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Synthesis and structural characterization of neutral hexacoordinate silicon(IV) complexes containing salophen and thiocyanato-*N* ligands

<https://doi.org/10.1515/mgmc-2017-0053>

Received November 14, 2017; accepted August 28, 2018; previously published online October 31, 2018

Abstract: The reaction of the H_2 salophen ligand, 2,2'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))diphenol, with one molar equivalent of $Si(NCS)_4$, $MeSi(NCS)_3$ (**13**), or $HMeSi(NCS)_2$ afforded neutral hexacoordinate silicon complexes, which have an-NCS bi-functionality (complex **1**) and mono-functionality (complex **14**). The reaction of $Si(NCS)_4$ with the H_2 salophen-type ligand 1,1'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene)) bis(naphthalen-2-ol) (H_2 Noph), afforded the hexacoordinate silicon complex **15**, which has an-NCS bi-functionality. Single-crystal X-ray structural and elemental analyses were used to characterize and confirm the structure of the starting material **13** and complexes **1**, **14**, and **15**. The complexes were characterized in solution by 1H , ^{13}C , and silicon-29 nuclear magnetic resonance (^{29}Si NMR) and in the solid state by ^{29}Si cross-polarization/magic angle spinning (CP/MAS) NMR. Because of the poor solubility of complex **1**, it was only possible to characterize it in the solid state by ^{13}C and ^{29}Si CP/MAS NMR and in solution by 1H NMR.

Keywords: ^{29}Si NMR spectroscopy; coordination chemistry; crystal structure; hexacoordinate silicon; salophen ligand; thiocyanato-*N* ligands.

Introduction

Bi-functional hexacoordinate silicon compounds played an important role as a building block for the preparation of novel oligosilanes containing hexacoordinate silicon backbones (Mucha et al., 1998, 1999; González-García et al., 2009) and as an initiator for ring-opening polymerization of ϵ -caprolactone (Lee et al., 2003). On the other hand, $Si(NCS)_4$ and $HMeSi(NCS)_2$ have proved to be useful starting materials for hypercoordinate silicon containing salen (Seiler et al., 2005; González-García et al., 2008, 2009, 2015), Schiff base (Seiler et al., 2007), and β -diketone ligands (Seiler et al., 2003; González-García et al., 2012) without adding an auxiliary base, such as triethylamine, which acts as a proton acceptor. In this work, the synthesis, single-crystal structure, and nuclear magnetic resonance (NMR) spectroscopy characterization of hexacoordinate silicon complexes containing salophen (**1** and **14**) or Noph (**15**) ligands and thiocyanato-*N* functional groups are reported. Complex **1** was previously prepared (Puri et al., 2009) starting from di-ethoxy di-thiocyanato-*N* silane, $(EtO)_2Si(NCS)_2$, and a H_2 salophen ligand (Scheme 1). However, the ^{29}Si NMR chemical shift at -132 ppm in a $CDCl_3$ /DMSO- D_6 solution for complex **1** appears to correspond to a pentacoordinate silicon species rather than a hexacoordinate one. Indeed, complex **1** contains two-NCS functional groups of silicon, and it is well-known that the NCS ligand causes a large displacement to higher field signals in the silicon-29 (^{29}Si) NMR chemical shift (Seiler et al., 2003). No further studies were performed to confirm the solution ^{29}Si NMR results, e.g. ^{29}Si solid-state NMR study or single-crystal X-ray analysis.

In this context, it is well known that the ^{29}Si NMR chemical shift is used as a tool to determine the silicon coordination number. Chart 1 shows selected examples of silicon compounds containing-NCS functionalities whose structure have been confirmed by a single-crystal X-ray diffraction analysis, and Table 1 shows the ^{29}Si chemical shift and the coordinating framework in the silicon center.

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Scheme 1: Synthesis of **1** starting from di-ethoxy di-thiocyanato-*N* silane, $(\text{EtO})_2\text{Si}(\text{NCS})_2$, and a $\text{H}_2\text{salophen}$ ligand.

Chart 1: Selected examples of silicon compounds containing-NCS functionalities whose structure have been confirmed by a single-crystal X-ray diffraction analysis.

Table 1: Selected examples of tetra-, penta-, and hexacoordinate silicon compounds containing-NCS functionalities showing the coordinating framework and ^{29}Si chemical shift.

Compound	Coordinating framework	^{29}Si solid-state NMR (ppm)	Reference
$\text{Si}(\text{NCS})_4$	SiN_4	-143.2	Seiler et al., 2003
$(O,N,O\text{-Schiff base})\text{Si}(\text{NCS})_2$	SiN_3O_2	-146.4	Seiler et al., 2007
$(N,N,O\text{-Schiff base})\text{MeSi}(\text{NCS})$	SiCN_3O	-107	González-García et al., 2008
$(N,N,O\text{-Schiff base})\text{MeSi}(\text{NCS})_2$	SiCN_4O	-172.9	González-García et al., 2008
$(O,N,N,O\text{-salen})\text{MeSi}(\text{NCS})$	SiCN_3O_2	-172.6	González-García et al., 2015
$(O,N,N,O\text{-salen})\text{Si}(\text{NCS})_2$	SiN_4O_2	-199.0; -209.3	González-García et al., 2009, 2015
$(O,N\text{-Schiff base})_2\text{Si}(\text{NCS})_2$	SiN_4O_2	-207.4; -204.3; -192.1	Seiler et al., 2005
$(O\text{-Schiff base})_2\text{Si}(\text{NCS})_4$	SiN_4O_2	-233.0	Seiler et al., 2005
$\text{Si}(\text{NCS})_6^{2-}$	SiN_6	-253.0; -256.5	Seiler et al., 2003

Results and discussion

The starting material methyltri(thiocyanato-*N*)silane, **13**, was synthesized in 70% yield by treatment MeSiCl_3 with three molar equivalent of NH_4SCN by following a

methodology reported (Voronkov and Dolgov, 1954), using toluene instead of benzene (Scheme 2).

The treatment of the $\text{H}_2\text{salophen}$ with one molar equivalent of $\text{Si}(\text{NCS})_4$, $\text{MeSi}(\text{NCS})_3$ or $\text{HMeSi}(\text{NCS})_2$ afforded complexes **1**, (salophen) $\text{Si}(\text{NCS})_2$, and **14**, (salophen)

Scheme 2: Synthesis of the starting material methyltri(thiocyanato-*N*)silane, **13**.

Scheme 3: Synthesis of complexes **1** and **14**.

Figure 1: ORTEP view of the asymmetric unit of the starting material **13** in crystal form.

Selected bond lengths [Å] and angles [°]: Si-N1 1.6994(19), Si-N2 1.705(2), Si-N3 1.7014(18), Si-C4 1.819(2); N1-Si-N2 105.94(9), N1-Si-N3 131.05(75), N1-Si-C4 112.95(9).

SiMe(NCS), with 59.0%, 45.0%, and 34.5% yields, respectively (Scheme 3).

Complex **15**, (Noph)Si(NCS)₂, was obtained analogously as complex **1** using 1,1'-(1*E*,1'*E*)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene)) bis(naphthalen-2-ol) (H₂Noph) (Abd-Elzaher, 2000) as the salophen-type ligand and Si(NCS)₄ as the starting material (yield 67%). The complexes **1** and **14** precipitated from the respective reaction mixture as yellow solids. A suitable crystal for the X-ray diffraction analysis of the starting material **13** was obtained by placing a neat sample at 10°C for 24 h. Figure 1 shows the asymmetric unit of **13** in the crystal structure. The starting material **13** displayed a distorted tetrahedral geometry and crystallized in a monoclinic system with the space group *P*2₁/*n*. Selected bond lengths for **13** are given in their figure caption.

Single crystals of complexes **1** and **14** were obtained by slow cooling in acetonitrile from 80°C to 20°C, while for complex **15**, a single-crystal was obtained by placing a saturated solution in a Schlenk tube at 55°C in an oven for

Figure 2: ORTEP view of the asymmetric unit of complex **1** in crystal form showing weak C-H...O intermolecular interactions.

Selected bond lengths [Å] and angles [°]: Si-O1 1.7093(13), Si-O2 1.7053(14), Si-N1 1.9183(17), Si-N2 1.9112(16), Si-N3 1.8375(17), Si-N4 1.8585(17), O1...H24a 2.54, O2...H24a 2.43; O1-Si-O2 89.94(7), O1-Si-N1 92.85(7), N1-Si-N2 82.69(7), O2-Si-N2 94.61(7), O1-Si-N2 174.67(8), O2-Si-N1 176.77(7), N3-Si-N4 174.75(8), C24-H24a...O1 123.8, C24-H24a...O2 175.9. All hydrogen atoms were refined and placed in idealized positions.

one night. Complexes **1** and **14** crystallized in a monoclinic system with the space groups *P*2₁/*c* and *P*2₁/*n*, respectively, while complex **15** crystallized in a triclinic system with the *P* $\bar{1}$ space group. The Si-coordination polyhedron for all complexes can be described as a distorted octahedron that maintains the-NCS functional group in a *trans* position in the coordination sphere with two-NCS functional groups for complexes **1** and **15** and one for complex **14**. In the asymmetric unit of the crystal structure of complex **1**, two molecules of acetonitrile solvent were present after the crystallization, and one molecule of CH₃CN showed weak C-H...O intermolecular interactions in the solid-state crystal structure (Figure 2), which can be best described as a larger type of electrostatic-based attractive force (Bakar

Figure 3: ORTEP view of the asymmetric unit of complex **14** in crystal form.

Selected bond lengths [Å] and angles [°]: Si-O1 1.7306(15), Si-O2 1.7292(15), Si-N1 1.9527(18), Si-N2 1.9592(16), Si-N3 1.921(2), Si-C21 1.895(2); O1-Si-O2 91.00(7), O1-Si-N1 92.64(7), N1-Si-N2 81.60(7), O2-Si-N2 93.31(7), O1-Si-N2 169.37(8), O2-Si-N1 170.06(8), N3-Si-C21 173.53(9).

Figure 4: ORTEP view of the asymmetric unit of complex **15** in crystal form.

Selected bond lengths [Å] and angles [°]: Si-O1 1.711(2), Si-O2 1.708(2), Si-N1 1.894(2), Si-N2 1.898(2), Si-N3 1.847(3), Si-N4 1.863(2); O1-Si-O2 93.59(10), O1-Si-N1 91.89(10), N1-Si-N2 82.54(10), O2-Si-N2 91.97(10), O1-Si-N2 174.31(11), O2-Si-N1 174.49(11), N3-Si-N4 175.75(12).

et al., 2017). The angle O1-Si-O₂ in complex **1** (89.9°) is significantly smaller with respect to that in complexes **14** (91.0°) and **15** (93.6°), this can be due to the attractive electrostatic force of the C-H₂4a...O1 and C-H₂4a...O₂ weak

intermolecular interactions. Complex **6** showed a similar weakly electrostatic interaction with another acetonitrile molecule in the asymmetric unit of the crystal structure (González-García et al., 2015).

Table 2: Summary of the crystallographic data and structure refinement results for compounds **1**, **13–15**.

	1	13	14	15
Formula	C ₂₆ H ₂₀ N ₆ O ₂ S ₂ Si	C ₄ H ₃ N ₃ S ₃ Si	C ₂₂ H ₁₇ N ₃ O ₂ Si	C ₃₀ H ₁₈ N ₄ O ₂ S ₂ Si
Formula mass (g mol ⁻¹)	540.69	217.36	415.53	558.69
Collection T (K)	150(2)	100(2)	293(2)	293(2)
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P2 ₁ /c	P2 ₁ /n	P2 ₁ /n	P $\bar{1}$
a (Å)	8.7274 (7)	7.6171(4)	8.3676(5)	8.7033(6)
b (Å)	21.9312 (10)	11.7556(6)	17.9978(9)	9.1667(9)
c (Å)	16.3230 (14)	10.5308(5)	13.5450(7)	17.4607(13)
α (deg)	90	90	90	104.453(8)
β (deg)	126.762 (13)	101.078(5)	103.461(5)	90.933(6)
γ (deg)	90	90	90	104.018(7)
V (Å ³)	2502.9 (3)	925.39(8)	1983.81(19)	1304.39(19)
Z	4	4	4	2
ρ (calcd) (Mg m ⁻³)	1.435	1.560	1.391	1.422
F(000)	1120.0	440.0	864.0	576.0
Crystal dimensions (mm)	0.4 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.1
2θ range (deg)	6.92–58.88°	6.94–52.74	6.47–52.74	6.65–52.75
No. of collected reflections	11 796	3952	9470	9684
No. of independent reflections/parameter	5787/336	1889/101	4052/263	5309/352
R _{int}	0.0305	0.0242	0.0251	0.0275
R ₁ (F) [F ² > 2σ(F ²)] ^a	0.0456	0.0340	0.0449	0.0568
wR ₂ (F ²) ^b (all data)	0.0995	0.0787	0.1060	0.1465
S ^c (all data)	1.043	1.076	1.034	1.051
Max./min. residual electron density (e Å ⁻³)	+0.35/−0.35	0.29/−0.31	+0.28/−0.23	+0.42/−0.29

^aR₁(F) = Σ(|F_o − |F_c||) / Σ|F_o| for the observed reflections [F² > 2σ(F²)].

^bwR₂(F²) = {Σ [w(F_o² − F_c²)²] / Σ w(F_o²)²}^{1/2}.

^cS = {Σ [w(F_o² − F_c²)²] / (n − p)}^{1/2}; (n = number of reflections, p = number of parameters).

As expected, for complex **14** (Figure 3), the Si-CH₃ and Si-NCS distances were significantly longer than the starting material **13**. In all the hexacoordinated silicon compounds, the Si-NCS distances were significantly shorter than the Si-N dative bonds.

The salophen ligand adopted a bowl conformation in the equatorial plane, which was more remarkable for complex **15** (Figure 4).

Selected bonds lengths for complexes **1**, **14**, and **15** are given in their figure captions. The crystal data and experimental parameters used for the crystal structure analyses of compounds **1**, and **13–15** are summarized in Table 2.

The ²⁹Si NMR chemical shift in the solid-state is at –200.4 ppm (Figure 5), and –177.1 and –202.3 ppm for complexes **1**, **14**, and **15**, respectively, which are consistent with a hexacoordinate silicon compound with SiN₄O₂ (**1** and **15**) and SiN₃O₂C (**14**) coordinating frameworks containing a salen-type ligand (González-García et al., 2009, 2015). The ¹³C CP/MAS NMR spectrum of complex **1** (see online-only supporting information) showed six signals, four in the aromatic region between 110 and 140 ppm and two for the imine carbons at approximately 160 ppm. The signals of NCS and the acetonitrile solvent were not detected, probably due by the coupling of the quadrupolar nucleus ¹⁴N and the loss of acetonitrile molecule during the cross-polarization/magic angle spinning (CP/MAS) NMR rotor spinning, respectively.

In the solution, ²⁹Si NMR analysis, complexes **14** and **15** showed signals at –167.1 and –187.9 ppm, respectively, which are consistent with hexacoordinate silicon species (Figure 6). Thus, the silicon atom maintained the hexacoordination in the DMSO-D₆ solution for both complexes.

Because of poor solubility, it was only possible to study complex **1** in solution by ¹H NMR in DMSO-D₆ and acetone-D₆. Freshly prepared samples of complex **1** in DMSO-D₆ and acetone-D₆ are shown in Figure 6. In both solvents, the ¹H NMR spectrum showed the presence of two resonance signals for the imine proton of the salophen ligand, which suggest the presence of **1** in a possible mixture of *trans*- and *cis*-isomers with a ratio of 1.00:0.75 and 1.00:0.22 in DMSO-D₆ and acetone-D₆ solution. A similar behavior was observed for complexes **14** and **15** in a DMSO-D₆ solution. Nevertheless, decomposition was observed for all three complexes in the DMSO-D₆ solution in a few days, as shown by the ¹H NMR analysis. In this context, further experimental and computational studies are needed to understand more clearly the nature of the possible stereoisomerization and decomposition process.

Figure 5: ²⁹Si CP/MAS NMR spectrum of complex **1**.

Figure 6: ²⁹Si spectra of complexes (A) **14** and (B) **15** in a DMSO-D₆ solution.

Conclusions

In this work was confirmed that complexes **1**, **14**, and **15** are hexacoordinate silicon compounds containing two thiocyanato-*N* functional or methyl groups in the *trans* position, and the salophen ligand is located at the equatorial plane in the crystal structure. Nevertheless, complex **1** was poorly soluble, which made studying it by ²⁹Si NMR in the solution state impossible. The analogous complexes **13** and **15** had good solubility in DMSO-D₆, which allowed us to confirm that both complexes maintained the hexacoordination of the silicon atom in a DMSO-D₆ solution by ²⁹Si NMR spectroscopy. The synthetic potential of MeSi(NCS)₃ (**13**) as starting material for neutral hexacoordinate silicon

complex was demonstrated. Complexes **1**, **14**, and **15** have the potential to be used as starting materials for the preparation of new neutral hexacoordinate silicon(IV) complexes using a substitution or condensation reaction with thiocyanato-*N* functionalities.

Experimental

General procedures

The reaction and manipulations were carried out under an inert atmosphere of ultra-high-purity nitrogen (99.999% Infracore, León, Guanajuato, Mexico) using standard Schlenk techniques. The organic solvents were dried and purified according to standard procedures and stored under nitrogen. Elemental analysis was carried out on PerkinElmer 2400 Series II CHNS/O Elemental Analyzer at the Chemistry Department of the Universidad de Guanajuato, Guanajuato, Mexico.

Nuclear magnetic resonance (NMR) analysis

The ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded at 25°C on a 400-MHz, 500-MHz NMR Bruker AvanceIII (Karlsruhe, Germany) or 600 NMR Varian/Agilent NMR spectrometer (Oxford Instruments, Oxfordshire, UK). DMSO- D_6 (99.9% D, Sigma-Aldrich, St Louis, MO, USA), CDCl_3 (99.8% D, Sigma-Aldrich, St Louis, MO, USA) and acetone- D_6 (99.9% D, Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA) were used as the solvents, and the chemical shifts (ppm) were determined relative to the internal residual signal of the solvent at 2.50, 7.26 and 2.05 ppm for $(\text{CHD}_2)_2\text{SO}$, CDCl_3 and $(\text{CHD}_2)_2\text{CO}$, respectively, for ^1H NMR and 39.05 and 77.16 ppm for ^{13}C NMR in DMSO- D_6 and CDCl_3 , respectively. Solid-state ^{13}C and ^{29}Si CP/MAS NMR spectra were recorded at 22°C on a Bruker Avance III HD 400 NMR (Karlsruhe, Germany) or Varian/Agilent 600 NMR spectrometer (Palo Alto, CA, USA). Rotors of ZrO_2 were used with 4.0 mm of diameter, $\pi/2$ pulse of 2.0 μs , 1.0 ms of contact time, and 5.0 s of recycling delay. Chemical shifts (ppm) were determined relative to the external adamantane (38.4 ppm) and talc (−90.0 ppm) and were spun at 9 kHz and 7 kHz for ^{13}C and ^{29}Si CP/MAS, respectively.

Single-crystal X-ray diffraction analysis

Suitable single crystals for X-ray single-crystal structural analysis were obtained by slow cooling from 80°C to 20°C of a clear acetonitrile solution of the complexes **1** or **14**. For complex **15**, a saturated solution was placed at 55°C inside an oven for one night. A single crystal for the starting material **13** was obtained from placing a neat sample at 10°C for 24 h. The crystals were mounted in an inert oil (perfluoroalkyl ether) on a SuperNova single source at the offset EosS2 diffractometer (Rigaku Oxford Diffraction, Oxfordshire, UK). The crystals were kept at 150(2) (complex **1**), 100(2) (**13**), or 293(2) K (complexes **14** and **15**) during data collection. Using Olex2 (Dolomanov et al., 2009), the structures were solved with the ShelXT (Sheldrick, 2015a) structure solution program using direct methods and refined with the ShelXL (Sheldrick, 2015b) refinement package using least squares minimization.

Synthesis of complex 1

A 0.5-g (1.7 mmol) sample of $\text{H}_2\text{salophen}$ was added to a stirred suspension of 0.4 g (1.6 mmol) of $\text{Si}(\text{NCS})_4$ in acetonitrile (20 mL). The reaction mixture was stirred for 24 h at room temperature producing a yellow solid that was dissolved by the appropriated amount of acetonitrile, and the solution was heated to ca. 80°C to obtain a clear solution then filtered. By slowly cooling it to 20°C, the yellow crystals that formed were filtered off, washed with 20 mL of diethyl ether, and dried under vacuum (0.1 mbar, 4 h). Yield: 0.5 g (0.9 mmol), 59.0%. Mp: decomposition over 270°C. Anal. Calc. $\text{C}_{26}\text{H}_{20}\text{N}_6\text{O}_2\text{S}_2\text{Si}$ (540.69): C, 57.76; H, 3.73; N, 15.54; S, 11.86. Found: C, 57.83; H, 3.78; N, 15.58; S, 11.77%.

^1H NMR (600 MHz, acetone- D_6) δ 9.54 (s, 1H), 8.25 (dd, $J=6.2$, 3.3 Hz, 1H), 7.84 (dd, $J=7.8$, 1.7 Hz, 1H), 7.77–7.73 (m, 2H), 7.16–7.13 (m, 1H), 7.10 (d, $J=8.4$ Hz, 1H); ^1H NMR (500 MHz, DMSO- D_6) δ 9.70 (s, 1H), 9.61 (s, 1H), 8.28–8.19 (m, 2H), 7.92 (dd, $J=7.7$, 1.5 Hz, 1H), 7.84 (dt, $J=5.6$, 2.8 Hz, 1H), 7.83–7.79 (m, 1H), 7.76 (dd, $J=8.1$, 6.4 Hz, 3H), 7.26–7.21 (m, 2H), 7.17 (t, $J=7.4$ Hz, 1H), 7.12 (t, $J=8.0$ Hz, 1H). ^{13}C CP/MAS δ 115.84, 121.66, 132.48, 138.93, 157.87, 160.26. ^{29}Si CP/MAS δ −200.4.

Synthesis of 13

Trichloro(methyl)silane (99%, Sigma-Aldrich, St Louis, MO, USA) 15.0 g (100 mmol) was added at 20°C to a stirred suspension of ammonium thiocyanate (97.5%, Sigma-Aldrich, St Louis, MO, USA), 23.0 g (300 mmol) in 100 mL of toluene. The reaction was refluxed for 4 h; after that, the mixture was cooled to 20°C; the resulting precipitate was filtered off and discarded. The solvent was distilled at normal pressure, and the residue was distilled *in vacuo* to give a colorless liquid (b.p. 84°–86°C, 0.2 mbar). Yield: 15.2 g (70 mmol) 70.0%. Anal. Calc. for $\text{C}_4\text{H}_3\text{N}_3\text{S}_3\text{Si}$ (217.36): C 22.10 H 1.39 N 19.33 S 44.25. Found: C 22.43 H 1.43 N 19.82 S 43.91. ^1H NMR (400 MHz, CDCl_3) δ 0.71 (s). ^{13}C NMR (101 MHz, CDCl_3) δ 143.91 (broad), 0.23. ^{29}Si NMR (79 MHz, CDCl_3) δ −74.5 (broad).

Synthesis of complex 14

Synthesis (a) A 0.9-g (2.8 mmol) sample of $\text{H}_2\text{salophen}$ was added to a solution of 0.6 g (2.7 mmol) of $\text{MeSi}(\text{NCS})_3$ in acetonitrile (20 mL). The reaction mixture was left undisturbed at room temperature for 24 h to produce a yellow crystalline solid. The yellow crystals that formed were filtered off, washed with 20 mL of diethyl ether, and dried under vacuum (0.1 mbar, 4 h). Yield: 0.7 g (1.4 mmol), 45.0%. Mp: decompose over 190°C. Anal. Calc. $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_2\text{SSi}$ (415.54): C, 69.88; H, 4.10; N, 8.15; S, 6.22. Found: C, 69.92; H, 4.13; N, 8.27; S, 6.27%. ^1H NMR (500 MHz, DMSO- D_6) δ 9.44 (s, 2H), 8.20 (dd, $J=6.1$, 3.4 Hz, 2H), 7.80 (d, $J=7.7$ Hz, 2H), 7.71–7.65 (m, 4H), 7.08 (dd, $J=15.2$, 7.8 Hz, 4H), −0.10 (s, 3H). ^{13}C NMR (126 MHz, DMSO- D_6) δ 160.37, 159.59, 138.72, 135.30, 134.19, 130.70, 130.19, 120.44, 119.86, 117.68, 117.66, 9.94. ^{29}Si NMR (99 MHz, DMSO- D_6) δ −167.1. ^{29}Si CP/MAS NMR δ −177.1.

Synthesis (b) A 1.1-g (3.4 mmol) sample of $\text{H}_2\text{salophen}$ was added to a solution of 0.5 g (3.3 mmol) of $\text{HMeSi}(\text{NCS})_2$ in acetonitrile (20 mL). The reaction mixture was stirred for 24 h at room temperature to produce a yellow solid. The solution was heated to ca. 80°C and then filtered to obtain a clear solution. By slowly cooling it to 20°C, the yellow crystals

that formed were filtered off, washed with 20 mL of diethyl ether, and dried under vacuum (0.1 mbar, 4 h). Yield: 0.5 g (1.1 mmol), 34.5%.

Synthesis of complex 15

A 0.27-g (0.65 mmol) of H_2Noph was added to a stirred suspension of 0.16 g of $Si(NCS)_4$ (0.61 mmol) in 20 mL of acetonitrile. The reaction mixture was stirred for 24 h at room temperature to produce a solid orange precipitate, which was placed at 55°C inside an oven for one night. The orange crystals that formed were filtered off, washed with 10 mL of diethyl ether, and dried under vacuum (0.1 mbar, 4 h). Yield 0.23 g (0.41 mmol), 67%.

Mp: decompose over 200°C. Anal. Calc. $C_{30}H_{18}N_4O_2S_2Si$ (558.71): C, 64.49; H, 3.25; N, 10.03; S, 11.48. Found: C, 64.33; H, 3.24; N, 10.12; S, 11.31%.

1H NMR (500 MHz, $DMSO-D_6$), mixture of *trans*- and *cis*- isomers. δ 9.71 (s, 1H), 9.37 (s, 1H), 8.55 (t, $J=12.2$ Hz, 1H), 8.26 (t, $J=10.0$ Hz, 1H), 8.02 (d, $J=27.2$ Hz, 2H), 7.92 (t, $J=9.8$ Hz, 1H), 7.88–7.80 (m, 1H), 7.67–7.52 (m, 2H), 7.51–7.42 (m, 1H), 7.38 (t, $J=7.4$ Hz, 2H), 7.25–7.16 (m, 2H), 7.09 (d, $J=9.1$ Hz, 1H), 6.83 (d, $J=8.9$ Hz, 1H). ^{13}C NMR (126 MHz, $DMSO-D_6$) δ 168.19, 163.12, 157.68, 152.02, 139.83, 138.39, 136.94, 133.63, 132.98, 131.74, 129.67, 129.26, 128.99, 128.76, 128.55, 128.42, 128.22, 127.51, 127.10, 126.93, 124.22, 124.01, 123.69, 121.70, 121.23, 120.70, 120.51, 119.83, 116.79, 109.20, 108.77. ^{29}Si NMR (99 MHz, $DMSO-D_6$) δ –187.9. ^{29}Si CP/MAS NMR δ –202.3.

Supplementary data

Data from the X-ray crystallographic analyses of complexes **1**, **14**, **15** and the starting material **13**, $MeSi(NCS)_3$ are available in a crystallographic information file (CIF) under CCDC No: 1534652, 1584246, 1584247, and 1862266, respectively. Online-only supplement: 1H , $^{13}C\{^1H\}$ and ^{29}Si NMR spectra of **13**; 1H NMR in the solution state and ^{13}C NMR in the solid-state CP/MAS spectra of **1**.

Acknowledgments: Financial support from the Universidad de Guanajuato by the project CIIC 1,105/2016 is acknowledged. The authors acknowledge the Laboratorio Nacional de Caracterización de Propiedades Físicoquímicas y Estructura Molecular (CONACYT-México, Project: 123732) and the Laboratorio de Cristalografía – Difracción de Rayos X de Monocristal (CONACYT-INFRA-2014-01-225496) for NMR and single-crystal diffraction analyses, respectively.

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Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/mgmc-2017-0053>).