator after checking the crystal quality by a rotational photo and determining a reasonable reduced cell. Further data: crystal size (mm³) 0.68 × 0.44 × 0.4, $T = 293(2) \text{ K}$, C₂₇H₆₈F₂Si₁₁, $M = 739.80$, colourless, part of prism, triclinic, space group (H.-M.) $P\bar{1}$, space group (Hall) $P1$, $a = 10.2190(10) \text{ \AA}$, $b = 12.4260(10) \text{ \AA}$, $c = 19.574(2) \text{ \AA}$, $\alpha = 89.140(10)^\circ$, $\beta = 75.390(10)^\circ$, $\gamma = 74.170(10)^\circ$, $V = 2310.1(4) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.064 \text{ mg m}^{-3}$, $\mu = 0.335 \text{ mm}^{-1}$, $F(0\ 0\ 0) = 804$, data collection range: $2.14 \leq \theta \leq 22.00^\circ$, index range: $-1 \leq h \leq 10$, $-12 \leq k \leq 13$, $-20 \leq l \leq 20$, 6813 reflections collected, 5644 independent reflections [$R_{\text{int}} = 0.0448$], 4573 observed [$I > 2\sigma(I)$], completeness to $\theta = 22.00^\circ$: 99.6%, $R_1 = 0.0451$ (observed), $wR_2 = 0.1154$ (observed), goodness-of-fit on $F^2 = 1.042$, max./min. residual electron density: $+0.253/-0.205 \text{ e \AA}^{-3}$. The weighting scheme was calculated according to $w^{-1} = \sigma^2(F_o^2) + (0.0504P)^2 + 1.2086P$ with $P = (F_o^2 + 2F_c^2)/3$. The structure was solved by direct methods (Bruker SHELXTL) and was refined by the full-matrix least-squares methods on F^2 (SHELXL-97) [14]. All non-hydrogen atoms were refined anisotropically, with the hydrogen atoms introduced into theoretical positions and refined according to the riding model. The Bruker SHELXTL [15] software package was used for the structure representations.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 206862 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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