

Synthesis of 1-cyclopropylmethylsilatrane and 1-cyclopropylmethyl-3,7,10-trimethylsilatrane. Crystal structure of 1-cyclopropylmethylsilatrane

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Received 15 March 1996

Abstract

1-Cyclopropylmethylsilatrane $N(CH_2CH_2O)_3SiCH_2-\triangleleft$ (**2a**) and 1-cyclopropylmethyl-3,7,10-trimethylsilatrane $N(CH_2CHMeO)_3SiCH_2-\triangleleft$ (**2b**) have been prepared in good yields by the reaction of the corresponding 1-allylsilatrane $N(CH_2CHRO)_3SiCH_2CH=CH_2$ (**1**) ($R = H$ (**a**), Me (**b**)) with diazomethane in the presence of $Pd(OAc)_2$ as a catalyst. 1-Cyclopropylmethylsilatrane (**2a**) has also been synthesized from the reaction of cyclopropylmethyltriethoxysilane (**3**) with triethanolamine. Compounds **2a**, **2b** and **3** have been characterized by 1H and ^{13}C NMR spectroscopy and elemental analyses. An X-ray structure determination of **2a** indicates the presence of an $N \rightarrow Si$ bond length of 2.149(4) Å.

Keywords: Silicon; Silatrane; Cyclopropanation; X-ray structure

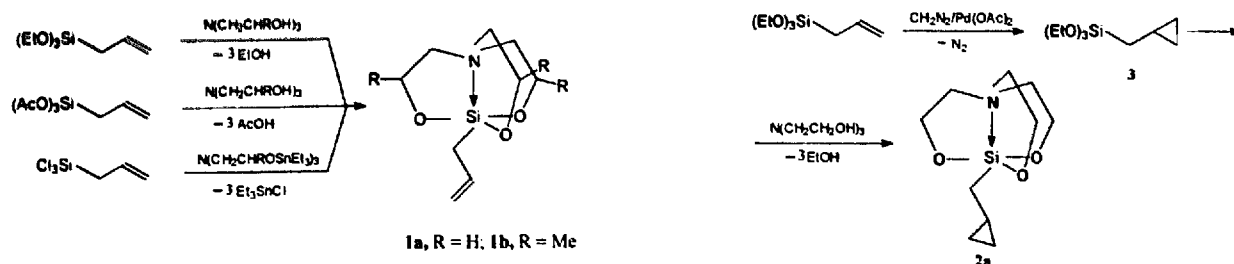
1. Introduction

Silatrane and related compounds have attracted great attention not only from the theoretical point of view as neutral pentacoordinated silicon species where the nature of the Si–N bond is the object of interest [1,2], but also due to the ability of these compounds to demonstrate a marked biological activity [3]. For the construction of functionalized silatrane containing a functionality near to the silicon atom we studied 1-alkenylsilatrane as versatile building blocks. Some useful reactions of these compounds involve participation of the carbon–carbon double bond that occurs with retention of the silatranyl fragment together with the silicon–carbon bond. For 1-vinylsilatrane such known reactions are hydrometalations and radical-initiated additions with species containing S–H, P–H, C–H, C–Br and C–I bonds, oxidation by *m*-CIPBA, or bromohydroxylation by the Br_2/H_2O system [4 and references

cited therein]. An important difference of the reactivity of 1-vinyl- and 1-allylsilatrane in the reaction with nBuLi was pointed out in a recent publication [5]. In 1-vinylsilatrane there was a simultaneous substitution of the Si–O bonds and an addition of nBuLi to the carbon–carbon double bond; a mixture of two products ($^nBuCH_2CH_2Si(OCH_2CH_2)_3N$ and $^nBuCH_2CH_2Si(^nBu)_3$), with a predominance of the tetraorganosilane, was obtained. In the case of 1-allylsilatrane no addition to the double bond took place; only the product of the cleavage reaction of the Si–O bonds, i.e. $CH_2=CHCH_2Si(^nBu)_3$, was isolated.

In our previous work we used the $CH_2N_2/Pd(OAc)_2$ system for the cyclopropanation of 1-vinylsilatrane and 1-vinyl-3,7,10-trimethylsilatrane and obtained the corresponding cyclopropylsilatrane in high yield [4]. In order to examine the reactivity and synthetic potential of 1-alkenylsilatrane we describe in this paper the application of the $CH_2N_2/Pd(OAc)_2$ system for the cyclopropanation of 1-allylsilatrane (**1**) as a convenient route to new functionalized silatrane, 1-cyclopropylmethylsilatrane (**2**), and give a characterization of these com-

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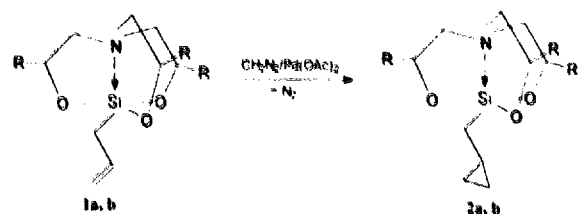
pounds by means of ^1H and ^{13}C NMR spectroscopy and X-ray crystallography for compound **2a**.

2. Results and discussion

1-Allylsilatrane (**1a,b**), the starting materials for cyclopropanation reactions, can be obtained in different ways: 1-allylsilatrane (**1a**) was prepared by published procedures from allyltriethoxysilane in 58% yield [6] and from allyltriacetoxysilane in 90% yield [7]. Allyltriacetoxysilane is the preferred reagent in reaction with trialkanolamines since it reacts under mild conditions without any need for a catalyst, giving compounds **1** in high yield (90–92%). The use of $\text{N}(\text{CH}_2\text{CHMeOSnEt}_3)_3$ and allyltrichlorosilane as starting materials also results in the formation of **1b** in high yield.

Cyclopropanation reactions were carried out in a temperature range from -10 to $+5^\circ\text{C}$, either by adding catalytic amounts of $\text{Pd}(\text{OAc})_2$ to an ethereal solution of a mixture of diazomethane and 1-allylsilatrane (**1**) or by adding an ethereal solution of diazomethane to a mixture of an ethereal solution of 1-allylsilatrane (**1**) and the catalyst. The mixtures were passed through a short column charged with neutral aluminium oxide to remove palladium species and, after evaporation of ether, **2a** was purified by recrystallization from chloroform/*n*-pentane and **2b** by sublimation in vacuo. In the absence of the catalyst, 1-allylsilatrane (**1a**) does not react with diazomethane.

In contrast to 1-allylsilatrane, cyclopropanation reaction of allyltriethoxysilane gives the corresponding cyclopropane **3** in only 15% yield, whereby under non catalytic conditions no reaction takes place.



Analogous reactivities of the carbon–carbon double bond in 1-allylsilatrane, compared with that in allyltriethoxysilane, are observed in reactions with alkanethiols [8]. In contrast to allyltriethoxysilane, vinyltriethoxysilane reacts readily with diazomethane to give the corresponding 1,3-cycloadduct [4].

A transesterification of **3** gave cyclopropylmethylsilatrane (**2a**) in good yield.

The structure of **2a** was confirmed by a single crystal X-ray analysis. The molecular structure of **2a** is shown in Fig. 1, important bond lengths and angles in Table 1. The coordination polyhedron of the silicon atom has a somewhat distorted trigonal bipyramidal geometry, bearing the nitrogen atom and the carbon atom of the cyclopropylmethyl group in the axial and the oxygen atoms in equatorial positions. The "atrane-skeleton" in the crystal is systematically disordered, showing two propeller-like cage structures. The occupation sites of both components are equal: for the carbon atoms of the cyclopropane fragment as well as for C(12) and C(12a)

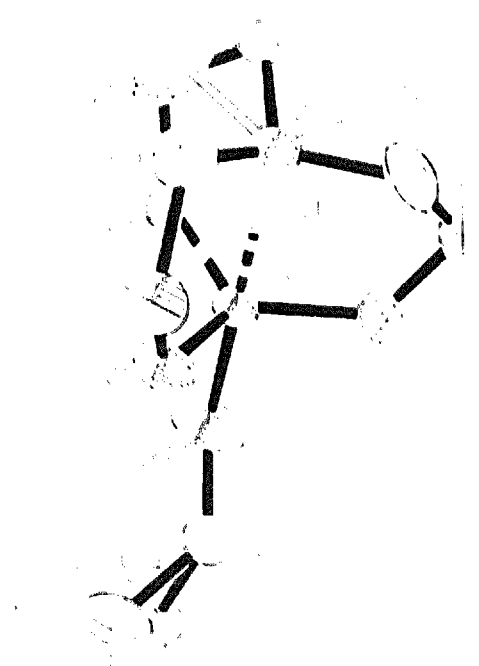


Fig. 1. View of the molecule **2a** with atomic numbering scheme and thermal motion ellipsoids scaled to 50% probability level.

Table 1
Selected bond lengths (Å) and angles (deg) for **2a**

Si(1)–O(2)	1.659(3)	O(2)–Si(1)–O(2a)	118.4(2)
Si(1)–O(2a)	1.659(3)	O(2)–Si(1)–O(1)	118.67(11)
Si(1)–O(1)	1.660(4)	O(2a)–Si(1)–O(1)	118.67(11)
Si(1)–C(1)	1.874(5)	O(2)–Si(1)–C(1)	95.67(13)
Si(1)–N(1)	2.149(4)	O(2a)–Si(1)–C(1)	95.67(13)
C(1)–C(2)	1.317(8)	O(1)–Si(1)–C(1)	99.2(2)
C(2)–C(4)	1.468(11)	O(2)–Si(1)–N(1)	83.18(11)
C(2)–C(3)	1.503(9)	O(2a)–Si(1)–N(1)	83.18(11)
C(3)–C(4)	1.488(10)	O(1)–Si(1)–N(1)	83.1(2)
C(3)–C(4)	1.488(10)	C(1)–Si(1)–N(1)	177.7(2)

they are exactly 50% due to the crystallographic mirror symmetry, while for the atoms C(22) and C(022) the occupancies of 50% could be refined. Unfortunately, this makes a precise assignment of the disordered components to a defined conformation of the molecule impossible. Refinement of the structure in a space group of lower symmetry, i.e. Pna_2 , instead of $Pnma$, provides a possibility of proving the correctness of such a model. In fact, the occupation sites of four, in this space group independent, components are nearly 50%, which indicates the choice of $Pnma$ as the correct space group and favours the assumed structural model.

The sum of the equatorial bond angles O(1)–Si(1)–O(3), O(1)–Si(1)–O(2) and O(2)–Si(1)–O(3) is 356° . The sum of the axial bond angles C(1)–Si(1)–O(1), C(1)–Si(1)–O(2) and C(1)–Si(1)–O(3) adds up to 290.5° . Deviation from an ideal trigonal bipyramidal structure is further demonstrated by the C(1)–Si(1)–N(1) angle of $177.7(2)^\circ$: the silicon atom is displaced by 0.2 Å from the trigonal plane defined by O(1), O(2) and O(3) atoms and is shifted towards the C(1) atom. The Si–N intramolecular distance of 2.149(4) Å can be compared with the longer (2.17 and 2.21 Å) bonds in 1-methyl- and 1-(γ -chloropropyl)silatrane [9] and with the shorter (2.11 and 2.12 Å) bonds in 2-silatranylacetaldehyde [10] and 1-chloromethylsilatrane [9] respectively. As to the structural characteristics of silatrane, the relationship between the Si–C and Si–N distances is a known phenomenon: a longer Si–C bond length (implying a weaker Si–X bonding interaction) generally results in a shorter Si–N distance (suggesting a stronger Si–N bonding interaction). The Si(1)–C(1) distance of 1.874(5) Å in **2a** is similar to the Si–C distance in 1-methyl- and 1-(γ -chloropropyl)silatrane (1.87–1.88 Å) [11] and somewhat shorter than that in 2-silatranylacetaldehyde and 1-chloromethylsilatrane (1.91 Å) [9].

All compounds were characterized completely by ^1H and ^{13}C NMR spectroscopy. The signals of the methylene protons of the silatrane skeleton appear in the ^1H NMR spectra as two markedly broadened triplets at 2.78 (NCH₂) and 3.75 (OCH₂) ppm, forming an AA'BB' spin system ($J_{\text{H-H}} = 5.6\text{--}5.8$ Hz). In the ^{13}C NMR

spectra signals of the carbon atoms of the "atrane-skeleton" appear at 51.0–51.3 (NCH₂) and 57.7–57.95 (OCH₂) ppm. The ^1H NMR spectra of the 3,7,10-trimethylsilatrane are extremely complex due to the asymmetry of the methyl substituted carbon atoms, which results in nonequivalence of the protons of the "atrane-skeleton", and also due to the presence of two diastereomers [12]; in this case the ^{13}C NMR spectra are more informative [13].

3. Experimental section

Solvents were dried by standard methods and distilled prior to use. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. Solution NMR spectra were recorded on Varian VXR-400 and Bruker AC-300 spectrometers at 400.133 and 300.133 MHz, using CDCl₃ as solvent for the internal deuterium lock. Chemical shifts (δ) of the ^1H and ^{13}C NMR resonances are given in parts per million relative to internal TMS. Assignment of the ^{13}C NMR data was supported by APT experiments. Mass spectra (EI-MS) were recorded on a Varian CH-7a device using electron impact with an ionization energy of 70 eV; all assignments were made with respect to the most abundant isotopes. 1-Allylsilatrane (**1a**), m.p. 121–123°C, lit. [6] 122–123°C. ^{13}C NMR (CDCl₃): δ 24.42 (SiCH₂), 51.04 (NCH₂), 57.73 (OCH₂), 110.81 (CH₂=), 138.67 (CH=).

3.1. Synthesis of 1-allyl-3,7,10-trimethylsilatrane, N(CH₂CHMeO)₃SiAlI (**1b**)

(a) A solution of triisopropanolamine (5 g, 26.4 mmol) in 10 ml CHCl₃ was slowly added to a solution of allyltriacetoxysilane (6.5 g, 26.4 mmol) in 10 ml CHCl₃, and cooled to ca. -5°C . The reaction mixture was stirred at 0°C for 1 h. After removal of the solvent in vacuo, acetic acid was removed by azeotropic distillation with 20 ml toluene. The residual oil was purified by sublimation in vacuo to yield 5.9 g (92%) of a pure product (**1b**); colourless crystals, m.p. 60–61°C, lit. [8] 61–62°C. ^1H NMR (CDCl₃): δ 1.35–1.45 (m, 2H, SiCH₂), 4.67–4.87 (m, 2H, CH₂=), 5.92–6.03 (m, 1H, CH=). ^{13}C NMR (CDCl₃): δ 24.45 (major isomer), 24.53 (minor isomer) (SiCH₂); 110.59 (major), 110.38 (minor) (CH₂=); 139.01 (major), 139.31 (minor) (CH=); 20.23, 20.36, 20.55, 23.15 (Me); 58.81, 61.50, 61.65, 63.30, 64.84, 64.91, 65.00, 66.66 (NCH₂, OCH) (two diastereomers). EI-MS, m/z (rel. int., assign.): 216 (100%, M-allyl).

(b) An n-pentane solution of N(CH₂CHMeOSnEt₃)₃ (11.2 g, 13.7 mmol) was slowly added to a solution of

allyltrichlorosilane (2.4 g, 13.7 mmol) in 10 ml pentane. The reaction mixture was stirred for 24 h. A solution of Et_3SnCl in *n*-pentane was separated. The crude oily product was sublimed in vacuo to give 3.4 g (96%) of **1b**.

(c) A mixture of triisopropanolamine (1.3 g, 6.8 mmol) and allyltriethoxysilane (1.4 g, 6.85 mmol) was heated at 80–85°C for 12 h in the presence of a catalytic amount of NaOH. Ethanol, formed during the reaction, was continuously removed by distillation. Sublimation of the residue in vacuo yields 1.1 g (63%) of **1b**.

3.2. Synthesis of cyclopropylmethyltriethoxysilane, $(\text{EtO})_3\text{SiCH}_2\text{-}\nabla$ (**3**)

A solution of diazomethane (17 mmol) in 50 ml of Et_2O was added dropwise to a stirred mixture of allyltriethoxysilane (1.8 g, 8.8 mmol) and 16 mg $\text{Pd}(\text{OAc})_2$ at –25°C. The mixture was filtered, distillation gave 0.3 g (15%) of **3**; b.p. 74–76°C/14 Torr. ^1H NMR (CDCl_3): δ 0.62 (m, 2H, SiCH_2), 0.64–0.76 (m, 1H, CH-cyclopropane), –0.05–0.07 (m, 2H, CH_2 -cyclopropane), 0.38–0.5 (m, 2H, CH_2 -cyclopropane), 3.81 (q, 6H, OCH_2), 1.2 (t, 9H, OCCH_3). ^{13}C NMR (CDCl_3): δ 15.87 (SiCH_2), 18.28 (OCCH_3), 58.30 (OCH_2), 4.84 (CH-cyclopropane), 6.58 (CH_2 -cyclopropane). Anal. Found: C, 54.88; H, 10.04; Si, 12.67. $\text{C}_{10}\text{H}_{22}\text{O}_3\text{Si}$ (218.13) Calc.: C, 55.01; H, 10.16; Si, 12.83%.

3.3. Synthesis of 1-cyclopropylmethylsilatrane, $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{SiCH}_2\text{-}\nabla$ (**2a**)

3.3.1. Method A

$\text{Pd}(\text{OAc})_2$ (2 mg) was added to a vigorously stirred mixture of 25 ml of diazomethane (8.5 mmol) in Et_2O and 1-allylsilatrane (**1a**) (0.22 g, 1 mmol) at –10°C. The mixture was filtered through neutral aluminium oxide. The aluminium oxide was washed with ether (20 ml) and then ether was evaporated from the combined filtrate. The residue was recrystallized from CHCl_3 /*n*-pentane to give colourless crystals of **2a**. Yield 0.18 g (82%), m.p. 141–142°C. ^1H NMR (CDCl_3): δ 0.39–0.42 (m, 2H, SiCH_2), 0.66–0.78 (m, 1H, CH-cyclopropane), –0.035–0.01 (m, 2H, CH_2 -cyclopropane), 0.34–0.39 (m, 2H, CH_2 -cyclopropane), 2.78 (t, 6H, NCH_2), 3.75 (t, 6H, OCH_2). ^{13}C NMR (CDCl_3): δ 6.85 (CH-cyclopropane); 6.65 (CH_2 -cyclopropane), 21.46 (SiCH_2), 51.24 (NCH_2), 57.92 (OCH_2). Anal. Found: C, 52.28; H, 8.24; Si, 12.17. $\text{C}_{10}\text{H}_{19}\text{NO}_3\text{Si}$ (229.34) Calc.: C, 52.37; H, 8.35; Si, 12.25%.

3.3.2. Method B

A mixture of 0.4 g (1.83 mmol) of cyclopropylmethyltriethoxysilane (**3**), 0.27 g (1.83 mmol) of triethanolamine, 15 ml of benzene and 1 pellet of KOH

was heated and the ethanol formed was removed together with benzene. The residue was dissolved in CHCl_3 and *n*-pentane was added; a white precipitate was filtered off and washed with *n*-pentane. After recrystallization from CHCl_3 /*n*-pentane and drying in vacuo, 0.33 g (80%) of **2a** was obtained.

3.4. Synthesis of 1-cyclopropylmethyl-3,7,10-trimethylsilatrane, $\text{N}(\text{CH}_2\text{CHMeO})_3\text{SiCH}_2\text{-}\nabla$ (**2b**)

A solution of diazomethane (8.5 mmol) in 25 ml Et_2O was added dropwise to a mixture of 1-allyl-3,7,10-trimethylsilatrane (**1b**) (0.2 g, 0.39 mmol) and 2 mg $\text{Pd}(\text{OAc})_2$ in 5 ml Et_2O at 5°C. The mixture was filtered through neutral aluminium oxide. The aluminium oxide was washed with ether (10 ml) and then ether of the combined filtrate was evaporated; the residual oil was purified by sublimation in vacuo, yielding 0.16 g (76%) of a pure product (**2b**) as colourless crystals, m.p. 73–75°C. ^1H NMR (CDCl_3): δ 0.36–0.48 (m, 2H, SiCH_2), 0.70–0.79 (m, 1H, CH-cyclopropane), 0.80–0.90 (m, 1H, CH-cyclopropane); –0.08–0.07 (m, 2H, CH_2 -cyclopropane), 0.28–0.38 (m, 2H, CH_2 -cyclopropane). ^{13}C NMR, gated decoupling, (CDCl_3): δ 7.00 (d), 7.07 (d), (CH-cyclopropane); 6.27 (major, t), 6.31 (minor, t), (CH_2 -cyclopropane); 20.26 (q), 20.36 (q), 20.70 (q), (CH_3); 23.02 (CH_3); 21.33 (major, t), 21.39 (minor, t), (SiCH_2); 58.96 (t), 61.72 (t), 62.00 (t), 65.24 (t), (NCH_2); 63.43 (d), 65.02 (d), 65.19 (d).

Table 2
Crystal data and structure refinement for **2a**

Empirical formula	$\text{C}_{10}\text{H}_{19}\text{NO}_3\text{Si}$
Formula weight	229.35
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	<i>Pnma</i> , $Z = 4$
Unit cell dimensions	$a = 13.755(3)$ Å, $\alpha = 90^\circ$ $b = 8.143(2)$ Å, $\beta = 90^\circ$ $c = 10.541(2)$ Å, $\gamma = 90^\circ$ $V = 1180.7(4)$ Å ³
Density (calculated)	1.290 g cm ^{–3}
Absorption coefficient	0.188 mm ^{–1}
$F(000)$	496
Crystal size	0.8 × 0.6 × 0.4 mm ³
Θ -range for data collection	2.43° to 24.94°
Index ranges	–16 ≤ h ≤ 0, –9 ≤ k ≤ 0, 0 ≤ l ≤ 12
Reflections collected	1079
Independent reflections	1016
Refinement method	Full-matrix least-squares on F^2
Data/parameters	1016/105
Goodness-of-fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0834$, $wR_2 = 0.2172$
R indices (all data)	$R_1 = 0.0955$, $wR_2 = 0.2324$
Extinction coefficient	0.042(13)
Largest difference peak and hole	0.628 and –0.890 e Å ^{–3}

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2a**

Atom	x	y	z	U_{eq}
Si(1)	3727(1)	2500	5971(1)	45(1)
C(1)	3949(4)	2500	7724(5)	90(3)
C(2)	4629(5)	1721(10)	8366(6)	57(2)
C(3)	5020(5)	2092(15)	9666(6)	74(4)
C(4)	5661(5)	2128(31)	8529(7)	85(8)
N(1)	3410(3)	2500	3974(3)	53(1)
O(1)	4870(2)	2500	5467(3)	60(1)
O(2)	3109(2)	750(3)	5946(2)	64(1)
C(11)	5122(4)	2500	4179(5)	67(2)
C(12)	4305(5)	1994(10)	3376(6)	66(3)
C(21)	2700(4)	80(6)	4835(5)	80(1)
C(22)	3181(8)	694(13)	3758(8)	74(4)
C(022)	2562(8)	1469(14)	3809(8)	64(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

66.99 (d), (OCH) (two diastereomers). Anal. Found: C, 57.74; H, 9.44; N, 5.19. $C_{13}H_{25}O_3Si$ (271.42) Calc.: C, 57.52; H, 9.28; N, 5.16%. MS-EI, m/z (rel. int., assign.) 216 (100%, M-allyl).

3.5. X-ray crystallographic study of **2a**

Experimental crystal data are summarized in Table 2, atomic coordinates with equivalent thermal displacement parameters are given in Table 3.

Intensity data were collected on an Enraf-Nonius CAD4 automated four-circle diffractometer. The data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom methods using SHELXS-86 [14]. All non-hydrogen atoms were refined anisotropically by least-squares procedure against F^2 using SHELXL-93 [15]. Although the locations of C(3), C(4) and C(12) were initially found on a special crystallographic position (i.e. at $y = 0.25$), the large thermal displacement parameter values were indicative of considerable disorder. Therefore, the positional constraints of these atoms were removed and a disordering model with occupation level of 50% was taken into the refinement. The components defined by the C(22) and C(022) carbon atoms could be freely refined, resulting in equal occupancies of 50% (see also Section 2). A quite large value of the U_{22} anisotropic displacement parameter ($0.167(8) \text{\AA}^2$) for C(1), as well as an unusually short distance C(2)–C(1) of $1.317(8) \text{\AA}$, also suggested disorder for this carbon atom, but all attempts to separate the positions in two components failed. The hydrogen atoms

were involved in the refinement procedure on calculated positions with $d(C-H) = 0.96 \text{\AA}$ and $U_{iso} = 0.08 \text{\AA}^2$. Additionally, an isotropic extinction parameter was refined. The final refinement cycle led to convergence with quite poor residuals: $R_1 = 8.34$, $wR_2 = 21.72\%$ and GOOF 1.035.

Acknowledgements

A research grant for G.S.Z. from the Deutscher Akademischer Austauschdienst (DAAD) and support from the Fonds der Deutschen Chemischen Industrie VCI (for J.L.) are gratefully acknowledged. E.V.A. thanks the Graduiertenkolleg "Metallorganische Chemie" of the Philipps University of Marburg for a doctoral fellowship. Support by the Russian Foundation for Basic Research under Grant No. 94-03-08418 for S.S.K. is also gratefully acknowledged.

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