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A Donor-Stabilized Silanethione or a Si-Substituted *N*-Heterocyclic Platinum Carbene?

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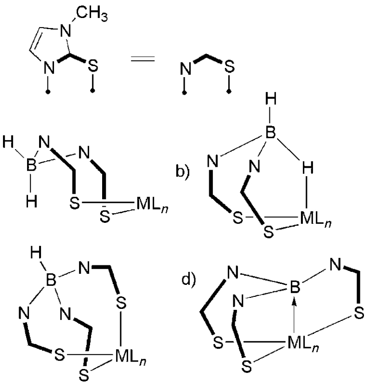
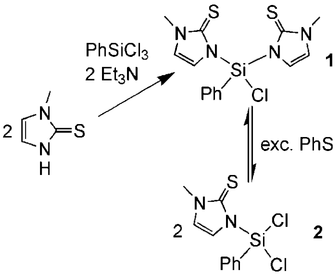
In recent years methimazole (2-mercapto-1-methylimidazole), methimazole-derived boranates and related systems have proven to be interesting ligands in transition-metal (TM) coordination chemistry (Scheme 1).[1] In particular, the first metallaboratranes were constructed with methimazolide acting as a hard–soft ambident buttressing moiety capable of stabilizing TM→B donor-acceptor interactions.[2] Although much effort has been directed towards exploring variations in the metal centre of poly(methimazolyl)borane and boranate complexes, little attention has been paid to the possibility of modifying the boron atom in these ligand systems other than replacement with carbon.[3] Bearing in mind the diagonal relationship between boron and silicon, it is therefore remarkable that no reports exist on the coordination chemistry of methimazolyl chelates based on silicon as the bridgehead atom.



Scheme 1. Coordination modes of a,b) bis(methimazolyl)boranates, c) tris(methimazolyl)boranates, and d) tris(methimazolyl)boranes.

We have therefore begun to explore both the synthesis and coordination chemistry of hitherto unknown methimazolylsilanes,[4] which has led through an unprecedented rearrangement process to the first N–Si-substituted *N*-heterocyclic carbene (NHC) complex. This unusual compound exhibits interesting structural features that suggest it might be described as a zwitterionic silicon substituted NHC complex or, alternatively, as a donor-stabilized silanethione.

As depicted in Scheme 2, the reactions of phenyltrichlorosilane and methimazole yielded the methimazolylsilanes **1** and **2**, the molecular structures of which were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy as well as single-crystal X-ray diffraction analysis.[5]



Scheme 2. Synthesis of methimazolylsilanes.

In an attempt to explore the reactivity of the Si–Cl bond in **2** towards low-valent metal centers, we have investigated its reaction with $[Pt(C_2H_4)(PPh_3)_2]$ but find that the product is not the simple Si–Cl oxidative addition product $[PtCl\{Si(mt)ClPh\}(PPh_3)_2]$. Rather, the Pt–Carbene complex **3** was obtained as pale yellow crystals, suitable for X-ray diffraction analysis (Scheme 3, Figure 1).[6]

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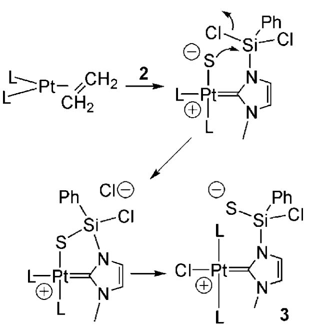


Scheme 3. Suggested mechanism for the reaction of **2** with $[Pt(CH_2{=}CH_2)L_2]$ (L = PPh_3).

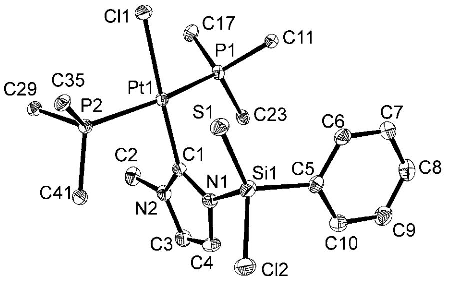
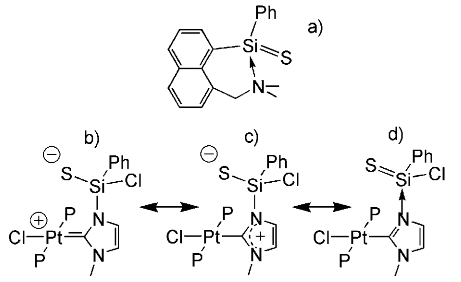


Figure 1. Molecular structure of one of the two crystallographically independent molecules of **3** in the crystal structure of **3**·THF.[6] (50% displacement ellipsoids; hydrogen atoms and phosphine phenyl groups omitted for clarity)

Compound **3** represents a Pt−Carbene complex with almost square planar coordination sphere around the Pt-atom (P1-Pt1-P2 164.79(2)°, Cl1-Pt1-C1 177.86(6)°). The structural features of the two crystallographically independent molecules are very similar; that based on Pt1 is discussed here. The phosphine ligands are *trans*-situated and the *N*-heterocyclic carbene ligand is, as expected, arranged perpendicular to the metal coordination plane of the Pt coordination sphere, the minimization of steric repulsion outweighing any modest electronic preference for in-plane coordination.[7] The bond length Pt1=C1 (1.992(2) Å) falls within the range typical of 4-coordinate platinum(II) carbene complexes.[8] Compound **3** exhibits a number of structural features of note: The square-planar Pt coordination sphere is lightly capped by atom S1 (Pt···S separation: 3.259(1) Å), the Si1−N1 bond (1.818(2) Å, noticeably longer than those in methimazolylsilanes **1** and **2**[5]) is comparable to those found in bis(trimethylsilyl)imidazolium bromide (mean 1.828(2) Å),[9] although the Si1−S1 bond (2.000(1) Å), is significantly shorter than the Si1−Cl2 bond (2.094(1) Å) and close to the Si=S bond lengths,[10] experimental data of which were reported by Kira (1.958(1) Å)[10a] and Okazaki (1.948(4) Å)[10b] for tricoordinate silanethiones. The presence of a further donor atom in donor-stabilized silanethiones causes a slight lengthening of the Si=S bond, as described by Corriu (Scheme 4a).[11] This suggests that contributions of various resonance structures to the bonding of **3** should be considered (Scheme 4b–d).



Scheme 4. a) A base-stabilized silanethione[11] and b–d) Canonical forms to describe **3**. In b) the Pt=C bond appears less important, whereas form c) accounts for the π-delocalization found along the NCN path and silanethione form d) accounts for the bond angles around the Si-atom, that is, the sum of the angles S-Si-Cl, S-Si-C, and Cl-Si-C (337.3°) is noticeably larger than expected for ideal tetrahedral coordination geometry (328.5°). Thus, the Si(Ph,S,Cl) environment can be regarded as 28% planarized.

Compound **3** is practically insoluble in solvents such as toluene, benzene, dichloromethane, chloroform and THF. Therefore, its ^{29}Si NMR shift was determined in the solid state (Figure 2).[12] In addition to the isotropic shift value characteristic of tetracoordinate silicon compounds ($\delta_{iso} = -2.7$ ppm) the remarkably large span of the signal ($\Omega = 256$ ppm) indicates a noticeable anisotropy of the contributions of the substituents to the shielding of the ^{29}Si nucleus,[13,14] hence indicating contributions of the silanethione canonical form to the overall bonding situation.

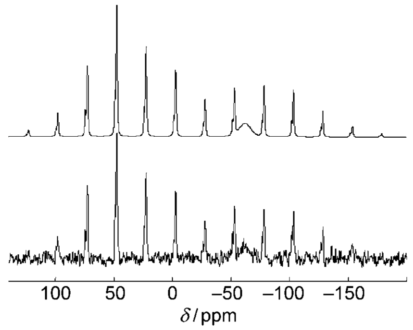
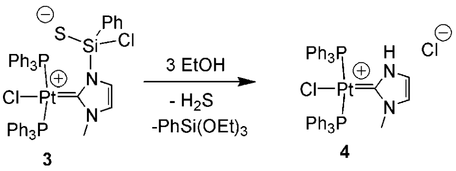


Figure 2. ^{29}Si CP/MAS NMR spectrum (top: fitted spectrum, bottom: experimental spectrum) of **3** at $\nu_{spin} = 2$ kHz. $\delta_{iso} = -2.7$, $\delta_{11} = 100.7$, $\delta_{22} = 46.4$, $\delta_{33} = -155.1$, $\Omega = 255.8$, κ 0.58.

The mechanism by which **3** forms under mild conditions remains speculative, however we note that zerovalent platinum reagents are capable of inserting into the C=S double bond of CS_2[15] and that thioureas[16] and imidazol-thiones[17] undergo C=S bond cleavage in the presence of, e.g., low-valent ruthenium. Thus, although terminal sulfido complexes of platinum have yet be isolated, a reactive intermediate of the form $[Pt({=}S)\{C(NMe)C_2H_2N(SiCl_2Ph)\}(PPh_3)_x]$ ($x = 1,2$) seems plausible and would be expected to display nucleophilic character at sulfur. The accessibility of hypervalent silicon geometries would then be expected to allow the exchange (concerted or ionic two-step) of sulfur and chloride between platinum and silicon sites to occur with ease, driven presumably by the thermodynamic preference for formation of a Pt−Cl bond over a Pt=S bond.

Treatment of **3** with "bench-top" (ethanol stabilized) chloroform, leads to the instant dissolution under formation of the solvolysis product **4** (Scheme 5), with H_2S evolution indicating the protolysis of the silanethione (or silanethiolate) moiety. The formation of colorless crystals of **4**·$(CHCl_3)_3$ provides easy access to this cationic N(*H*)-substituted carbene complex. Previously, only one N(*H*)-functionalized Pt-NHC complex had been structurally characterized,[18] joined now by **4**·$(CHCl_3)_3$ (Figure 3).[19]



Scheme 5.

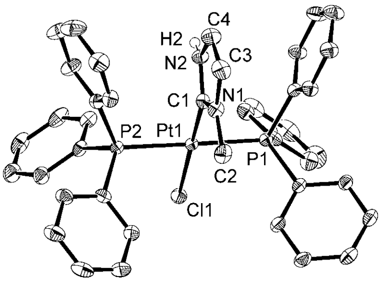


Figure 3. Molecular structure of the cation of **4** in a crystal of **4**·$(CHCl_3)_3$.[19] (50 % displacement ellipsoids; most hydrogen atoms omitted for clarity).

As in **3**, the triphenylphosphine ligands in **4** are *trans*-disposed with Pt−P bond lengths of 2.312(1) and 2.315(1) Å (cf **3**: Pt−P 2.306(1), 2.336(1) Å). As in **3** the plane of the carbene ligand is perpendicular to the nearly square planar Pt− Coordination sphere. Both the Pt−C (1.970(3) Å) and Pt−Cl (2.358(1) Å) bonds are noticeably contracted relative to those in **3** (1.992(2), 2.376(1) Å, respectively), which may be attributed to the loss of the weak sulfur-capping interaction that distorts the geometry of **3** towards 5-coordination with attendant bond elongation and platinum trigonal bipyramidalization.

In conclusion, oxidative addition of the first example of a methimazolylsilane to Pt^0 provided easy access to a novel *N*-silylated *N*-heterocyclic carbene complex. Compound **3** exhibited structural features consistent with a donor-stabilized silanethione, thus contributing to the pool of Si=X bonding patterns,[20] although its hydrolysis product **4** is a representative of the scarcely explored N(*H*)-substituted NHC class of complexes. The NH moiety of the latter may allow for further substitution reactions thus representing a convenient entrance into functionalized NHC coordination chemistry, the applicability of which is subject to further investigations.

Experimental Section

Syntheses were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk techniques and dry solvents. ^{1}H, ^{13}C, ^{29}Si, and ^{31}P solution NMR spectra were recorded by using a Varian INOVA 300 spectrometer using TMS as internal standard for ^{1}H, ^{13}C, ^{29}Si, and 85 % H_3PO_4 as external standard for ^{31}P. Elemental analyses were performed by the microanalytical services of the Research School of Chemistry, ANU, Canberra. Single crystal X-ray data were collected by using a NONIUS KappaCCD-diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved using SHELXS-97 (direct methods and Patterson method) and refined with full-matrix least-squares methods (refinement of F^2 against all reflections with SHELXL-97). All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were refined isotropically in idealized positions, except the N-bonded H-atom of **4** which was located from residual electron density and refined without restraints. CCDC 699124(**1**), 699123(**2**), 699125(**3**), and 699126(**4**) 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

Synthesis of compound 3: A solution of **2** (0.26 g, 0.90 mmol) in THF (3 mL) was stirred at 0 °C and a solution of $[Pt(C_2H_4)(PPh_3)_2]$ (0.67 g, 0.90 mmol) in THF (7 mL) was added drop-wise. The resulting yellow solution was then stored at room temperature. Within 36 h some white precipitate (some mg) had formed. The yellow solution was filter-cannulated into a new Schlenk flask and stored at room temperature for further 2 weeks during which time pale yellow crystals of **3**·THF formed. The solution was decanted, the crystals washed with THF (3 mL) and briefly dried in vacuo. Yield: 0.63 g (0.58 mmol, 65 %). ^{29}Si CP/MAS NMR (79.5 MHz, $\nu_{spin} = 2$ kHz) : $\delta_{iso} = -2.7$ ppm. elemental analysis calcd (%) for $C_{50}H_{48}Cl_2ON_2P_2PtSSi$: C 55.55, H 4.48, N 2.59, S 2.97, Cl 6.56; found: C 55.23, H 4.80, N 2.86, S 2.74, Cl 6.27.

Synthesis of compound 4: At room temperature **3** (0.32 g, 0.30 mmol) was dissolved in a mixture of reagent grade chloroform (3 mL) and 3 drops of methanol. Within 24 h **4**.$(CHCl_3)_3$ crystallized from this solution. The solution was decanted, the crystals washed with chloroform (0.3 mL) and dried in air. Yield: 0.23 g (0.19 mmol, 58 %); ^{1}H NMR (299.9 MHz, CD_2Cl_2): $\delta = 3.23$ (s, 3H; N-CH_3), 6.04 and 6.28 (2 m, 2H; N-CH=CH-N), 7.15–7.25 and 7.85–7.95 (2 m, 18 and 12H; phenyl), 14.46 ppm (s, broad, 1H; NH); ^{13}C NMR (75.4 MHz, CD_2Cl_2): $\delta = 37.2$ (N-CH_3), 120.5 (2 signals, N-CH=CH-N), 128.9, 131.3, 134.9, 135.1 (phenyl), 144.2 ppm (Pt=C), ^{31}P NMR (121.4 MHz, CD_2Cl_2): $\delta = 20.07$ ppm (^1J(Pt-P) = 2584 Hz). elemental analysis calcd (%) for $C_{43}H_{39}Cl_{11}N_2P_2Pt$: C 41.96, H 3.19, N 2.28; found: C 41.95, H 2.98, N 2.35.

Acknowledgements

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Keywords: carbenes · donor stabilization · oxidative addition · silanethione · silicon

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[5] Compounds **1** and **2** will be published and discussed in detail in another report. Syntheses and spectroscopic details in brief: **Compound 1**: A solution of methimazole (10.0 g, 87.7 mmol) and triethylamine (10.0 g, 99 mmol) in THF (120 mL) was stirred at 0 °C and phenyltrichlorosilane (9.30 g, 44.0 mmol) was added. After storing the mixture at 20 °C over night the precipitate of Et_3NHCl formed was filtered and washed with THF. Removal of the solvent from the filtrate and recrystallization of the crude product from toluene yielded colorless crystals of **1** and of the solvate **1**·toluene (both compositions found by single crystal X-ray structure analyses). The solution was decanted and the crystals briefly dried in a vacuum. Yield: 12.8 g **1**·(toluene)$_{0.25}$, composition determined by ^{1}H NMR (32.8 mmol, 75 %). ^{1}H NMR (299.9 MHz, $CDCl_3$): $\delta = 2.85$ (s, 6H; CH_3), 5.72 (d, ^3J(H,H) 2.4 Hz, 1H), 6.62 (d, ^3J(H,H) 2.4 Hz, 1H), 7.1–7.2 ppm (m, 3H), 8.2–8.3 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 33.8$, 119.0, 120.3, 127.9, 128.2, 132.2, 136.6, 169.9 ppm; ^{29}Si NMR (59.6 MHz, $CDCl_3$): $\delta = -28.5$ ppm. Crystal data for **1**·toluene: $C_{21}H_{23}ClN_4S_2Si$, $M_r = 459.09$, $T = 100(2)$ K, triclinic, space group P-1 (No. 2), $a = 7.2963(2)$, $b = 9.5355(3)$, $c = 17.0013(6)$ Å, $\alpha = 99.635(2)$ $\beta = 101.711(2)$ $\gamma = 94.944(2)°$, $V = 1133.01(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.346$ Mgm^{-3}, μ(Mo-K$_\alpha$) = 0.421 mm^{-1}, $F(000) = 480$, $2\theta_{max} = 58.0°$, 30102 collected reflections, 5993 unique reflections ($R_{int} = 0.0700$), 265 parameters, $S = 1.046$, $R_1 = 0.0471$ ($I > 2\sigma(I)$), wR_2(all data) = 0.1206, max./min. residual electron density +0.727/−0.404 e Å^{-3}. **Compound 2**: **1** (1.5 g, 3.8 mmol) was dissolved in phenyltrichlorosilane (5.0 g, 23.6 mmol) at 110 °C. After 3 min the solution was allowed to cool to room temperature whereupon **2** crystallized as colorless needles. After 5 days these crystals were filtered, washed with $PhSiCl_3$/hexane 1:1 (2 mL), $PhSiCl_3$/hexane 1:2 (3 mL) and hexane (2×2 mL) and dried in a vacuum. Yield: 1.1 g (3.8 mmol, 50 %). NMR spectra of solutions of **2** in $CDCl_3$ and C_6D_6 revealed decomposition under formation of **1** and $PhSiCl_3$. In THF, however, **2** appeared stable for an extended period of time (up to hours with less ligand scrambling). ^{29}Si NMR (59.6 MHz): $\delta = -17.0$ ($CDCl_3$), −17.5 (C_6D_6), −18.3 ppm (THF). Crystal data for **2**: $C_{10}H_{10}Cl_2N_2SSi$, $M_r = 289.25$, $T = 100(2)$ K, monoclinic, space group Cc, $a = 7.4317(2)$, $b = 24.7920(8)$, $c = 7.5343(2)$ Å, $\beta = 111.129(2)°$, $V = 1304.25(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.473$ Mgm^{-3}, μ(Mo-K$_\alpha$) = 0.723 mm^{-1}, $F(000) = 592$, $2\theta_{max} = 66.0°$, 12155 collected reflections, 4494 unique reflections ($R_{int} = 0.0498$), 146 parameters, $S = 1.048$, $R_1 = 0.0306$ ($I > 2\sigma(I)$), wR_2(all data) = 0.0765, max./min. residual electron density +0.253/−0.349 e Å^{-3}. Selected bond lengths [Å]: **1**: Si−Cl 2.038(1), Si−C 1.841(2), Si−N 1.751(2) and 1.752(2); **2**: Si−Cl 2.031(1) and 2.047(1), Si−C 1.840(2), Si−N 1.753(1).

[6] Crystal data for **3·THF**: $C_{50}H_{48}Cl_2N_2OP_2PtSSi$, $M_r = 1080.98$, $T = 100(2)$ K, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.6020(1)$, $b = 15.5442(1)$, $c = 24.1972(2)$ Å, $\alpha = 105.323(1)$ $\beta = 98.003(1)$ $\gamma = 90.505(1)°$, $V = 4521.76(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.588$ Mgm^{-3}, μ(Mo-K$_\alpha$) = 3.405 mm^{-1}, $F(000) = 2168$, $2\theta_{max} = 60.0°$, 153088 collected reflections, 26340 unique reflections ($R_{int} = 0.0513$), 1091 parameters, $S = 1.034$, $R_1 = 0.0249$ ($I > 2\sigma(I)$), wR_2(all data) = 0.0573, max./min. residual electron density +1.095, −1.922 e Å^{-3}.

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[12] ^{29}Si CP/MAS NMR measurements were carried out on a Bruker AVANCE 400 WB spectrometer using a 4 mm CP/MAS probe with zirconia rotor. The number of spinning sidebands for tensor evaluation was adjusted to an optimum value recommended by Hodgkinson and Emsley.[13a] Deconvolution of the spectra was done using DMFIT.[13b] The principal components of the chemical shift tensor were calculated from spinning sideband spectra using the program HBMAS (D.Fenzke, Universität Leipzig 1989). Data are given according to the Hertzfeld–Berger convention.[13c,d]

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[14] Whereas di-, tri- and pentacoordinate silicon compounds, such as silylenes, disilynes, disilenes, silenes and pentacoordinate silicon complexes, are known to exhibit remarkably large-span CSA tensors (**A**), the chemical shift anisotropy for silicon coordination spheres of higher symmetry, that is, tetrahedral and octahedral coordination, was found to be significantly smaller in many cases (**B**). For (**A**) see: a) J. D. Cavalieri, R. West, *J. Am. Chem. Soc.* **1993**, *115*, 3770–3771; b) R. West, J. D. Cavalieri, J. J. Buffy, C. Fry, K. W. Zilm, J. C. Duchamp, M. Kira, T. Iwamoto, T. Müller, Y. Apeloig, *J. Am. Chem. Soc.* **1997**, *119*, 4972–4976; c) R. West, J. J. Buffy, M. Haaf, T. Müller, B. Gehrhus, M. F. Lappert, Y. Apeloig, *J. Am. Chem. Soc.* **1998**, *120*, 1639–1640; d) J. J. Buffy, R. West, M. Bendikov, Y. Apeloig, *J. Am. Chem. Soc.* **2001**, *123*, 978–979; e) V. Kravchenko, R. Kinjo, A. Sekiguchi, M. Ichinohe, R. West, Y. S. Balazs, A. Schmidt, M. Karni, Y. Apeloig, *J. Am. Chem. Soc.* **2006**, *128*, 14472–14473; f) J. H. Iwamiya, G. E. Maciel, *J. Am. Chem. Soc.* **1993**, *115*, 6835–6842; g) T. Müller, *J. Organomet. Chem.* **2003**, *686*, 251–256; h) K. W. Zilm, D. M. Grant, J. Michl, M. J. Fink, R. West, *Organometallics* **1983**, *2*, 193–194; i) D. Gerlach, E. Brendler, T. Heine, J. Wagler, *Organometallics* **2007**, *26*, 234–240; j) J. Wagler, U. Böhme, E. Brendler, G. Roewer, *Z. Naturforsch. B* **2004**, *59*, 1348–1352; k) R. Bertermann, A. Biller, M. Kaupp, M. Penka, O. Seiler, R. Tacke, *Organometallics* **2003**, *22*, 4104–4110. For (**B**) see: l) M. R. Hansen, R. J. Jacobsen, J. Skibsted, *Inorg. Chem.* **2003**, *42*, 2368–2377; m) D. H. Brouwer, G. D. Enright, *J. Am. Chem. Soc.* **2008**, *130*, 3095–3105; n) R. K. Harris, T. N. Pritchard, E. G. Smith, *J. Chem. Soc. Faraday Trans.* **1989**, *85*, 1853–1860; o) R. West, J. D. Cavalieri, J. Duchamp, K. W. Zilm, *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *93/94*, 213–216; p) J. Wagler, U. Böhme, E. Brendler, S. Blaurock, G. Roewer, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2907–2913; q) G. W. Fester, J. Wagler, E. Brendler, U. Böhme, G. Roewer, E. Kroke, *Chem. Eur. J.* **2008**, *14*, 3164–3176; r) J. Wagler, U. Böhme,

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