

Synthesis and structure of 3-(cyclohexylamino)propyldimethylsilanol¹

Wolfgang Ziche, Bernhard Herrschaft², Friedemann Hahn³, Peter John⁴, Johann Weis⁴,
Norbert Auner^{*}

Institut für Anorganische und Allgemeine Chemie, Humboldt Universität zu Berlin, Hessische Straße 1–2, 10115 Berlin, Germany

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Abstract

3-(Cyclohexylamino)propylmethoxydimethylsilane **1** is readily hydrolyzed to give the silanol 3-(cyclohexylamino)propyldimethylsilanol **2**, which forms hydrogen bonded chains in the solid state. © 1997 Elsevier Science S.A.

Keywords: Silicon; Silanol; Hydrogen bond; Crystal structure

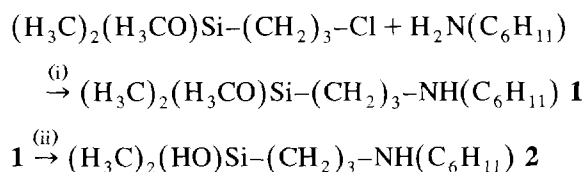
1. Introduction

In connection with our studies on five-membered cyclic azasilanes [1], we synthesized linear precursors that should yield the cyclic compounds with elimination of methanol. An example of such a precursor is 3-(cyclohexylamino)propyldimethylmethoxysilane **1**. This compound is quite moisture-sensitive, and as a product of complete hydrolysis we obtained the corresponding solid silanol **2**, which is stable against condensation in the presence of a base.

Silanol structures are of interest because of their extended hydrogen bonded systems in the solid state [2]. To elucidate the hydrogen bond network of **2**, an X-ray crystallographic study has been carried out.

2. Synthesis and analysis

The synthesis of **1** and **2** is carried out according to the scheme below:



Reaction conditions: (i) **1** reflux 6 h, 2 (H₂NCH₂)₂; (ii) atmospheric moisture.

The amination of the 3-chloropropylsilane gives **1** as the main product. Minor amounts of the bis-substituted product (C₆H₁₁)N[(CH₂)₃Si(OCH₃)(CH₃)₂]₂, cyclo-[–Si(CH₃)₂–(CH₂)₃N(C₆H₁₁)–] and the disiloxane **3** from the condensation of **2** are formed.

The composition of **1** and **2** is confirmed by mass spectrometry, elemental analysis and NMR spectroscopy. A full assignment of resonances was obtained for **1** by ¹H¹H–COSY and ¹H¹³C–HSQC spectra (Fig. 1).

The OH and NH resonances of **2** are very broad (solvent CDCl₃), and indicate hydrogen bonding. In order to confirm this assumption, IR spectra in the solid state (KBr) and in solution (CS₂) were measured. In both cases a strong band from 3100 to 3600 cm^{–1} is

^{*} Corresponding author.

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² Crystal structure determination.

³ STOE&Cie GmbH, Hilpertstr. 10, 64295 Darmstadt, Germany.

⁴ Wacker Chemie GmbH, Johannes-Hess-Str. 24, 84480 Burghausen, Germany.

observed, in addition a sharp strong band at 3240 cm^{-1} is found for the KBr pellet. This is characteristic of a silanol group involved in hydrogen bonding. [Shift from a free O–H stretching frequency of ca. 3600 cm^{-1} by coordination to a base [3]; low polar solvents (CS_2) lead to increasing $\nu(\text{OH})$ and decrease of the relative intensity [4].]

3. Crystallography

3.1. Data collection, structure solution and refinement

A colourless crystal of approximate dimensions $0.12 \times 0.20 \times 0.50\text{ mm}^3$ was mounted on glass fibre and transferred to an IPDS (Stoe & Cie, Darmstadt GmbH,

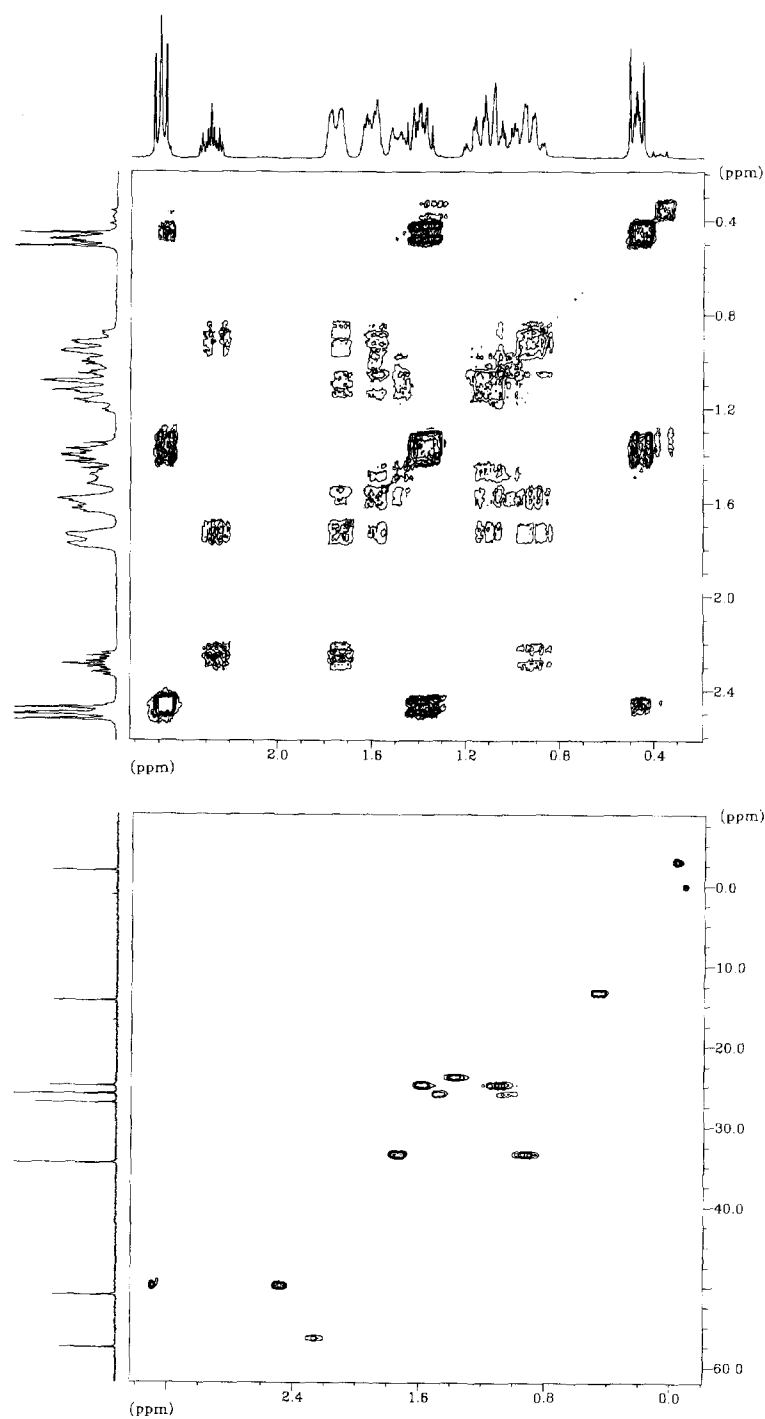


Fig. 1. ^1H – ^1H -COSY and ^1H – ^{13}C -HSQC spectra of **1**.

Table 1
Crystal data and structure refinement for 2

Empirical formula	$C_{22}H_{50}N_2O_2Si_2$
Formula weight	430.92
$F(000)$	960
Crystal size (approx.) [mm ³]	0.50 × 0.20 × 0.12
Crystal system, Laue class	monoclinic, 2/m, second setting
Space group	$P2_1/n$ (No. 14)
Unit cell dimensions [pm, °]	$a = 720.93(4)$ $b = 1995.2(3), \beta = 91.775(5)$ $c = 1936.2(1)$
Volume [10 ⁶ pm ³]	$V_{EZ} = 2783.7(5)$
Unit number $C_{22}H_{50}N_2O_2Si_2$	$Z = 4$
Density (calc.) [Mg m ⁻³]	$d_{calc} = 1.028$
Absorption coefficient [mm ⁻¹]	$\mu = 0.112$
Diffractometer	IPDS (Stoe & Cie, Darmstadt, Germany)
Temperature [K]	293(2)
Wavelength [pm], monochromator	$\lambda = 71.073$, graphite
Scan technique	rotation
Theta range [°] for data collection	$5.17 < \theta < 23.00$
Index ranges	$h = -8/8, k = -25/26, l = -25/24$
Reflections, collected	9348
Reflections, independent	3709, $R_{int} = 0.0351$
Starting coordinates	Si, O C, N, H _N , H _O
Structure factor calculation	direct methods, SHELXS-86
Refinement method	difference Fourier syntheses, SHELXL-93
Atom form-factors	minimum function $\sum w(F_o^2 - F_c^2)$
Absorption correction	full-matrix least-squares calculations based on F_{rel}^2
Extinction correction	neutral atoms [6]
Hydrogen atoms	none
Weighting scheme	none
Number of reflections $F_{rel}^2 > 4\sigma(F_{rel}^2)$	calculated, not refined, included in the structure factor calculation
Number of variables	$w = [\sigma^2(F_o^2) + 0.00195P^2 + 0.5627P]; P = (F_o^2 + 2F_c^2)/3$
GoF based on F_{rel}^2	3690
Final R index [$F_{rel}^2 > 4\sigma(F_{rel}^2)$]	273
R index for all data	1.037; $GoF = \{[\sum w(F_o^2 - F_c^2)]/(n - m)\}^{-1/2}$
Largest parameter shift [e.s.d.]	$wR_2 = 0.0872$ (conventional R index $R_1 = 0.0374$)
Largest difference electron density peak and hole [$e \times 10^{-6}$ pm ⁻³]	$wR_2 = 0.0987$ (conventional R index $R_1 = 0.0600$)
	0.0002
	0.143, -0.131

Germany). After 15 h from 170 exposures, a total of 15796 reflections were taken (Mo K α radiation, graphite monochromator, 293 K, $0^\circ \leq \varphi \leq 120^\circ$, oscillation angle 1° , detector distance 60 mm). Owing to loss of 21% of

the mean intensity, a linear decay correction had to be applied to the data set. After data reduction, 6287 independent reflections survived ($R_{int} = 5.08\%$), of which 6286 were considered observed (Table 1).

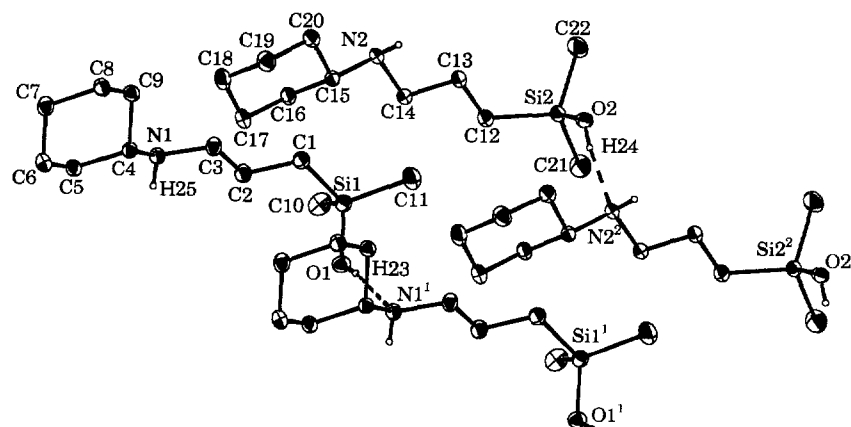


Fig. 2. ORTEP [9] drawing of 3-(cyclohexylamino)propyldimethylsilanol (ellipsoids enclose 30% probability) showing the chain structure by hydrogen bonding: O1–H23 72 pm, H23 \cdots N1' 205 pm, O1 \cdots N1' 276 pm, N1'–H23–O1 171°; O2–H24 76 pm, H24 \cdots N2' 198 pm, O2 \cdots N2' 273 pm, N2'–H24–O2 170°. Generating symmetry operation 1: $1 + x, y, z$.

The metrics of the initial unit cell and the observed systematic extinctions (observed $h0l$ for $h+l=2n$ and $00l$ for $l=2n$) made the space group $P2_1/n$ (No. 14) reliable. Trial structure solution with direct methods (SHELXS-86 [5]), assuming $P2_1/n$ to be the correct space group, led to a weighted E -map from which two molecules of the assumed constitution emerged (Table 2).

The subsequent structure refinement by difference Fourier syntheses (atom form-factors for neutral atoms [6], full-matrix least-squares refinement) based on F_{rel}^2 . No absorption correction was applied. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were assumed in their idealized positions and only included in the structure factor calculations. The positions of amino- and hydroxyl-hydrogen atoms respectively were taken from a difference Fourier map and refined isotropically [7].

3.2. Structure discussion

Two crystallographically independent molecules of 3-(cyclohexylamino)propyldimethylsilanol on general

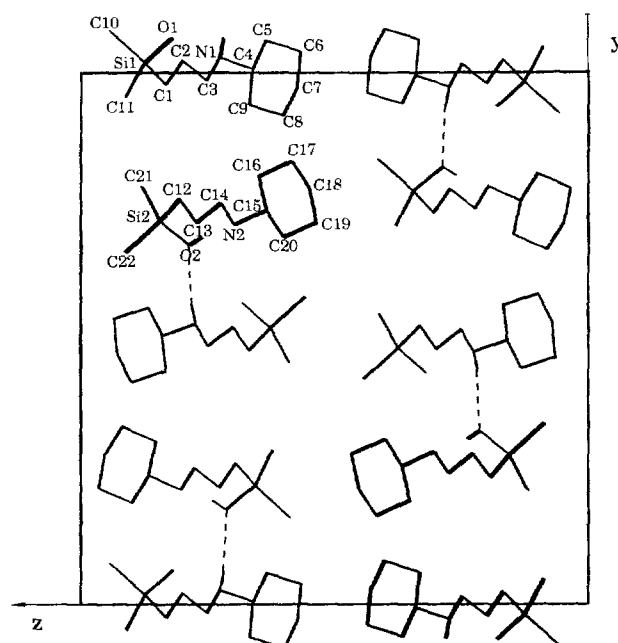


Fig. 3. Packing diagram (ORTEP [9]) of the crystal structure viewing along $[-100]$ and the asymmetric unit with numbering scheme. Dashed lines visualize the hydrogen bonding.

Table 2

Atomic coordinates^a and equivalent isotropic displacement parameters^{b,c} for **2**

Atom	x	y	z	U_{eq}^c
Si(1)	2791(1)	10191(1)	8751(1)	56(1)
Si(2)	2167(1)	7216(1)	8456(1)	52(1)
O(1)	-1712(2)	10654(1)	8207(1)	63(1)
O(2)	3160(2)	6765(1)	7884(1)	60(1)
N(1)	9143(2)	10271(1)	7254(1)	52(1)
N(2)	-4218(2)	7143(1)	6974(1)	52(1)
C(1)	4799(3)	9765(1)	8320(1)	62(1)
C(2)	6290(3)	10216(1)	7996(1)	63(1)
C(3)	7604(3)	9849(1)	7506(1)	58(1)
C(4)	10000(3)	10053(1)	6593(1)	47(1)
C(5)	11341(3)	10585(1)	6322(1)	57(1)
C(6)	12264(3)	10377(1)	5638(1)	62(1)
C(7)	13247(3)	9712(1)	5701(1)	65(1)
C(8)	11915(3)	9179(1)	5975(1)	59(1)
C(9)	10991(3)	9388(1)	6660(1)	54(1)
C(10)	-3579(4)	10771(2)	9426(1)	92(1)
C(11)	-1216(4)	9539(2)	9121(2)	98(1)
C(12)	83(3)	7636(1)	8068(1)	59(1)
C(13)	-1388(3)	7184(1)	7732(1)	61(1)
C(14)	-2688(3)	7556(1)	7249(1)	59(1)
C(15)	-5093(3)	7414(1)	6335(1)	49(1)
C(16)	-6144(3)	8056(1)	6476(1)	56(1)
C(17)	-7028(3)	8335(1)	5819(1)	65(1)
C(18)	-8309(4)	7826(1)	5471(1)	79(1)
C(19)	-7299(4)	7175(1)	5340(1)	76(1)
C(20)	-6384(3)	6902(1)	6000(1)	66(1)
C(21)	3766(4)	7869(1)	8804(2)	95(1)
C(22)	1497(4)	6623(2)	9138(1)	92(1)

^a Coordinates multiplied by 10^4 .

^b $[U_{\text{eq}}] = [10^3 \text{Å}^2]$; e.s.d.s in parentheses.

^c $U_{\text{eq}} = \frac{1}{3} \sum_{i < j} U_{ij} a_i^* a_j^* a_i a_j$.

positions constitute the asymmetric unit of the structure (Fig. 2). The C–Si distances are in the normal range observed for C–Si bonds of silahydrocarbons in the solid state. The C–C and C–N distances in the azahydrocarbon backbone also show no special features. Intermolecular $\text{N} \cdots \text{H}-\text{O}$ hydrogen bonds give rise to a chain structure (Fig. 3). Slightly longer $\text{N} \cdots \text{H}-\text{O}$ contact distances with a slightly more bent hydrogen bridge hold the rods running along $[100]$ together, and establish a distorted tetragonal rod packing.

The hydrogen bond motif found for **2** is analogous to that of some sila drugs, which are also silanols having an amino-functional substituent [8].

4. Experimental section

The preparation of **1** was carried out with exclusion of moisture. 30 g (0.3 mol) dry cyclohexylamine was put into a flask equipped with a stirrer, dropping funnel and a thermometer, and heated to reflux. 20 g (0.12 mol) 3-chloropropylmethoxydimethylsilane was added slowly. The temperature rose to 145°C . After complete addition, the temperature was held for another 5 h. Colourless leafy crystals formed when the mixture was cooled to 120°C . 8 g dry ethylenediamine was added, and a heavy melt formed which solidified upon cooling. The remaining light-yellow liquid phase was separated and distilled under reduced pressure to give 20 g (0.087 mol, 72% yield) **1** as a colourless liquid, b.p. $100^\circ\text{C}/2 \text{ mbar}$.

1 is moisture sensitive, and on standing in air for 24 h gave slightly wet colourless crystals of **2**. **2** was recrystallized from pentane; m.p. 65–67°C. Mass spectra were obtained on a HP5995B spectrometer (EI) or a GC/MS couple (Chrompack CP 9000, 10 m CP-Sil-5CB-MS; Finnigan ITD 800, CI). NMR spectra were performed on Bruker AM300 and DPX300 spectrometers. IR spectra were measured with a Bruker IFS-55 FT-IR spectrometer.

NMR parameters for the $^1\text{H}^1\text{H}$ -COSY experiment (gradient pulses for selection) of **1**: preceded by 16 dummy scans, two scans for each of the 128 t_1 values recorded in 2K data blocks with a relaxation delay of 1.5 s and a spectral width of 730 Hz. The data matrix was zero-filled to $2\text{K} \times 0.25\text{K}$ and apodized with sine bell window functions in both dimensions. $^1\text{H}^{13}\text{C}$ -HSQC (gradient pulses for selection): preceded by eight dummy scans, two scans for each of the 256 t_1 values recorded in 1K data blocks with a relaxation delay of 2 s and a spectral width of 1092 Hz in f_2 (^1H) and 5360 Hz in f_1 (^{13}C). The data matrix was zero-filled to $2\text{K} \times 0.5\text{K}$ and apodized with shifted square sine bell window functions in both dimensions.

4.1. 3-(Cyclohexylamino)propylmethoxydimethylsilane **1**

^1H NMR (300 MHz, CDCl_3 , 20°C): δ [ppm] –0.03 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 0.43–0.48 (m, 2H, $\text{Si}-\text{CH}_2$), 0.65–0.85 (s, br, 1H, NH), 0.92–1.09, 1.71–1.76 (m, AB, 4H, $\text{N}-\text{CH}-\text{CH}_2$), 0.90, 1.50 (m, AB, 2H, $\text{N}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2$), 1.09–1.15, 1.56–1.61 (m, AB, 4H, $\text{N}-\text{CH}-\text{CH}_2-\text{CH}_2$), 1.31–1.50 (m, $\text{Si}-\text{CH}_2-\text{CH}_2$), 2.22–2.29 (m, 1H, $\text{N}-\text{CH}$), 2.47 (tr, br, 2H, $J(\text{H},\text{H}) = 7.3$ Hz, $\text{N}-\text{CH}_2$), 3.28 (s, 3H, OCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3 , 20°C): δ [ppm] –2.95 ($\text{Si}(\text{CH}_3)_2$), 13.29 ($\text{Si}-\text{CH}_2$), 23.92 ($\text{Si}-\text{CH}_2-\text{CH}_2$), 24.88 ($\text{N}-\text{CH}-\text{CH}_2-\text{CH}_2$), 26.00 ($\text{N}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2$), 33.53 ($\text{N}-\text{CH}-\text{CH}_2$), 49.97 ($\text{O}-\text{CH}_3$), 49.97 ($\text{N}-\text{CH}_2$), 56.54 ($\text{N}-\text{CH}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, CDCl_3 , 20°C): δ [ppm] 18.65. MS (CI): m/z (%) 229 (1.7) [$\text{M}^+ + 1$], 154 (14.1), 112 (100), 98 (5.1), 89 (27.3), 70 (5.9), 59 (31.7), 30 (90.1). Anal. Found: C, 62.41; H, 11.82; N, 6.08. $\text{C}_{12}\text{H}_{27}\text{ONSi}$ (229.44) Calc.: C, 62.82; H, 11.86; N, 6.10%.

4.2. 3-(Cyclohexylamino)propyldimethylsilanol **2**

^1H NMR (300 MHz, CDCl_3 , 20°C): δ [ppm] 0.10 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 0.64 (tr, br, 2H, $J(\text{H},\text{H}) = 7.0$ Hz, $\text{Si}-\text{CH}_2$), 0.98–1.34 (m, 5H, CH_2), 1.55–1.78 (m, 5H, CH_2), 1.82–1.97 (m, 2H, CH_2), 2.32–2.46 (m, 1H, $\text{N}-\text{CH}$), 2.66 (tr, br, 2H, $J(\text{H},\text{H}) = 5.6$ Hz, $\text{N}-\text{CH}_2$),

2.8–4.7 (s, br, 2H, NH, OH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3 , 20°C): δ [ppm] –0.22 ($\text{Si}(\text{CH}_3)_2$), 17.21 ($\text{Si}-\text{CH}_2$), 24.04 ($\text{Si}-\text{CH}_2-\text{CH}_2$), 24.99 ($\text{N}-\text{CH}-\text{CH}_2-\text{CH}_2$), 25.95 ($\text{N}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2$), 33.12 ($\text{N}-\text{CH}-\text{CH}_2$), 48.80 ($\text{N}-\text{CH}_2$), 56.80 ($\text{N}-\text{CH}$). ^{29}Si NMR (^1H) (59.6 MHz, CDCl_3 , 20°C): δ [ppm] 12.51. IR (CS_2): ν (cm^{-1}) 3100–3600 (s, $\text{O}-\text{H} \cdots \text{N}$). IR (KBr): ν (cm^{-1}) 3100–3600 (s), 3240 (s) ($\text{O}-\text{H} \cdots \text{N}$). MS (EI): m/z (%) 215 (3.05) [M^+], 200 (2.05), 172 (7.61), 154 (4.89), 112 (74.87), 98 (7.12), 75 (39.34), 30 (100). Anal. Found: C, 61.57; H, 11.82; N, 6.48. $\text{C}_{11}\text{H}_{25}\text{ONSi}$ (215.41) Calc.: C, 61.33; H, 11.70; N, 6.50%.

4.3. Bis(3-(cyclohexylamino)propyl)tetramethyldisiloxane **3**

^{29}Si NMR (^1H) (59.6 MHz, CDCl_3 , 20°C): δ [ppm] 7.65. MS (EI): m/z (%) 413 (0.32) [$\text{M}^+ + 1$], 397 (0.22), 329 (0.45), 198 (10.05), 133 (12.72), 112 (68.96), 83 (31.81), 73 (11.74), 55 (36.26), 30 (100).

5. Supplementary material available

Tables of complete bond distances and angles, anisotropic displacement parameters and atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

References

- [1] W. Ziche, B. Ziemer, P. John, J. Weis and N. Auner, *J. Organomet. Chem.*, 521 (1996) 29.
- [2] P. Lickiss, *Adv. Inorg. Chem.*, 42 (1995) 147.
- [3] R. West and R.H. Baney, *J. Am. Chem. Soc.*, 81 (1959) 6145; R.M. Badger and S.H. Bauer, *J. Chem. Phys.*, 5 (1937) 839.
- [4] O. Nillius and H. Kriegsmann, *Spectrochim. Acta*, 26A (1970) 121.
- [5] G.M. Sheldrick, SHELXS-86, Universität Göttingen, Germany, 1986.
- [6] *International Tables of X-ray Crystallography*, Vol. C, Kluwer Academic, Dordrecht, Netherlands, 1995.
- [7] G.M. Sheldrick, SHELXL-93, Universität Göttingen, Germany, 1993.
- [8] M. Söderholm, *Acta Chem. Scand.*, B38 (1984) 31, 95; R. Tacke, H. Lange, W.S. Sheldrick, G. Lambrecht, U. Moser and E. Mutschler, *Z. Naturforsch.*, 38 (1983) 738; W.S. Sheldrick, H. Linoh, R. Tacke, G. Lambrecht and U. Moser, *J. Chem. Soc., Dalton Trans.*, (1985) 1743; R. Tacke, J. Pikies, F. Weisenberger, L. Ernst, D. Schomburg, M. Waelbroeck, J. Christophe, G. Lambrecht, J. Gross and E. Mutschler, *J. Organomet. Chem.*, 466 (1994) 15.
- [9] C.K. Johnson, ORTEP II, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations, ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.