Organometallics **2005,** *24,* 6059−6062

Zwitterionic λ^5*Si*-Silicates with an *Si*S_4C or *Si*S_2O_2C Skeleton, Compounds Containing a Square-Pyramidal or Trigonal-Bipyramidal Si-Coordination Polyhedron

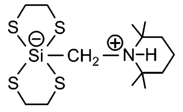
Oliver Seiler, Matthias Büttner, Martin Penka, and Reinhold Tacke*

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland,
D-97074 Würzburg, Germany

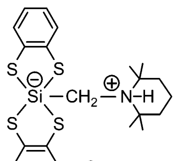
Received June 8, 2005

*Summary: Treatment of [2-(dimethylamino)phenyl]-silane (**8**) with 2 molar equivs of benzene-1,2-dithiol or 2-mercaptoacetic acid yields bis[benzene-1,2-dithiolato-(2−)][2-(dimethylammonio)phenyl]silicate (**6**) and [2-(dimethylammonio)phenyl]bis[2-mercaptoethanoato(2−)-O,S]silicate (**7**), respectively. The zwitterionic λ^5Si-silicates were structurally characterized by solid-state NMR spectroscopy (^{13}C, ^{15}N, ^{29}Si) and single-crystal X-ray diffraction. Compound **6** is the first zwitterionic λ^5Si-silicate with Si−S bonds that contains a square-pyramidal Si-coordination polyhedron.*

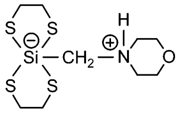
In almost all cases reported so far, pentacoordination of silicon is accomplished by strongly electronegative ligand atoms, such as fluorine, oxygen, nitrogen, and chlorine atoms, as well as carbon atoms (for reviews dealing with higher-coordinate silicon compounds, see ref 1). We have recently reported on the synthesis of the zwitterionic λ^5*Si*-silicates **1**,[2] **2**,[2] **3**·CH_3CN,[3] **4**,[4] and **5**,[4] demonstrating that sulfur atoms can also act as ligand atoms in pentacoordinate silicon compounds. The electronegativity of sulfur is similar to that of carbon (Allred-Rochow values: S, 2.44; C, 2.50) but significantly lower than those of fluorine (4.10), oxygen (3.50), nitrogen (3.07), and chlorine (2.83). As shown by single-crystal X-ray diffraction, the Si-coordination polyhedra of **1**, **2**, **3**·CH_3CN, and **4** are somewhat distorted trigonal bipyramids, with the carbon atom and two sulfur atoms in the three equatorial positions. In all cases, the carbon ligand atoms are characterized by sp^3-hybridization, with Si−C bond distances ranging from 1.906(2) to 1.939(4) Å. We have now succeeded in synthesizing the first pentacoordinate silicon compounds with *Si*S_4C and *Si*S_2O_2C skeletons that contain an sp^2-hybridized carbon ligand atom, the zwitterionic λ^5*Si*-silicates **6** and **7**. Both compounds were characterized by solid-state NMR spectroscopy and single-crystal X-ray diffraction.



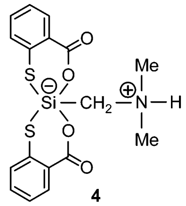
1



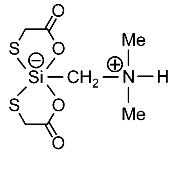
2



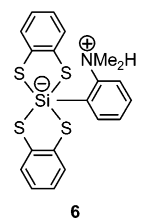
3



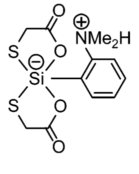
4



5



6



7

The zwitterionic λ^5*Si*-silicates **6** and **7** were synthesized according to Scheme 1 by treatment of [2-(dimethylamino)phenyl]silane (**8**) with 2 molar equivs of benzene-1,2-dithiol or 2-mercaptoacetic acid at 20 °C in acetonitrile. The products were isolated as crystalline solids (yields: **6**, 89%; **7**, 62%), and their identities were established by elemental analyses (C, H, N), solid-state VACP/MAS NMR experiments (^{13}C, ^{15}N, ^{29}Si), and single-crystal X-ray diffraction.

---

* To whom correspondence should be addressed. E-mail: r.tacke@mail.uni-wuerzburg.de.

(1) Selected reviews dealing with compounds of higher-coordinate silicon: (a) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 1, pp 227−303. (b) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 1, pp 839−892. (c) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 2, pp 1241−1288. (d) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17−31. (e) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448. (f) Tacke, R.; Becht, J.; Lopez-Mras, A.; Sperlich, J. *J. Organomet. Chem.* **1993**, *446*, 1−8. (g) Wong, C. Y.; Woollins, J. D. *Coord. Chem. Rev.* **1994**, *130*, 175−241. (h) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233−295. (i) Tacke, R.; Dannappel, O. In *Tailor-made Silicon-Oxygen Compounds—From Molecules to Materials*; Corriu, R., Jutzi, P., Eds.; Vieweg: Braunschweig-Wiesbaden, Germany, 1996; pp 75−86. (j) Lukevics, E.; Pudova, O. A. *Chem. Heterocycl. Compd (Engl. Transl.)* **1996**, *32*, 1381−1418. (k) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927−950. (l) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 2, pp 1339−1445. (m) Pestunovich, V.; Kirpichenko, S.; Voronkov, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 2, pp 1447−1537. (n) Chuit, C.; Corriu, R. J. P.; Reye, C. In *Chemistry of Hypervalent Compounds*; Akiba, K.-y., Ed.; Wiley-VCH: New York, 1999; pp 81−146. (o) Tacke, R.; Pülm, M.; Wagner, B. *Adv. Organomet. Chem.* **1999**, *44*, 221−273. (p) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000; pp 97−114. (q) Tacke, R.; Seiler, O. In *Silicon Chemistry: From the Atom to Extended Systems*; Jutzi, P., Schubert, U., Eds.; Wiley-VCH: Weinheim, Germany, 2003; pp 324−337. (r) Kost, D.; Kalikhman, I. *Adv. Organomet. Chem.* **2004**, *50*, 1−106.

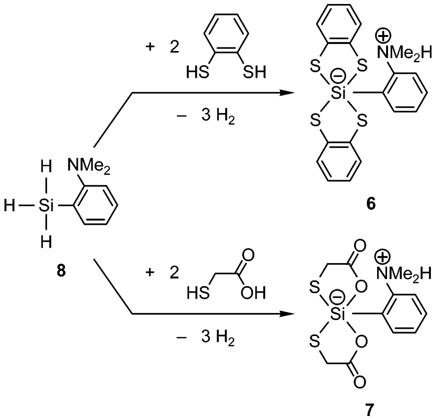
(2) Tacke, R.; Mallak, M.; Willeke, R. *Angew. Chem.* **2001**, *113*, 2401−2403; *Angew. Chem., Int. Ed.* **2001**, *40*, 2339−2341.

(3) Bertermann, R.; Biller, A.; Kaupp, M.; Penka, M.; Seiler, O.; Tacke, R. *Organometallics* **2003**, *22*, 4104−4110.

(4) Willeke, R.; Tacke, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1537−1541.

10.1021/om058032o CCC: $30.25

Scheme 1



The solid-state ^{13}C, ^{15}N, and ^{29}Si NMR data of compounds **6** and **7** are compatible with their molecular structures in the crystal (for details, see Experimental Section). The isotropic chemical shift obtained in the ^{29}Si VACP/MAS NMR studies of **6** ($\delta = -50.2$) is similar to those of compounds **1** ($\delta = -53.0$), **2** ($\delta = -57.2$), and **3**·CH$_3$CN ($\delta = -64.1$), which all contain an SiS$_4$C skeleton. The isotropic ^{29}Si chemical shift of **7** ($\delta = -73.4$) is similar to that of **5** ($\delta = -69.8$), but these values differ significantly from that of **4** ($\delta = -98.5$), although compounds **4**, **5**, and **7** contain an SiS$_2$O$_2$C skeleton. These differences might be explained by the different sizes of the five- (**5**, **7**) and six-membered (**4**) chelate rings of these zwitterions (in this context, see ref 5).

The crystal data and the experimental parameters used for the crystal structure analyses of **6** and **7** are given in Table 1. The molecular structures in the crystal are shown in Figures 1 and 2; selected bond distances and angles are given in the respective Figure legends.

The Si-coordination polyhedron of **6** can be described as a slightly distorted square pyramid (Berry distortion, 96.2%),[6] with each of the two benzene-1,2-dithiolato(2−) ligands spanning two of the four basal sites and the carbon atom of the aryl group occupying the apical site. To the best of our knowledge, this is the first pentacoordinate silicon compound with Si−S bonds that has been reported to have a square-pyramidal Si-coordination polyhedron. The Si−S bond lengths of **6** range from 2.2251(7) to 2.2558(6) Å. These Si−S distances are longer than the equatorial (2.1588(9)−2.1728(9) Å) and shorter than the axial (2.2871(7)−2.3475(8) Å) Si−S bonds in compounds **1**−**4**, which all contain a trigonal-bipyramidal Si-coordination polyhedron. The Si-coordination polyhedron of **7** is also best described as a distorted trigonal bipyramid (Berry distortion, 25.6%),[6] with each of the two 2-mercaptoethanoato(2−) ligands spanning one axial (O1, O2) and one equatorial (S1, S2) site. The Si−S distances amount to 2.1474(6) and 2.1632(6) Å, and the Si−O distances range from 1.7821(11) to 1.8074(11) Å. The Si−C distances of compounds **6** and **7** (sp^2-hybridization of the carbon ligand atom) amount to 1.9032(15) and 1.8938(14) Å, respectively, indicating a shortening compared to the Si−C distances of **1**, **2**, **3**·CH$_3$CN, and **4** (1.906(2)−

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 6 and 7

	6	7
empirical formula	$C_{20}H_{19}NS_4Si$	$C_{12}H_{15}NO_4S_2Si$
formula mass, g mol^{-1}	429.69	329.46
collection T, K	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group (No.)	$P2_1/c$ (14)	$P2_1/n$ (14)
a, Å	10.0162(15)	12.8836(19)
b, Å	13.5118(17)	7.3143(9)
c, Å	15.4322(19)	16.792(2)
β, deg	105.046(16)	108.268(16)
V, Å^3	2016.9(5)	1502.6(4)
Z	4	4
D(calc), g cm^{-3}	1.415	1.456
μ, mm^{-1}	0.535	0.445
F(000)	896	688
cryst dimens, mm	0.5 × 0.5 × 0.1	0.5 × 0.4 × 0.3
2θ range, deg	5.18−53.94	6.12−52.80
index ranges	$-12 \le h \le 12$, $-17 \le k \le 17$, $-19 \le l \le 19$	$-16 \le h \le 16$, $-9 \le k \le 9$, $-20 \le l \le 20$
no. of collected reflns	21 992	21 546
no. of indep reflns	4341	3059
R_{int}	0.0872	0.0502
no. of reflns used	4341	3059
no. of params	240	186
S^a	1.063	1.051
weight params a/b^b	0.0567/0.3816	0.0522/0.1908
$R1^c$ [$I > 2\sigma(I)$]	0.0359	0.0298
$wR2^d$ (all data)	0.0974	0.0815
max./min. residual electron density, e Å^{-3}	+0.429/−0.373	+0.299/−0.235

^{a} $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. ^{b} $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$. ^{c} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{d} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

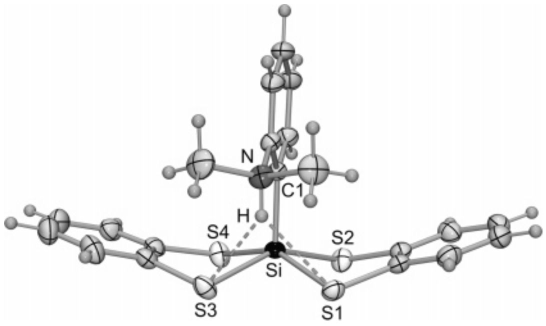


Figure 1. Molecular structure of **6** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths (Å) and angles (deg): Si−S1 2.2558(6), Si−S2 2.2251(6), Si−S3 2.2374(6), Si−S4 2.2343(6), Si−C1 1.9032(15); S1−Si−S2 88.84(2), S1−Si−S3 82.41(2), S1−Si−S4 152.24(2), S1−Si−C1 103.52(5), S2−Si−S3 150.08(2), S2−Si−S4 85.42(2), S2−Si−C1 103.96(5), S3−Si−S4 89.15(2), S3−Si−C1 105.89(5), S4−Si−C1 104.23(5). The dashed lines indicate the presence of an intramolecular bifurcate N−H···S1/S3 hydrogen bond: N−H 0.91(2), H···S1 2.58(2), N···S1 3.3142(15), H···S3 2.48(2), N···S3 3.2474(15); N−H···S1 138.7(17), N−H···S3 142.2(17), S1···H···S3 71.7(6).[7]

---

[5] (a) Kemmitt, T.; Milestone, N. B. *Aust. J. Chem.* **1995**, *48*, 93−102. (b) Tacke, R.; Heermann, J.; Pülm, M.; Richter, I. *Organometallics* **1998**, *17*, 1663−1668. (c) Narula, S. P.; Shankar, R.; Meenu; Anand, R. D. *Polyhedron* **1999**, *18*, 2055−2059. (d) Seiler, O.; Burschka, C.; Penka, M.; Tacke, R. *Silicon Chem.* **2002**, *1*, 355−365.

[6] (a) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748−1756. (b) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318−3326. (c) The degree of distortion was calculated by using the dihedral angle method described in refs 6a,b. All nine dihedral angles and the values for the reference geometry of the ideal square pyramid given in ref 6a were considered for this calculation.

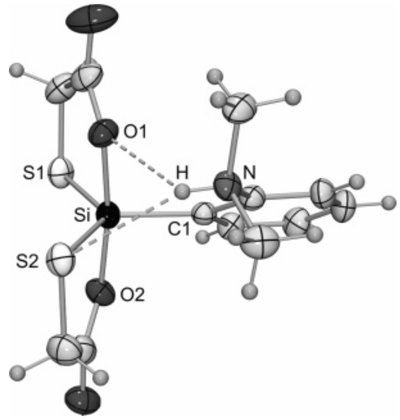


Figure 2. Molecular structure of **7** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths (Å) and angles (deg): Si−S1 2.1474(6), Si−S2 2.1632(6), Si−O1 1.8074(11), Si−O2 1.7821(11), Si−C1 1.8938(14); S1−Si−S2 128.92(2), S1−Si−O1 89.96(4), S1−Si−O2 87.46(4), S1−Si−C1 115.01(5), S2−Si−O1 85.34(4), S2−Si−O2 90.37(4), S2−Si−C1 116.03(5), O1−Si−O2 171.97(5), O1−Si−C1 93.16(5), O2−Si−C1 94.83(6). The dashed lines indicate the presence of an intramolecular bifurcate N−H···S2/O1 hydrogen bond: N−H 0.84(2), H···S2 2.62(2), N···S2 3.4064(14), H···O1 2.339(19), N···O1 2.9069(18); N−H···S2 156.1(18), N−H···O1 125.4(13), S2···H···O1 65.7(5).[7]

1.939(4) Å, sp^3-hybridization of the carbon ligand atoms).

The zwitterion **6** forms an intramolecular bifurcate N−H···S1/S3 hydrogen bond in the crystal,[7] resulting in slightly longer Si−S1/S3 distances compared to the Si−S2/S4 distances. Compound **7** forms an intramolecular bifurcate N−H···S2/O1 hydrogen bond,[7] resulting in an elongation of the Si−S2 and Si−O1 bonds compared to the Si−S1 and Si−O2 bonds.

The Berry pseudorotation process is a major feature in the stereodynamics of pentacoordinate silicon compounds (in this context, see for example refs 1d,o and the relevant literature cited therein). Almost nothing is known about the dynamic behavior of λ^5*Si*-silicates with *Si*S_4C skeletons in solution, due to solubility and/or stability problems with the compounds of this type known so far.[2,3] The Si-coordination polyhedra of **1**−**3** in the crystal are best described as trigonal bipyramids, suggesting that this particular structure is the energetically most stable one. However, the existence of the square-pyramidal Si-coordination polyhedron of **6** in the crystal clearly indicates that the energy difference between the trigonal-bipyramidal and square-pyramidal structure must be rather small. Thus, it is likely that the stereodynamics of λ^5*Si*-silicates with *Si*S_4C frameworks in solution can also be described in terms of a Berry-type process (with the square-pyramidal structure as the transition state), as it is well established for structurally related pentacoordinate silicon compounds with *Si*O_4C skeletons. However, further investigations are necessary to confirm this hypothesis, whereby the synthesis of compounds with an *Si*S_4C framework that are suitable for solution NMR studies remains the major goal.

Experimental Section

General Procedures. The syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The ^{1}H, ^{13}C, and ^{29}Si solution NMR spectra were recorded at 23 °C on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz) using C_6D_6 as the solvent. Chemical shifts (ppm) were determined relative to internal C_6HD_5 (^{1}H, δ 7.28), internal C_6D_6 (^{13}C, δ 128.0), or external TMS (^{29}Si, δ 0). Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Solid-state ^{13}C, ^{15}N, and ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter, 7 mm) containing ca. 300 mg of sample (^{13}C, 100.6 MHz; ^{15}N, 40.6 MHz; ^{29}Si, 79.5 MHz; external standard, TMS (^{13}C, ^{29}Si; δ 0) or glycine (^{15}N, δ −342.0); spinning rate, 5−6 kHz; contact time, 1 ms (^{13}C), 3 ms (^{15}N), or 5 ms (^{29}Si); 90° ^{1}H transmitter pulse length, 3.6 μs; repetition time, 4 s).

Preparation of Bis[benzene-1,2-dithiolato(2−)][2-(dimethylammonio)phenyl]silicate (6). Compound **8** (200 mg, 1.32 mmol) was added at 20 °C to a stirred solution of benzene-1,2-dithiol (376 mg, 2.64 mmol) in acetonitrile (10 mL), and the mixture was stirred at 20 °C for 30 min (evolution of hydrogen) and then kept undisturbed at 20 °C for 16 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **6** in 89% yield as a colorless crystalline solid (504 mg, 1.17 mmol); mp 210 °C. ^{13}C VACP/MAS NMR: δ 49.8 (2 C, NCH_3), 120.5−146.5 (18 C, C_6H_4). ^{15}N VACP/MAS NMR: δ −324.3. ^{29}Si VACP/MAS NMR: δ −50.2. Anal. Calcd for $C_{20}H_{19}NS_4Si$ (429.7): C, 55.90; H, 4.46; N, 3.26. Found: C, 56.01; H, 4.56; N, 3.24.

Preparation of [2-(Dimethylammonio)phenyl]bis[2-mercaptoethanoato(2−)-*O*,*S*]silicate (7). Compound **8** (200 mg, 1.32 mmol) was added at 20 °C to a stirred solution of 2-mercaptoacetic acid (243 mg, 2.64 mmol) in acetonitrile (10 mL), and the mixture was stirred at 20 °C for 3 h (evolution of hydrogen). The solution was then concentrated to a volume of ca. 1 mL, and the resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **7** in 62% yield as a colorless crystalline solid (268 mg, 813 μmol); mp 166 °C (dec). ^{13}C VACP/MAS NMR: δ 31.5 (CH_2), 33.6 (CH_2), 47.3 (NCH_3), 47.8 (NCH_3), 118.7, 130.0, 131.3, 136.3, 136.6, and 146.9 (C_6H_4), 169.4 (C=O), 170.9 (C=O). ^{15}N VACP/MAS NMR: δ −322.7. ^{29}Si VACP/MAS NMR: δ −73.4. Anal. Calcd for $C_{12}H_{15}NO_4S_2Si$ (329.5): C, 43.75; H, 4.59; N, 4.25. Found: C, 43.72; H, 4.61; N, 4.55.

Preparation of [2-(Dimethylamino)phenyl]silane (8). A solution of [2-(dimethylamino)phenyl]trimethoxysilane[8] (5.00 g, 20.7 mmol) in diethyl ether (20 mL) was added dropwise at 0 °C over a period of 1 h to a stirred suspension of lithium aluminum hydride (786 mg, 20.7 mmol) in diethyl ether (20 mL). The resulting mixture was stirred at 20 °C for 18 h and then under reflux for a further 4 h. The remaining solid was filtered off and washed with diethyl ether (15 mL) and was then discarded. The filtrate and the wash solution were combined, the solvent was removed at 40 °C under normal pressure, and the residue was distilled under reduced pressure to give **8** in 79% yield as a colorless liquid (2.48 g, 16.4 mmol); bp 45−47 °C/6 mbar. ^{1}H NMR (C_6D_6): δ 2.56 (s, 6 H, NCH_3), 4.55 (s, 3 H, SiH), 6.98−7.71 (m, 4 H, C_6H_4). ^{13}C NMR (C_6D_6): δ 45.5 (NCH_3), 119.7, 124.4, 126.9, 131.9, 138.3, and 161.2 (C_6H_4). ^{29}Si NMR (C_6D_6): δ −63.9. Anal. Calcd for $C_8H_{13}NSi$ (151.3): C, 63.52; H, 8.66; N, 9.26. Found: C, 63.78; H, 8.33; N, 9.01.

---

(7) The hydrogen-bonding systems were analyzed by using the program system *PLATON*: Spek, A. L. *PLATON*; University of Utrecht: Utrecht, The Netherlands, 1998.

(8) Tacke, R.; Wiesenberger, F.; Lopez-Mras, A.; Sperlich, J.; Mattern, G. *Z. Naturforsch.* **1992**, *47b*, 1370−1376.

Crystal Structure Analyses. Suitable single crystals of **6** and **7** were isolated directly from the respective reaction mixtures. The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS diffractometer; graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods.[9] The non-hydrogen atoms were refined anisotropically.[10] A riding model was employed in the refinement of the C*H* hydrogen atoms. The N*H* hydrogen atoms were localized in difference Fourier syntheses and refined freely.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-286582 (**6**) and CCDC-286583 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM058032O

---

(9) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

(10) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.