Polyhedron 41 (2012) 127-133

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Pentacoordinate mono(β -diketonato)- and hexacoordinate *bis*-(β -diketonato)-silicon(IV) complexes obtained from (thiocyanato-*N*)hydridosilanes

Gerardo González-García^a, Eleuterio Álvarez^b, J. Alfredo Gutiérrez^{a,*}

^a Departamento de Química, Universidad de Guanajuato, Noria Alta s/n, 36050 Guanajuato, Gto., Mexico ^b Instituto de Investigaciones Químicas, CSIC – Universidad de Sevilla, Avda. Américo Vespucio, 49, Isla de La Cartuja, 41092 Sevilla, Spain

ARTICLE INFO

Article history: Received 12 December 2011 Accepted 25 April 2012 Available online 7 May 2012

Keywords: Silicon Hypercoordinate Hydridosilanes (Thiocyanato-N)silanes β-Diketones

ABSTRACT

Three novel neutral hypercoordinate silicon(IV) complexes containing the O,O'-donor deprotonated β -diketone ligands 1,3-diphenylpropane-1,3-dione (**HL**¹) and 1-phenylbutane-1,3-dione (**HL**²) were synthesized starting from the hitherto unknown diphenyl(thiocyanato-N)silane [HPh₂Si(NCS)] and methyldi(thiocyanato-N)silane [HMeSi(NCS)₂], a class of silicon source with Si-NCS and Si-H reactive functionalities. The reaction of HL¹ with the new starting material HPh₂Si(NCS) only afforded a neutral pentacoordinate silicon complex containing one β -diketonato ligand coordinated in a bidentate fashion (complex 16). The reaction of HL^1 and HL^2 with HMeSi(NCS)₂ yielded *bis*- β -diketonato neutral hexacoordinate silicon complexes (17 and 18, respectively). The three compounds 16-18 were characterized using solution ¹H, ¹³C and ²⁹Si INEPT NMR and FT-IR spectroscopies, and compounds **17** and **18** were also studied using solid-state ²⁹Si CP/MAS NMR. Elemental analysis and single-crystal X-ray diffraction were used to establish the composition and the structure of all of the new complexes. The ²⁹Si INEPT NMR solution studies confirmed that compounds 16-18 maintain the same hypercoordination in solution that they have in the solid state. Compound 16 has a SiO_2NC_2 coordinating framework and represents the first example of a pentacoordinate silicon β -diketonato whose X-ray single crystal structure has been elucidated, and compounds 17 and 18 are the first neutral, non-zwitterionic, hexacoordinate silicon complexes with a SiO₄NC coordinating framework bearing only one –NCS functionality. The usefulness of the (thiocyanato-N)hydridosilanes HPh₂Si(NCS) and HMeSi(NCS)₂ as starting materials for the preparation of hypercoordinate organosilicon complexes is confirmed.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

The chemistry of hypercoordinate β -diketonato silicon(IV) complexes encompasses compounds containing one [1], two [2–14] and three [15,16] β -diketonato ligands. This type of compound has been known since Dilthey reported the reaction of silicon tetrachloride with acetylacetone (Hacac) to obtain the cationic hexacoordinate complex *tris*-(acetylacetonato), [Si(acac)₃]⁺ (1), more than one hundred years ago [15]. The family of hypercoordinate silicon β -diketonates has continued to grow [1,14]; however, only hexacoordinate complexes have been structurally characterized using single crystal X-ray diffraction [1,10–14] (see below), and no examples of pentacoordinate silicon β -diketonates have been studied with this technique. In fact, for several years, hypercoordinate silicon β diketonates have been characterized mainly with the help of IR and UV–Vis spectroscopies, elemental analyses [2–5,7–9] and, in some cases, ¹H or ¹³C NMR [3b,4,7], molecular weight determinations [3,8,9] and mass spectrometry [8,9]. Thus, several structural features of these compounds remain unknown. It was only in relatively recent times that silicon complexes began to be systematically studied by means of solution ²⁹Si NMR spectroscopy: Cella et al. concluded that this analytical tool is very powerful for determining the coordination number in silicon compounds after analyzing several previously synthesized penta- and hexa-coordinate silicon complexes and a number of new hypercoordinate silicon complexes that they had prepared [6].

A search in the Cambridge Structural Data Base (CSD) revealed that the first X-ray crystal structures for silicon β -diketonatos were reported from 1979 to 1993, and these structures correspond to several examples of the hexacoordinate cation [Si(acac)₃]⁺ (1), which only differs in the counterion (ClO₄⁻, C₁₂H₄N₄⁻, HCl₂⁻ and Ag₂Cl₄²⁻) [16]. In addition to **1** [16], the CSD showed that the hexacoordinate compounds **2** [10], **3** [11], **4** [12], **5** [13], **6**, **7** [14] and **8–10** [1] (Chart 1) are the only silicon β -diketonates that have been studied using X-ray single crystal diffractometry.





^{*} Corresponding author. Tel./fax: +52 473 732 0006x8134. *E-mail address:* jagutier@ugto.mx (J.A. Gutiérrez).

^{0277-5387/\$ -} see front matter @ 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2012.04.030



Chart 1. Silicon(IV) β-diketonates studied by single-crystal X-ray diffraction.

In the first studies with silicon β -diketonatos, it has been observed that silicon acetylacetonato complexes are prone to decomposition [2,4,5] or the production of silicon dienolates [7,17]; these problems can be circumvented by using β -diketone-bearing groups without enolizable protons, such as dibenzoylmethane (1,3diphenylpropane-1,3-dione) [3c,5,7,13] 2-thenoyltrifluoroacetone [4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione] [3c] and dipivaloylmethane (2,2',6,6'-tetramethylheptane-3,5-dione) [12]. Another strategy to stabilize the silicon B-diketonatos is to increase the Lewis acidity of the silicon atom with the use of electron-withdrawing groups [18] such as chloro [2], carboxylatos [3,13,14], alkoxides [14] and catecholatos [9] as well as *N*-thiocyanato (-NCS) [8,10] and N-cyanato (-NCO) [11] anions. Tacke et al. have demonstrated the high synthetic potential of Si(NCO)₄ and Si(NCS)₄ as starting materials for the synthesis of hypercoordinate silicon complexes [10,11] because the –NCX ligands (X = O, S) are able to easily stabilize the hypercoordination of the silicon center (as was observed earlier by Narula in the case of –NCS [8]), but they are also good as leaving groups; thus, the hexacoordinate *bis*-(β -diketonato) complexes 2 [10] and 3 [11] (Chart 1) can be obtained from Si(N-CO)₄ and Si(NCS)₄, respectively. In this regard, we recently reported the preparation of (thiocyanato-N)hydridosilane, HMeSi(NCS)₂ (**11**) [19], which contains a labile Si-H functionality in addition to Si-NCS bonds, making it a suitable reagent for nucleophilic substitution at the silicon center with byproducts that are easily eliminated. We demonstrated the usefulness of **11** in the preparation of neutral penta- and hexacoordinate silicon complexes with SiON₃C and SiON₄C coordinating frameworks by its reaction with tridentate N,N,O-donor Schiff base ligands (12 and 13, respectively; Scheme 1) [19] as well as a silicon complex with a SiO_2N_3C coordinating framework (14, Scheme 1) by the reaction of 11 with a salen-type ligand [20]. In fact, one can consider that the hydridosilane functionality, Si-H, provides a strong base (H⁻) that easily and cleanly abstracts acidic protons from the β -diketone ligands (see below), thus avoiding the use of bases such as pyridine [2], triethylamine [17] or imidazole, which may give rise to complex reactions in the presence of β -diketones [7], or other strategies that require the prior preparation of a deprotonated derivative of the β-diketone [1,2,5,12,21].

To the best of our knowledge, no structural information has been reported for pentacoordinate silicon β -diketonato complexes [5,6]. Therefore, we are now reporting the preparation and detailed characterization of the first example of this type of compound, starting from the hitherto unknown silane HPh₂Si(NCS) (**15**). We also report the synthesis and X-ray crystal structure of two new neutral *bis*- β -diketonato hexacoordinate silicon complexes, which were prepared from the already known silane reagent HMe-Si(NCS)₂ (**11**) [19,20] and which, like **15**, also contain the useful Si-H functionality.

2. Results and discussion

The new starting material, diphenyl(thiocyanato-*N*)silane [HPh₂Si(NCS), **15**] was obtained as a colorless liquid in 64% yield by treating HPh₂SiCl with an excess of NH₄NCS (25%). Complex **15** reacts with the β -diketone ligand **HL**¹ (1,3-diphenylpropane-1,3-dione) only via the Si–H functionality to yield complex **16** (Scheme 1) in a 44% yield as a yellow crystalline solid and H₂ as a byproduct (evidenced by a pressurization of the reaction vessel and the explosive combustion of a small balloon filled with the gas liberated). Complex **16** was the only silicon complex isolated from this reaction in spite of the fact that two equivalents of the β -diketone were added without displacement of the Si–NCS functional group that could yield the *bis*- β -diketonato silicon complex Ph₂Si(L¹)₂ (Scheme 2), which is an analog of the previously reported Ph₂Si(acac)₂ [7].

Complex **16** crystallizes in the space group *Pc* with two independent molecules in the asymmetric unit. The silicon coordination polyhedron is a nearly perfect trigonal bipyramid (TBP) with 98.9% of ideal TBP [22]. The maximum deviations from the ideal 90° and 180° angles of **16** are $4.26(7)^{\circ}$ and $4.34(7)^{\circ}$, respectively. The sum of the bond angles around the Si1 atom, which form the equatorial plane (C16, C22, O2), is 359.93(8)°. The structure complex **16** is depicted in Fig. 1, and the crystal data and the experimental parameters used for the crystal structure analysis are summarized in Table 1.

In the TBP complex 16, the silicon atom is coordinated in the equatorial positions by two phenyl ligands (Si1-C16, Si1-C22) and one oxygen in the β -diketonato ligand (Si1–O2), whereas the axial positions are occupied by the thiocyanato-N ligand (Si1-NCS) and the second oxygen in the β -diketonato ligand (Si1–O1). As expected, the Si1–O1 bond in the axial position [1.8792(13)] is significantly longer than the Si1-O2 bond in the equatorial position [1.6957(14)]. The two molecules in the asymmetric unit of complex **16** show intermolecular π - π and H··· π interactions (see supplementary information for details), but these molecules are not structurally identical. A slight difference in the dihedral angle of one phenyl ring of the order of 28.99(9)°, probably either to avoid intermolecular steric hindrance or to increase the aromatic interactions (edge-to-face or offset stacked orientations), is enough to break the inversion symmetry for this structure; the former situation originates that complex 16 crystallizes in a non-centrosymmetric space group (Pc).

In a CDCl₃ solution, the ²⁹Si INEPT NMR spectrum of a sample of **16** in a sealed tube under high vacuum exhibits only one sharp signal at δ –99.9, which indicates that this pentacoordinate silicon(IV) complex exists only as one diastereomer in this solvent at room temperature. The ²⁹Si NMR signal of **16** is shifted significantly upfield (*ca.* 70 ppm) with respect to the starting material **11**, which is consistent with a strong O–Si–O coordination by the β -diketonato ligand. Attempts to study **16** using solid state ²⁹Si NMR failed; although the sample for the NMR measurements was prepared under a N₂ atmosphere, two signals developed at δ –109.7 (broad) and δ –38.9 (sharp) during the first minutes of the spectral



Scheme 1. Preparation of some hypercoordinate silicon complexes from (thiocyanato-N)hydridosilanes as silicon sources.



Scheme 2. Preparation of diphenyl(thiocyanato-*N*)silane (**15**) and its reaction with 1,3-diphenylpropane-1,3-dione (**HL**¹).



acquisition, indicating the fast decomposition of **16**, probably catalyzed by traces of oxygen or water. The ²⁹Si chemical shift of complex **16** is similar to that of analogous neutral pentacoordinate silicon complexes with a SiO_2NC_2 skeleton containing *O*,*N*,*O*-donor Schiff base ligands and two phenyl [23–25] or two vinyl ligands [25].

Compound **16** could be considered to be a stable intermediate species in a nucleophilic substitution reaction to produce *bis*-(β -diketonato)hexacoordinate silicon compounds (see below); the Si–NCS functionality that is present in **16** could be useful in further condensation [20,26,27] or substitution [14,28–31] reactions to prepare novel hypercoordinate silicon compounds.

The reaction of one equivalent of $HMeSi(NCS)_2$ (11) with two equivalent of 1,3-diphenylpropane-1,3-dione (HL^1) or 1-phenylbutane-1,3-dione (HL^2) at 25 °C in acetonitrile leads to the formation of the neutral hexacoordinate silicon(IV) complexes 17 and 18 in 70% and 73% yield, respectively (see Scheme 3). All the compounds here reported are very reactive making difficult the obtainment of

Fig. 1. ORTEP view of compound **16** drawn at the 50% probability level. The crystallographic asymmetric unit presents two independent molecules of compound **16** which only differ slightly in the dihedral angle of one phenyl ring; only one independent molecule is shown. The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–N1 1.8716(17), Si1–O1 1.8792(13), Si1–O2 1.6957(14), Si1–C16 1.8641(19), Si1–C22 1.8664(19), N1–C28 1.163(2), S1–C28 1.6160(18); N1–Si1–O1 175.74(7), O2–Si1–C16 116.73(8), O2–Si1–C22 121.85(8), C16–Si1–C22 121.34(8), C28–N1–Si1 173.51(16), N1–C28–S1 179.70(18), O2–Si1–N1 85.66(7), C16–Si1–N1 93.99(7), C22–Si1–N1 92.96(8), O2–Si1–O1 90.31(6), C16–Si1–O1 89.07(7), C22–Si1–O1 87.98(7).

good elemental analyses; this was particularly hard in the case of compound **17** (see Section 4).

The molecular structures of **17** and **18** in a crystal are shown in Figs. 2 and 3, respectively; selected bond distances and angles are given in the figure legends. The crystal data and the experimental parameters used for the crystal structure analyses of **17** and **18** are given in Table 1. Both complexes crystallize in the space group $P2_1/c$.

Table	1
Table	

Summary of the crystallographic data and structure refinement results for 16-18.

Complexes	16	17	18
Complexes Formula Formula mass (g mol ⁻¹) Collection T (K) λ (Mo K α) (Å) Crystal system Space group a (Å) b (Å) c (Å) β (°) V (Å ³) Z ρ (Calc.) (Mg m ⁻³) F (000) Crystal dimensions (mm) θ range (°) No. of collected reflections No. of independent reflections/parameters	16 $C_{28}H_{21}NO_2SSi$ 463.61 $100(2)$ 0.71073 monoclinic Pc $13.6456(6)$ $10.6108(6)$ $17.5293(10)$ $112.184(2)$ $2350.2(2)$ 4 $0.50 \times 0.40 \times 0.30$ $3.25-31.85$ 39705 $12.211/595$	$\begin{array}{c} \textbf{17} \\ \hline C_{32}H_{25}NO_4SSi \\ 547.68 \\ 100(2) \\ 0.71073 \\ monoclinic \\ P_{2,1}/c \\ 14.7078(9) \\ 9.8037(6) \\ 19.9540(12) \\ 108.146(2) \\ 2734.1(3) \\ 4 \\ 1.331 \\ 1144 \\ 0.54 \times 0.50 \times 0.26 \\ 2.91-30.91 \\ 33822 \\ 8584/353 \\ \hline \end{array}$	18 $C_{22}H_{21}NO_4SSi$ 423.55 $100(2)$ 0.71073 monoclinic $P_2, /c$ $12.8759(7)$ $14.4162(8)$ $11.6962(7)$ $109.579(2)$ $2045.5(2)$ 4 1.375 888 $0.50 \times 0.16 \times 0.11$ $2.33-30.57$ 45448 $6259/265$
$R_{\text{int}} = R_{*}(F) \left[F^{2} > 2\sigma(F^{2})\right]^{a}$	0.0399	0.0484	0.0708
$ \begin{array}{l} \kappa_{\text{int}} \\ R_1(F) \left[F^2 > 2\sigma(F^2) \right]^a \\ \qquad $	0.0399	0.0484 0.0436 0.1202	0.0708
S^{c} (all data) max/min residual electron density (e Å ⁻³)	1.060 +0.388/-0.346	1.002 0.384 and -0.368	1.024 0.416 and -0.477

^a $R_1(F) = \sum_{i} (|F_0| - |F_c|) / \sum_{i} |F_0|$ for the observed reflections $[F^2 > 2\sigma(F^2)]$. ^b $wR_2(F^2) = \{\sum_{i} [w(F_0^2 - F_c^2)^2] / \sum_{i} w(F_0^2)^2\}^{1/2}$. ^c $S = \{\sum_{i} [w(F_0^2 - F_c^2)^2] / (n - p)\}^{1/2}$; (*n* = number of reflections, *p* = number of parameters).



Scheme 3. Reaction of methyldi(thiocyanato-N)silane (15) with 1,3-diphenylpro pane-1,3-dione (HL¹) and with 1-phenylbutane-1,3-dione (HL²).

The Si-coordination polyhedron for the two neutral hexacoordinate silicon complexes 17 and 18 can be described as a distorted octahedron with a SiO₄NC coordinating framework with two βdiketonato ligands located in a relative cis position. As expected, the Si-C and Si-N distances, as well as the analogous angles and Si-O distances in the coordinating framework for complexes 17 and 18, are quite similar; for instance, the shorter Si-O distance for both complexes is that for a Si-O bond trans to another Si-O bond (Si1-O1 1.7883 Å for 17 and Si1-O2 1.7858 Å for 18); similarly, the angles formed by the O-Si-C trans bonds are O(2)-Si(1)-C(32) 177.90(7) for 17 and O(1)-Si(1)-C(21) 176.92(9) for 18, and the angles of the O-Si-N trans bonds are O(4)-Si(1)-N(1) 175.13(6) for **17** and O(4)–Si(1)–N(1) 171.03(9) for **18**. In the case of the complex with the unsymmetrical β-diketonato ligand (18. see Fig. 3), it can be observed that each pair of analogous groups on the two β -diketonato ligands (phenyl groups or methyl groups), are mutually located in a relative *cis* position with respect to the silicon center.

The FT-IR signals of the C–N stretching mode of the N-thiocyanato ligands in the hexacoordinate silicon complexes 16, 17 and 18 appear at 2099, 2085 and 2113 cm⁻¹, respectively, and are shifted to higher energy with respect to the starting materials 11



Fig. 2. ORTEP view of compound 17 drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Si1-N1 1.8843(15), Si1-O1 1.7883(13), Si1-O2 1.8111(11), Si1-O3 1.8017(13), Si1-O4 1.8171(12), Si1-C32 1.8875(15), N(1)-C31 1.171(2), S(1)-C31 1.6079(17); O(4)-Si(1)-N(1) 175.13(6), O(1)-Si(1)-O(3) 172.69(5), O(2)-Si(1)-C(32) 177.90(7), O(1)-Si(1)-O(2) 89.36(5), O(3)-Si(1)-O(2) 83.51(5), O(3)-Si(1)-C(32) 95.91(7), O(1)-Si(1)-C(32) 91.27(7).

 (2019 cm^{-1}) and **15** (2066 cm^{-1}) . Similar behavior has been observed for some hexacoordinate β-diketonato silicon complexes [8a] and was ascribed to the predominance of the N \equiv C-S^{δ -} canonical form in the silicon hypercoordinate complexes, whereas for **11** and **15**, the $^{\delta-}$ N=C=S canonical form must have a higher contribution; this observation is consistent with C-N and C-S crystallographic distances for the -NCS ligand in complexes 16-17 as



Fig. 3. ORTEP view of compound **18** drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Si1–N1 1.8591(19), Si1–O1 1.8304(17), Si1–O2 1.7858(14), Si1–O3 1.8103(15), Si1–O4 1.8166(15), Si1–C21 1.881(2), N(1)–C22 1.161(3), S(1)–C22 1.605(2); O(4)–Si(1)–N(1) 171.03(9), O(2)–Si(1)–O(3) 175.04(8), O(1)–Si(1)–C(21) 176.92(9), O(1)–Si(1)–O(2) 91.38(7), O(1)–Si(1)–O(3) 83.66(7), O(3)–Si(1)–C(21) 93.27(9), O(2)–Si(1)–C(21) 91.68(9).

compared, for instance, with those corresponding to the tetracoordinate compound Si(NCS)₄ [10].

Complexes 17 and 18 were studied using solution and solidstate ²⁹Si NMR. In the solid state, the isotropic ²⁹Si chemical shifts obtained in the CP/MAS NMR studies are guite similar for both complexes (17: δ –169.0; 18: δ –170.0) and are in good agreement with the ²⁹Si chemical shifts obtained in solution [17 (CDCl₃): δ -174.2; **18** (CDCl₃): δ -174.8, (C₆D₆): δ -175.5)]. These results indicate that compounds 17 and 18 maintain the hexacoordination of the silicon atom in solution and that only one diastereomer is present in both cases. The ²⁹Si chemical shift resonance of complexes 17 and 18 (SiO₄NC skeleton) are in the expected region for hexacoordinate silicon complexes containing two β-diketonato ligands; some examples of this type of compound that illustrate this fact are the following (skeleton, chemical shift, solvent): SiO₄CCl, δ -149.5, CDCl₃ [6]; SiO₄C₂, δ -161.7, THF-d₈ [7]; SiO₄N₂ (2), δ -208.7, CDCl₃ [10]; SiO₄N₂ (**3**), δ -204.2, CD₂Cl₂ [11]; SiO₄C₂ (**4**), δ -138.87, C₆D₆ [12]; SiO₆ (**5**), δ -176.1, CD₂Cl₂ [13]; SiO₆ (**6**), δ -190.3, CD₂Cl₂ [14]; SiO₆ (7), δ -174.1, CD₂Cl₂ [14]; (see Chart 1 for the structures of 2–7). As observed from the above data, the presence of two -NCS or -NCO ligands in these complexes causes a large high-field chemical shift of the ²⁹Si resonance (complexes 2 [10] and 3 [11]).



Chart 2. Hexacoordinate silicon complexes with a SiO₄NC skeleton.

According to the literature, the anionic (**19** [32] and **20** [33]) and the zwitterionic (**21** [34] and **22** [35]) silicon complexes shown in Chart 2, are the only analogous hexacoordinate silicon complexes of **17** and **18** with a SiO_4NC coordinating framework that have been structurally characterized using single-crystal X-ray diffraction.

It is interesting to compare some structural data for the SiO_4NC skeleton of the neutral hexacoordinate silicon complexes **17** and **18** with those of complexes **19–21** whose silicon centers are formally charged (-1). Although they possess a SiO_4NC skeleton, compound **22** has Si–C and Si–N bonds in a relative *trans* position, whereas the corresponding bonds in complexes **17–21** are in a relative *cis* position. Table 2 shows the data for some comparable bonds distances for the above-mentioned compounds.

According to the data in Table 2, the Si-C and Si-N bonds in complexes **19–21** are consistently longer, and three of the four Si-O bonds are consistently shorter, compared with the analogous bond distances for 17 and 18 (of the two Si-O bonds that are mutually trans for all complexes in Table 2, the shorter bonds have similar values, whereas the longer bonds are slightly shorter for 19-21). This difference in bond distances can be explained by considering the presence of the two dianionic 0,0'-donor catecholato ligands for compounds **19–21**, which in virtue of their charge (-1)on each oxygen atom, act as very strong donors toward the silicon center, and this is particularly favored by the presence of a neutral amino donor atom of the second ligand that, compared with the -NCS ligand, is a relatively poor donating atom. In the case of each β -diketonato ligand of **17** and **18**, only one of the oxygen donor atoms formally has a -1 charge, whereas the second atom is formally neutral. However, these complexes also contain a strong Ndonor anionic ligand, -NCS, in addition to the methyl ligand, which is also an electron donating (+I) group [36]. These latter two factors diminish the average donating power of the β-diketonate ligands, which is reflected in three larger Si–O distances for 17 and 18 with respect to the *bis*-catecholate complexes **19–21**.

In the reaction of the Si-H bond of tetravalent hydridosilanes 10 and **15** with the β-diketones **HL**¹ and **HL**² to yield the five- and sixcoordinate silicon complexes 16-18. the question arises as to whether these are acid-base reactions or nucleophilic substitutions at the silicon center through a hypercoordinate silicon intermediate. This subject was analyzed by Corriu in the case of the reactions of a set of pentacoordinate dihydridosilicates $[H_2Si(OR)_3]^-$ with alcohols (ROH) to yield the corresponding pentacoordinate silicates [HSi(OR)₄]⁻, and he concluded that a nucleophilic substitution reaction mechanism at the silicon atom was occurring via a hexacoordinate intermediate [18a,37]. By analogy, in the present case, it can be considered that the reaction initiates with a nucleophilic attack at the silicon atom of hydridosilanes **10** and **15** by the sp³ enolic oxygen of the β -diketone ligand (the ketonic oxygen with an sp^2 hybridization is more electronegative [38] and thus less basic) to yield a pentacoordinate intermediate; the intramolecular reaction between the hydride and the enol proton then follows with the coordination of the second oxygen of the ligand to yield a neutral pentacoordinate complex. In the three reactions that produce complexes 16-18, the acid base reaction for the former step can be ruled out by considering that this pathway would produce a low-valent tricoordinate silicon intermediate [37]. However, two pathways follow: in the case of the hydridosilane 15, a second molecule of the βdiketone ligand would be unable to carry out an additional nucleophilic attack at the silicon center of complex 16 due to steric hindrance, causing the reaction to end at this point; in the case of the pentacoordinate intermediates derived from the hydridosilane 11, a second molecule of the β -diketones HL¹ and HL² could attack at the intermediate via one of their oxygen atoms, following the liberation of HNCS and the coordination of the second oxygen atom to yield hexacoordinate complexes 17 and 18.

Bond	17	18	19 ^a	20 ^b	21 ^c
Si-C	1.885	1.881	1.917	1.943	1.954
Si–N	1.884	1.859	2.157	2.085	2.173
Si-O trans to Si-C	1.811	1.830	1.776	1.771	1.795
Si-O trans to Si-N	1.817	1.816	1.785	1.778	1.767
Si–O mutually trans	1.788, 1.801	1.785, 1.810	1.779, 1.785	1.768, 1.796	1.787, 1.793

Comparison of some crystallographic bond distances (Å) for some silicon compounds with a SiO₄NC coordinating framework.

^a Reference [32].

Table 2

^b Reference [33].

^c Reference [34]. See Scheme 2 for structures of **17** and **18** and Chart 2 for structures of **19–21**.

3. Concluding remarks

The (thiocyanato-N)hydridosilanes HPh₂Si(NCS) and HMe-Si(NCS)₂ proved to be useful silicon sources for the production of novel neutral penta- and hexa-coordinate silicon compounds containing β -diketonato ligands; in a more general sense, the primary usefulness of the (thiocyanato-N)hydridosilanes will be in those cases in which anionic protonated ligands are involved, which, to avoid the presence of acidic protons during the synthesis, require the use of external bases such as pyridine, triethylamine or imidazole or the preparation of a deprotonated derivative of the β-diketonate ligand. In this regard, the synthetic route exemplified here with HPh₂Si(NCS) and HMeSi(NCS)₂ as starting materials could be extended to prepare other novel pentacoordinate and hexacoordinate silicon complexes by the displacement of the hydride ligand from the silicon atom upon reaction with protonated monoanionic bidentate ligands. This type of reaction could be extended, for instance, to other chelating monoanionic, hard-donor ligands, analogous to β -diketones such as those of the type R₂P(O)-X-P(O)R₂ (X = NH) [39]. Alternatively, given the fact that complexes 16-18 retain one -NCS group in the coordination sphere, this functionality could be used, for instance, in further Wurtz-type coupling or substitution reactions to obtain novel hypercoordinate silicon complexes.

4. Experimental

4.1. General procedures

The reactions were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. The organic solvents were dried and purified according to standard procedures and stored under a nitrogen atmosphere. The ${}^{1}\mathrm{H}$ and ${}^{13}\mathrm{C}$ solution NMR spectra were recorded at room temperature on either a Varian Gemini 200 (200 MHz ¹H and 50 MHz ¹³C) or a Varian Unity Plus 300 spectrometer. CDCl₃ and C₆D₆ were used as solvents for the NMR experiments and were dried using 4A molecular sieve (Aldrich). The chemical shifts (δ) were determined relative to the residual signal of the solvent (CDCl₃: ¹H δ 7.26; ¹³C δ 77.0). The assignment of the ¹³C NMR data was supported by DEPT 135 experiments. The solution (CDCl₃ or C₆D₆)²⁹Si INEPT NMR and the solid-state ²⁹Si CP/MAS spectra were recorded on a Varian Unity Plus 300 spectrometer (²⁹Si, 59.6 MHz), and the chemical shifts (δ) were determined relative to external TMS (δ 0.0). The FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer using Nuiol mulls for **11** and **15**, and a KBr disk for complexes 16-18. The melting points were determined in sealed capillaries and are not corrected, and the elemental analyses were performed by ALS Environmental (Tucson, USA) or using a LECO TruSpec CHNS instrument at the Instituto de Investigaciones Químicas CSIC, Universidad de Sevilla, Spain. The starting material, HMeSi(NCS)₂, was prepared as reported in the literature [19]. The β -diketone ligands **L**¹**H** and **L**²**H** were purchased from Aldrich and were recrystallized in ethanol and dried for 2 h in a vacuum before use. The HPh_2SiCl (90%) was purchased from Aldrich and was distilled before use.

4.2. Synthesis of diphenyl(thiocyanato-N)silane (15)

Chloro(diphenyl)silane (9.7 g, 44.0 mmol) was added at 20 °C to a stirred suspension of ammonium thiocyanate (4.2 g, 55.0 mmol) in toluene (30 mL). The reaction mixture was stirred under reflux for 4 h. After the mixture was cooled to 20 °C, the resulting precipitate was filtered off and discarded. The solvent was removed from the filtrate by distillation at normal pressure, and the residue was distilled in a vacuum to yield a colorless liquid (bp: 98–100 °C/ 20 mbar). Yield: 64% (6.8 g, 28.0 mmol). ¹H NMR (200 MHz, CDCl₃): δ 5.5 (s, 1H, SiH; satellites: d ¹J (¹H–²⁹Si) 233.5 Hz), 7.5–7.7 (m, 10H, SiPh). ¹³C NMR (50 MHz, CDCl₃): δ 128.51, 131.36, 134.58 (CH aromatic); 129.83 (C_{ipso} –Si); 144.28 (NCS). ²⁹Si INEPT NMR (56.9 MHz, CDCl₃): δ –30.0. FT-IR: v(–NCS) 2066 cm⁻¹; v(Si–H) 2169 cm⁻¹; v(C–H) 3072, 3053 cm⁻¹. *Anal.* Calc. for C₁₃H₁₁NSSi (FW 241.38): C, 64.69; H, 4.59; N, 5.80; S, 13.28. Found: C, 64.94; H, 4.99; N, 5.60; S, 13.51%.

4.3. Synthesis of diphenyl-[1,3-diphenylpropan-1,3-dionato(1–)-0,0 '](thiocyanato-N)silicon(IV) (**16**)

1,3-Diphenylpropane-1,3-dione (**HL**¹, 1.40 g, 6.24 mmol) was added at 25 °C to a stirred solution of HPh₂Si(NCS) (0.75 g, 3.11 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 72 h at 20 °C and produced a yellow crystalline solid. The solid product was filtered and recrystallized in acetonitrile (20 mL) by slow cooling from 80 to -20 °C. The yellow crystals formed were filtered, washed with diethyl ether (10 mL) and dried under a vacuum (0.01 mbar) for 2 h. Yield 46.3% (0.67 g, 1.44 mmol); mp: 220–222 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.18 (s, 1H, O-C=CH), 7.25-8.17 (m, 20H, CH aromatic). ¹³C NMR (50 MHz, CDCl₃): δ 95.61 (O-C=CH); 127.66, 128.65, 129.22, 129.48, 134.32 (CH aromatic); 133.62 (Cipso-Si); 138.90 (Cipso-C=O); 183.40 (C_{ipso}-C=O); resonance signal of -NCS ligand not detected. ²⁹Si INEPT NMR (79.5 MHz, CDCl₃): δ –99.9. FT-IR: ν (–NCS) 2099 cm⁻¹; v(C-H) 3013, 3064 cm⁻¹. Anal. Calc. for C₂₈H₂₁NO₂SSi (FW 463.62): C, 72.54; H, 4.57; N, 3.02; S, 6.92. Found: C, 72.72; H, 4.87; N, 2.98; S, 7.26%.

4.4. Synthesis of methyl-bis[1,3-diphenylpropan-1,3-dionato(1–)-0,0 '](thiocyanato-N)silicon(IV) (**17**)

1,3-Diphenylpropane-1,3-dione (HL^1 , 3.72 g, 16.72 mmol) at room temperature was added to a solution of HMeSi(NCS)₂ (1.31 g, 8.17 mmol) in acetonitrile (30 mL). The reaction mixture was stirred at 25 °C for 24 h. The precipitate solid that formed was recrystallized by slow cooling from 80 to 20 °C, and the crystalline solid obtained was filtered and washed with diethyl ether (20 mL) and then dried in a vacuum (0.01 mbar for 2 h). Yield 70% (3.14 g, 5.73 mmol); mp >250 °C (dec). ¹H NMR (200 MHz, CDCl₃): δ 0.61 (s, 3H, SiCH₃); 7.04 (s, 2H, O–C=CH), 7.3–8.2 (m, 20H, CH aromatic; two broad signals). ¹³C NMR (50.3 MHz, CDCl₃): δ 12.20 (SiCH₃); 93.83 (O–C=CH); 128.23, 128.77, 133.56, (CH aromatic); 135.1 (C_{ipso}), 183.30 broad (C=O); resonance signal of –NCS ligand not detected. ²⁹Si INEPT NMR (59.6 MHz, CDCl₃): δ –174.2. ²⁹Si CP/MAS NMR (59.6 MHz): δ –169.0 (broad). FT-IR: ν (–NCS) 2085 cm⁻¹; ν (C–H) 3063 cm⁻¹. *Anal.* Calc. for C₃₂H₂₅NO₄SSi (FW 547.69): C, 70.17; H, 4.60; N, 2.56; S, 5.85. Found: C, 70.02; H, 4.66; N, 2.39; S, 4.85%.

4.5. Synthesis of methyl-bis[1-phenylbutan-1,3-dionato(1–)-O,O'] (thiocyanato-N)silicon(IV) (**18**)

1-Phenylbutane-1.3-dione (1.47 g. 9.07 mmol) at room temperature was added to a solution of HMeSi(NCS)₂ (0.73 g, 4.53 mmol) in acetonitrile (30 mL): the reaction mixture was stirred at 25 °C for 2 h; the precipitate solid that formed was recrystallized by slow cooling from 80 to -20 °C in acetonitrile (40 mL). The crystalline solid obtained was filtered and washed with diethyl ether (20 mL) and dried in a vacuum (0.01 mbar for 2 h). Yield 73% (1.40 g, 3.30 mmol); mp >150 °C (dec). ¹H NMR (200 MHz, CDCl₃): δ 0.38 (s, 3H, SiCH₃), 2.23 (s, 6H, O=C-CH₃); 6.26 (s, 2H, O-C=CH); 7.40–8.19 (m, 10H, CH aromatic).¹³C NMR (75 MHz, CDCl₃): δ 9.65 (SiCH₃), 26.6 (O=C-CH₃), 97.46 (O-C=CH); 128.22, 128.76, 134.48 (CH aromatic); 133.54 (O=C-C_{ipso}); 134.87 (-NCS). ²⁹Si INEPT NMR (59.6 MHz) CDCl₃, δ -174.8; C₆D₆, δ -175.5. ²⁹Si CP/MAS NMR (59.6 MHz): δ –170.0. FT-IR: v(–NCS) 2113 cm⁻¹; v(C–H) 2966 cm⁻¹. Anal. Calc. for C₂₂H₂₁NO₄SSi (FW 423.56): C, 62.38; H, 5.00; N, 3.31; S, 7.57. Found: C, 62.51; H, 5.36; N, 3.40; 7.55%.

4.6. Crystallographic structure determination

Suitable single crystals of **16–18** were obtained by slow cooling in acetonitrile, after which they were coated with dry perfluoropolyether and mounted on a glass fiber under a cold nitrogen stream [T = 100(2) K]. Data collection was performed on a Bruker-Nonius X8APEX-II CCD diffractometer using monochromatedgraphite radiation λ (Mo K α) = 0.71073 Å by means of ω and ϕ scans. The structures were resolved using direct methods with a SIR 2004 [40] and refined using full-matrix least-squares procedures utilizing SHELXL-97 [41].

Acknowledgments

Financial support from PROMEP (Secretaría de Educación Pública) is acknowledged. G.G.G. gratefully acknowledges a Ph.D. scholarship from Consejo Nacional de Ciencia y Tecnología (CONACYT) and the Universidad de Guanajuato. We are grateful to the Consejo Superior de Investigaciones Científicas (CSIC) of Spain for the award of a license for the use of the Cambridge Crystallographic Data Base (CSD).

References

[1] S. Metz, C. Burschka, R. Tacke, Organometallics 28 (2009) 2311.

- [2] R. West, J. Am. Chem. Soc. 80 (1958) 3246.
- [3] (a) R.M. Pike, R.R. Luongo, J. Am. Chem. Soc. 87 (1965) 1403;
 (b) C.E. Holloway, R.R. Luongo, R.M. Pike, J. Am. Chem. Soc. 88 (1966) 2060;
 (c) R.M. Pike, R.R. Luongo, J. Am. Chem. Soc. 88 (1966) 2972.
- [4] D.W. Thompson, Inorg. Chem. 8 (1969) 2015.
- [5] G. Schott, K. Golz, Z. Anorg. Allg. Chem. 383 (1971) 314.
- [6] J.A. Cella, J.D. Cargioli, E.A. Williams, J. Organometal. Chem. 186 (1980) 13.
- [7] K.M. Taba, W.V. Dahlhoff, J. Organometal. Chem. 280 (1985) 27.
- [8] (a) S.P. Narula, R. Shankar, B. Kaur, S. Soni, Polyhedron 10 (1991) 2463;
 (b) S.P. Narula, S. Soni, R. Shankar, Main Group Met. Chem. 15 (1992) 293.
 [9] K. Yamaguchi, K. Ueno, H. Ogino, Chem. Lett. (1998) 247.
- O. Seiler, R. Bertermann, N. Buggisch, C. Burschka, M. Penka, D. Tebbe, R. Tacke, Z. Anorg, Allg, Chem. 629 (2003) 1403.
- [11] R. Tacke, R. Bertermann, M. Penka, O. Seiler, Z. Anorg. Allg. Chem. 629 (2003) 2415.
- [12] C. Xu, T.H. Baum, A.L. Rheingold, Inorg. Chem. 43 (2004) 1568.
- [13] O. Seiler, M. Penka, R. Tacke, Inorg. Chim. Acta 357 (2004) 1955.
- [14] O. Seiler, C. Burschka, T. Fenske, D. Troegel, R. Tacke, Inorg. Chem. 46 (2007) 5419.
- [15] W. Dilthey, Chem. Abstr. (1903) 162105.
- [16] Cambridge Structural Data Base (CSD, version 5.32; November 2010): F.H. Allen, Acta Crystallogr. B58 (2002) 380. The references cited in CSD concerning the X-ray crystal structures of the cation [Si(aca)₃]* with different anions are the following: (a) Anion ClO₄⁻: T. Adam, T. Debaerdemaeker, U. Thewalt, Eur. Cryst. Meeting 5 (1979) 325; (b) Anion Cl2_{H4}N₄⁻: K. Ueyama, G.-E. Matsubayashi, J. Chem. Res. 48 (1985) 801; (c) Anion HCl₂⁻: U. Thewalt, U. Link, Z. Naturforsch. B Chem. Sci. 46 (1991) 293; (d) Anion Ag₂Cl4₂⁻: D. Hogerle, U. Link, U. Thewalt, Z. Naturforsch. B Chem. Sci. 48 (1983) 691.
- [17] J.A. Cella, T.D. Mitchell, J. Organometal. Chem. 244 (1983) C5.
- [18] (a) C. Chuit, R.J.P. Corriu, C. Reye, J.C. Young, Chem. Rev. 93 (1993) 1371;
 (b) D. Kotz, I. Kalikhman, in: Z. Rappoport, Y. Apeilgon (Eds.), The Chemistry of Organosilicon Compounds, vol. 2, John Wiley and Sons, Ltd, 1998 (Chapter 2).
- [19] G. Gonzalez-Garcia, J.A. Gutierrez, S. Cota, S. Metz, R. Bertermann, C. Burschka, R. Tacke, Z. Anorg. Allg. Chem. 634 (2008) 1281.
- [20] G. Gonzalez-Garcia, E. Alvarez, A.M. Marcos-Fernandez, J.A. Gutierrez, Inorg. Chem. 48 (2009) 4231.
- [21] N. Serpone, K.A. Hersh, J. Organometal. Chem. 84 (1975) 177.
- [22] N. Kano, A. Kikuchi, T. Kawashima, Chem. Commun. (2001) 2096.
- [23] J. Wagler, E. Brendler, Z. Naturforsch. 62b (2007) 225.
- [24] U. Böhme, B. Günther, Inorg. Chem. Commun. 10 (2007) 482.
- [25] U. Böhme, S. Wiesner, B. Günther, Inorg. Chem. Commun. 9 (2006) 806.
- [26] K. Tamao, M. Asahara, T. Saeki, A. Toshimitsu, Angew. Chem., Int. Ed. 38 (1999) 3316.
- [27] F. Mucha, U. Bohme, Chem. Commun. (1998) 1289.
- [28] K. Junold, C. Burschka, R. Bertermann, R. Tacke, Dalton Trans. 39 (2010) 9401.
- [29] S. Metz, C. Burschka, R. Tacke, Organometallics 27 (2008) 6032.
- [30] S. Metz, B. Theis, C. Burschka, R. Tacke, Chem. Eur. J. 16 (2010) 6844
- [31] C. Breliere, R.J.P. Corriu, G. Royo, W.W.C. Wong Chi Man, J. Zwecker, Organometallics 9 (1990) 2633.
- [32] F. Carré, G. Cerveau, C. Chuit, R.J.P. Corriu, C. Réyé, Angew. Chem., Int. Ed. 28 (1989) 489.
- [33] F. Carré, C. Chuit, R.J.P. Corriu, A. Mehdi, C. Reyé, J. Organomet. Chem. 446 (1993) C6.
- [34] F. Carré, C. Chuit, R.J.P. Corriu, A. Fanta, A. Mehdi, C. Reyé, Organometallics 14 (1995) 194.
- [35] I. Kalikhman, V. Kingston, O. Girshberg, D. Kost, Organometallics 20 (2001) 4713.
- [36] J. March, Advanced Organic Chemistry. Reaction, Mechanisms, and Structure, fourth ed., John Wiley and Sons, New York, 1992. p. 18.
- [37] R.J.P. Corriu, C. Guerin, B.J.L. Henner, Q. Wang, Organometallics 10 (1991) 3200.
- [38] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry. Principles of Structure and Reactivity, fourth ed., Harper Collins College Publishers, New York, 1993. p. 187 (Chapter 5).
- [39] M. Correa-Ascencio, E.K. Galvan-Miranda, F. Rascon-Cruz, O. Jimenez-Sandoval, S.J. Jimenez-Sandoval, R. Cea-Olivares, V. Jancik, R.A. Toscano, V. Garcia-Montalvo, Inorg. Chem. 49 (2010) 4109.
- [40] M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L.G.C. De Caro, G. Polidori, R. Spagna, J. Appl. Crystallogr. 38 (2005) 381.
- [41] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.