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Unexpected Formation of a Silicon-Centered Spirocyclic Oligosiloxane Bearing Eight Pendant Ferrocene Units

Sonia Bruña ^{1,*} , Isabel Cuadrado ¹ and Josefina Perles ² 

¹ Departamento de Química Inorgánica, Institute for Advanced Research in Chemical Sciences (IAdChem), Facultad de Ciencias, Universidad Autónoma de Madrid, Avd. Francisco Tomás y Valiente 7, Campus de Cantoblanco, 28049 Madrid, Spain

² Laboratorio de Difracción de Rayos X de Monocristal, Servicio Interdepartamental de Investigación (SIdI), Universidad Autónoma de Madrid, Avd. Francisco Tomás y Valiente 7, Campus de Cantoblanco, 28049 Madrid, Spain

* Correspondence: sonia.brunna@uam.es

Abstract: An intriguing but rare silicon-centered spirocyclic compound, spiro[5.5]octaferrocenylpenta siloxane (**4**) featuring silicon fused six-membered ferrocenyl-functionalized siloxane rings, has been obtained during the thermally induced transformation of triferrocenylsilane Fc₃Si-H (**1**) into triferrocenylsilanol Fc₃Si-OH (**2**), when N,N-dimethylformamide (DMF) was used as a solvent in the presence of the metal carbonyl Mo(CO)₆. The unexpected formation of the maximally ferrocenyl substituted silicon centered spirocyclic **4** involves the obtention, and subsequent condensation, of different ferrocenylsilanol intermediates. Spirocyclic silicate **4** has been characterized using a combination of MALDI-TOF mass spectrometry, elemental analysis, and single crystal X-ray diffraction analysis.

Keywords: spirocyclic; siloxanes; ferrocene; cyclosiloxanes; inorganic macrocycles; SCXRD



Citation: Bruña, S.; Cuadrado, I.; Perles, J. Unexpected Formation of a Silicon-Centered Spirocyclic Oligosiloxane Bearing Eight Pendant Ferrocene Units. *Crystals* **2022**, *12*, 1122. <https://doi.org/10.3390/cryst12081122>

Academic Editor: Chang Seop Hong

Received: 7 July 2022

Accepted: 9 August 2022

Published: 11 August 2022

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1. Introduction

Organosilicon molecules bearing Si–O–Si siloxane bonds are an important type of functional compound exhibiting valuable applications in various fields such as catalysis, materials, energy, and bioscience, due to their high thermal stability and hydrophobicity, chemical inertness, and unique electronic, optical, and biocompatibility properties [1–4]. Concerning the chemical properties of siloxanes, in the last few years, the field of siloxane coordination chemistry has significantly advanced and sophisticated methods have been established to enable the Si–O–Si bond for coordination. Accordingly, experimental features, as well as comprehensive quantum chemical calculations, have been provided to confirm siloxane coordination ability [5].

Moreover, cyclic siloxanes, which formally resemble silicon analogs of crown ethers, have received considerable interest concerning their host–guest chemistry [5–12]. The key specific characteristics of organosilicon compounds bearing siloxane bonds are: (1) the bond lengths of Si–O bonds, ranging from 1.63 to 1.67 Å; (2) the Si–O–Si bond angles between 130 and 150°, which are considerably larger than the range for the C–O–C angles in aliphatic ethers (105–115°) [2–5]; (3) the O–Si–O angles, which vary within a narrower range, from 110 to 120°. Due to the large open and variable angle of the Si–O–Si linkage, siloxane compounds present unusual conformational flexibility. Essentially, the high flexibility of the siloxane bond is a key feature that is outstandingly useful for assembling siloxane-containing small molecules into more complex inorganic macromolecules [4,5]. It is also well known that unexpected, novel silicon- and siloxane-containing compounds, which in most cases cannot be synthesized by other means, can be obtained by reacting organosiloxanes with selected organometallic reagents [5–13].

On the other hand, over the past few decades, the design of multiferrocenyl macromolecular structures has evolved to be one the most appealing subjects within various areas

of research, including organometallic and supramolecular chemistries, electrochemistry, catalysis, biomolecules, sensors, and molecular recognition [14–20].

In this context, from years ago, our research interest concerns the chemistry of silicon- and siloxane-containing multiferrocenyl molecules [21–25]. As a contribution to this field, we have reported the synthesis of triferrocenylsilane $\text{Fc}_3\text{Si-H}$ (**1**) and have shown that the Si–H bond in this redox-active hydrosilane can be metalated, as it oxidatively adds to the Co(0) metal center of $\text{Co}_2(\text{CO})_8$ to give the silyl-Co(I) compound $\text{Fc}_3\text{Si-Co}(\text{CO})_4$ [24]. More recently, our studies have been focused on ferrocene-functionalized silanols, such as $\text{Fc}_2\text{Si}(\text{OH})_2$ and $\text{Fc}_2(\text{HO})\text{Si-O-Si}(\text{OH})\text{Fc}_2$, and we have investigated their ability to act as new electroactive anion receptors for either acetate or chloride anions [26]. As a continuation of this research and with the intention to further expand the family of multiferrocenyl siloxane-containing compounds, we now report an evaluation of the reactivity of triferrocenylsilane $\text{Fc}_3\text{Si-H}$ (**1**). Specifically, we investigate here the transformation of the Si–H (hydrosilane) bond of **1** into a Si–OH (silanol) group, using two polar aprotic solvents, *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), as the oxygen source and in the presence of different transition metal catalysts (of Pt(0) or Mo(0)) [27–29].

In all cases, the desired triferrocenylsilanol $\text{Fc}_3\text{Si-OH}$ (**2**) was formed as the major product. Nevertheless, these reactions have also given rise to secondary chemical processes originating from the great affinity of the Si–OH group to undergo intermolecular condensation reactions. Particularly, using $\text{Mo}(\text{CO})_6$ as catalyst and DMF as the oxygen source, at elevated temperatures, some intermediate species are assumed to be formed, such as diferrocenylsilanediol $\text{Fc}_2\text{Si}(\text{OH})_2$ and tetraferrocenyldisiloxanediol $\text{Fc}_2(\text{OH})\text{Si-O-Si}(\text{OH})\text{Fc}_2$, which in turn would condense in order to form the cyclic compound hexaferrocenylcyclotrisiloxane (**3**). Remarkably, as a result of such condensation reactions, a new and unexpected octaferrocenyl-siloxane-based compound **4** has also been isolated; **4** is a molecular spirocyclic silicate that contains two cyclosiloxane rings, connected by one silicon atom. This molecule is the first example reported to date of a spirocyclic silicate with electroactive ferrocenyl units.

2. Materials and Methods

Synthesis. All reactions and compound manipulations were performed in an oxygen- and moisture-free Ar atmosphere using standard Schlenk techniques. The functionalized precursor $\text{Fc}_3\text{Si-H}$ (**1**) was synthesized from monolithioferrocene (generated in situ from the reaction between ferrocene and *t*-BuLi, at low temperature) according to the procedure already described [24]. Platinum-divinyltetramethyldisiloxane complex in xylene (3–3.5% Pt concentration) (Karstedt's catalyst, available from Merck-Sigma-Aldrich, Europe) was used as received. $\text{Mo}(\text{CO})_6$ (available from Merck-Sigma-Aldrich) was sublimated before use. Silica gel (70–230 mesh) (Merck-Sigma-Aldrich) was used for column chromatography purifications. Elemental analyses were performed in a LECO CHNS-932 elemental analyzer equipped with an MX5 Mettler Toledo microbalance. All NMR spectra were recorded on Bruker Avance III-Hd Nanobay 300 MHz and Bruker Avance 300 MHz spectrometers. Chemical shifts were reported in parts per million (δ) with reference to CDCl_3 residual solvent resonances for ^1H (δ 7.26 ppm) and ^{13}C (δ 77.2 ppm). MALDI-TOF mass spectra were recorded using a Bruker-Ultraflex III TOF/TOF mass spectrometer equipped with a nitrogen laser emitting at 337 nm. Dichloromethane solutions of the matrix (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB), 10 mg/mL) and dichloromethane solutions of the corresponding compound (1 mg/mL) were mixed in the ratio 20:5. Then, 0.5–1 μL of the mixture was deposited on the target plate using the dried droplet method.

Method 1: using Karstedt's catalyst: a suspension of triferrocenylsilane **1** (300 mg, 0.51 mmol) in 6 mL of DMSO or DMF and in the presence of 30 μL of Karstedt's catalyst, was heated to 100 °C. A darkening in the color of the reaction mixtures was observed with time. After 48 h for the reaction in DMSO, and 7 days for the reaction in DMF, solvent removal afforded dark brown oils that were purified by column chromatography on silica

gel (2 cm × 15 cm). Using a mixture of hexane/CH₂Cl₂ (10:3) as the eluent, a first band containing unreacted **1** was obtained, and subsequently, a second major orange band was eluted with CH₂Cl₂. Solvent removal afforded the desired tetrametallic silanol **2** as an air-stable, orange, crystalline solid. Yield: 0.20 g (65% for the reaction in DMSO) and 0.14 g (46% for the reaction in DMF). **2**: Anal. Calc. for C₃₀H₂₈OSiFe₃ (%): C, 60.04; H, 4.70. Found (%): C, 60.23; H, 4.68. ¹H NMR (CDCl₃, 300 MHz, ppm): δ 2.17 (s, 1H, OH), 4.14 (s, 15H, C₅H₅), 4.37, 4.43 (m, 12H, C₅H₄). ¹³C{¹H} NMR (CDCl₃, 75 MHz, ppm): δ 68.6 (C₅H₅), 69.3 (*ipso*-Fc), 71.0, 73.9 (C₅H₄). ²⁹Si{¹H} NMR (CDCl₃, 59 MHz, ppm): δ −2.7 (*Si*-OH). MS (MALDI-TOF): *m/z* 600.1 [M⁺].

Method 2: using Mo(CO)₆ as catalyst: a solution of triferrocenylsilane **1** (200 mg, 0.34 mmol) in 4 mL of DMF was added to a solution of Mo(CO)₆ (4.49 mg, 0.017 mmol) in 2 mL of DMF. After 72 h at 90 °C the dark brown oily product was purified by column chromatography on silica gel. Using hexane as the eluent, a first band containing ferrocene was collected. Subsequently, with a mixture of hexane/CH₂Cl₂ (10:5) two new fractions were eluted; the first one afforded cyclosiloxane **3** (yield: 39 mg, 28%) and the second one corresponded to a mixture of compound **3** and spiro-silicate **4**. Orange needlelike crystals of **4** were isolated and analyzed by SCXRD. Finally, on eluting with CH₂Cl₂, triferrocenylsilanol **2** was obtained (yield: 0.11 g, 52%). **3**: Anal. Calc. for C₆₀H₅₄O₃Si₃Fe₆ (%): C, 58.00; H, 4.38. Found (%): C, 57.82; H, 4.41. ¹H NMR (CDCl₃, 300 MHz, ppm): δ 4.10 (s, 30H, C₅H₅), 4.47, 4.57 (m, 24H, C₅H₄). ¹³C{¹H} NMR (CDCl₃, 75 MHz, ppm): δ 66.8 (*ipso*-Fc), 68.9 (C₅H₅), 71.2, 73.8 (C₅H₄). ²⁹Si{¹H} NMR (CDCl₃, 59 MHz, ppm): δ −26.8 (Fc−Si). MS (MALDI-TOF): *m/z* 1241.9 [M⁺]. **4**: Anal. Calc. for C₆₀H₅₄O₃Si₃Fe₆ (%): C, 55.97; H, 4.23. Found (%): C, 56.12; H, 3.98. MS (MALDI-TOF): *m/z* 1716.9 [M⁺].

X-ray crystal structure determination. Suitable orange crystals of **4** were isolated and coated with mineral oil, and mounted on Mitegen MicroMounts. Diffraction data were collected in a Bruker D8 KAPPA series II diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Full details of the data collection and refinement can be found in the supplementary material (see Section 2). The redundancy in data allows empirical absorption corrections (SADABS) [30] to be applied using multiple measurements of symmetry-equivalent reflections. Raw intensity data frames were integrated with the SAINT program [31], which also applied corrections for Lorentz and polarization effects. SHELXTL was used for space group determination, structure solution, and refinement [32]. The space group determination was based on a check of the Laue symmetry and systematic absences were confirmed using the structure solution. The structures were solved by direct methods (SHELXS-97), completed with different Fourier syntheses, and refined with full-matrix least-squares using S minimizing $\omega(F_o^2 - F_c^2)^2$ [33,34]. Weighted *R* factors (*R_w*) and all goodness of fit *S* are based on *F*²; conventional *R* factors (*R*) are based on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.10 program library. The crystal structure of compound **4** has been deposited at the Cambridge Crystallographic Data Centre with deposit number CCDC 2182627.

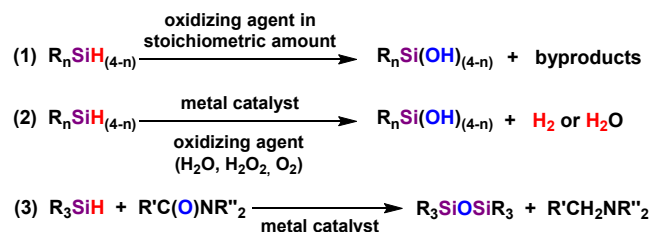
3. Results and Discussion

3.1. Transformation of Triferrocenylsilane **1** into Triferrocenylsilanol **2**

With the dual purpose of investigating the reactivity of triferrocenylsilane **1**, previously synthesized by our group [24] and obtaining the triferrocenylsilanol **2**, we tried the Si–H to Si–OH transformation.

In this regard, it must be said that triferrocenylsilanol **2** was first isolated in a moderate yield, 5%, as a secondary product of a Friedel–Crafts reaction between ferrocene and bis(*N,N*-dimethylamino)dichlorosilane [35]. In 2000, Ian Manners's group synthesized it through hydrolysis of triferrocenylchlorosilane in the presence of triethylamine [36]. In general, a Si–H bond within an organosilane can be oxidized through a stoichiometric reaction using strong oxidizing agents or through a catalytic oxidation, mainly with transition metal catalysts, in aqueous media (Scheme 1); however, neither of the two first methods

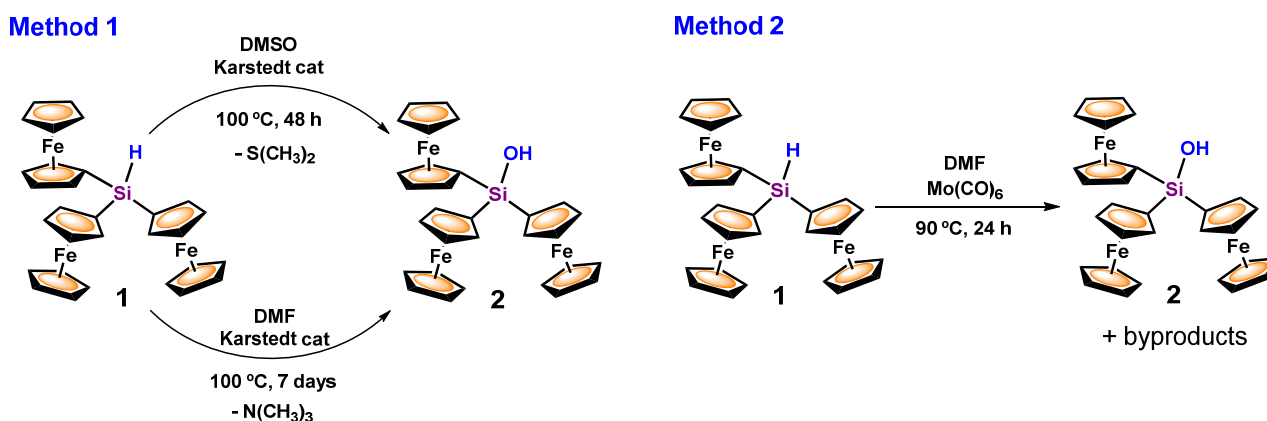
mentioned in Scheme 1 could be useful in our case, because the three ferrocenyl units could be oxidized at the same time. A ferrocene (Fe^{II}) oxidation to ferricenium (Fe^{III}) would decrease the solubility of the organometallic species formed, compromising the Si–H to Si–OH transformation.



Scheme 1. Synthetic methods to obtain a silanol or siloxane from a silane (Si–H bond).

Through a more in-depth bibliographic search on silanes reactivity, we found that some transition metal derivatives can act as catalysts for reducing amides with silanes of the $\text{R}_3\text{Si-H}$ type, being this also an efficient method to prepare disiloxanes, following reaction 3 in Scheme 1 [27,28,37]. Catalysts involved in these transformations are normally metallic carbonyls, such as $\text{CpFe}(\text{CO})_2\text{Me}$ [37] or $\text{Mo}(\text{CO})_6$ [28], or platinum complexes, for example, Karstedt's catalyst [27].

On the other hand, $\text{Fc}_3\text{Si-OH}$ (**2**) must be very stable against condensation. As a result of the electronic effect of the three ferrocenyl donor groups, the acidic strength of the Si–OH group must be necessarily low, above all if it is compared to organosilanol with electron-withdrawing substituents, which easily tend to condense [38]. Based on these facts, we decided to investigate the triferrocenylsilane **1** transformation to the triferrocenylsilanol **2** using polar and oxygen-containing solvents (DMF or DMSO) and a metallic catalyst: Karstedt's catalyst (Method 1 in Scheme 2) or $\text{Mo}(\text{CO})_6$ (Method 2 in Scheme 2).



Scheme 2. Reactions to obtain triferrocenylsilanol **2** following Methods 1 and 2.

Following Method 1, with Karstedt's catalyst in dimethyl sulfoxide (DMSO), after heating the reaction of silane **1** at 100 °C for 48 h, the yield of isolated silanol **2** was 65%. The same reaction using *N,N*-dimethylformamide (DMF) as oxygen-donor solvent was considerably slower than the reaction in DMSO, and after 7 days, a 46% yield of silanol **2** was obtained.

With the purpose of increasing the yield of the $\text{Fc}_3\text{Si-H}$ (**1**) \rightarrow $\text{Fc}_3\text{Si-OH}$ (**2**) transformation, Method 2, involving molybdenum hexacarbonyl as a catalyst and DMF as the source of oxygen, was also investigated. After heating the reaction at 90 °C for 24 h, the ^1H NMR spectrum (Figure 1A) showed that the reaction had progressed to the formation of triferrocenylsilanol **2**, although an important amount of unreacted silane **1** was also detected. In addition, two new signals in the ferrocenyl region were observed, one at δ 4.16 ppm (labeled as F) corresponding to unbonded ferrocene and a second one at δ 4.10 ppm (&) corresponding to bonded ferrocene.

that did not correspond to either compound **1** or **2**. These new and unexpected signals led us to assume that one of the two triferrocenylsilanes, or the two of them, could be experiencing interesting chemical transformations. To verify this, the reaction was heated at 90 °C for another 24 h, after the addition of more catalyst. The new ^1H NMR spectrum (Figure 1B) showed better progress of the reaction, with a higher triferrocenylsilanol **2**/triferrocenylsilane **1** ratio, but the Si–H signal was still present. The relative intensities of the signals at δ 4.16 and 4.10 ppm had also increased. Finally, after 72 h of reaction, the ^1H NMR spectrum (Figure 1C) showed: (a) no signal at δ 5.47 ppm for the Si–H group; (b) the formation of triferrocenylsilanol **2** as the main organometallic product; and (c) a greater increase in the signals at δ 4.16 (Fc) and 4.10 ppm, at the expense of silanol **2** signals, therefore the reaction was stopped.

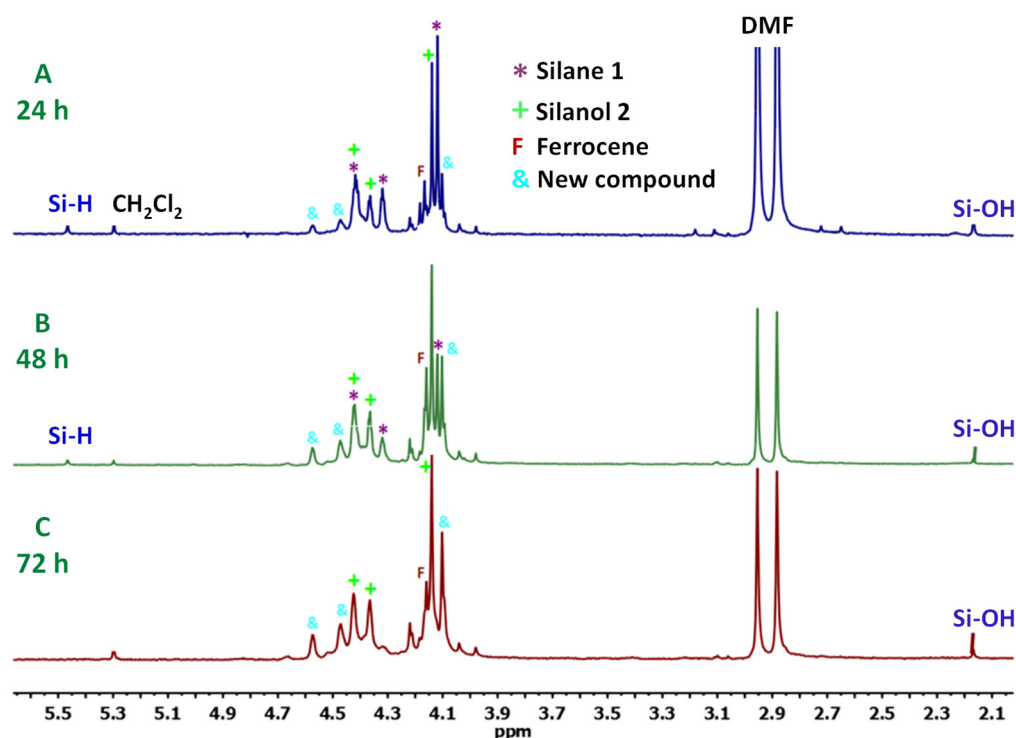
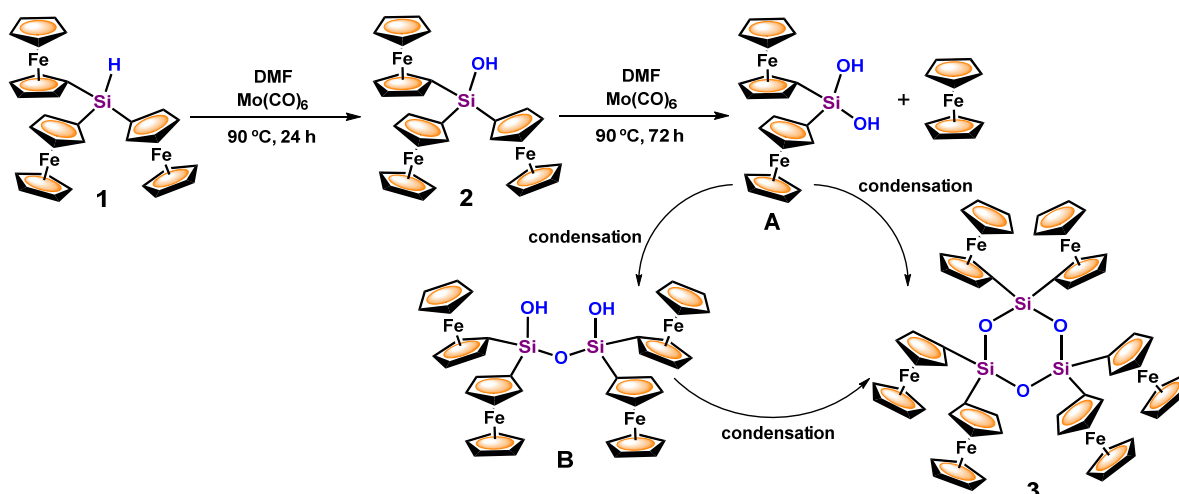


Figure 1. ^1H NMR spectra (CDCl_3 , 300 MHz) of the reaction between silane **1** and DMF, with $\text{Mo}(\text{CO})_6$ as a catalyst, after 24 (A), 48 (B), and 72 (C) h.

The brown oil obtained was purified by column chromatography. The first fraction eluted with hexane corresponded to ferrocene, proving a decomposition process during the reaction. Triferrocenylsilanol **2** was eluted with CH_2Cl_2 and isolated as an orange solid in 52% yield. During the purification process, another two fractions (FA and FB) were obtained with a 10:5 mixture of hexane: CH_2Cl_2 . The ^1H NMR spectrum for the first of these two fractions (FA) showed a pure compound with signals only in the ferrocenyl region, while the MALDI-TOF spectrum showed a peak at m/z 1241.9, corresponding to the cyclotrisiloxane **3**. This compound had already been isolated and fully characterized by Manners group, including its single crystal X-ray structure [39]. They obtained it by heating siloxanediol **B** (Scheme 3) in ethanol and in the presence of NaOH. Moreover, we had already obtained $[\text{Fc}_2\text{SiO}]_3$ (**3**) as a side product of the reactions we developed for the synthesis of multiferrocenyl silanols **A** and **B** (depicted in Scheme 3) [26].



Scheme 3. Proposed route for the formation of cyclotrisiloxane 3.

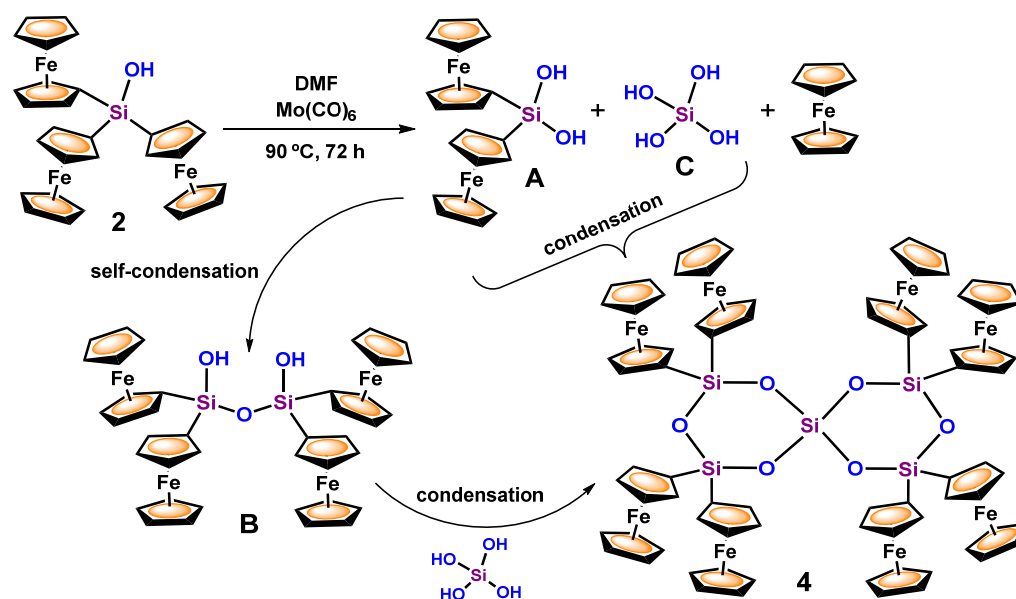
On the basis of our previous experience [26], and Manners group reactions [39], it seems reasonable to assume that, after forcing reaction conditions in the presence of $\text{Mo}(\text{CO})_6$ and heat, the diferrocenylsilanol **A** was formed, also supporting the ferrocene formation. Then, this disilanol **A** would condense to form a stable cyclosiloxane, the hexaferrocenylcyclotrisiloxane **3** (Scheme 3). Alternatively, and/or simultaneously, disilanol **A** could also condense to form the tetraferrocenyldisiloxanediol **B**, which in turn would form cycle **3**.

The ^1H NMR and MALDI-TOF spectra for the second unexpected fraction obtained from the column chromatography (FB), showed a mixture of two species. One of them was easily identified as hexaferrocenylcyclotrisiloxane **3**, and the other one had a mass of m/z 1716.9, consistent with eight ferrocenyl units. After several attempts, suitable crystals for single crystal X-ray diffraction studies were obtained. This analysis unambiguously confirmed the structure of the new and unexpected species **4**, with a surprising spirocyclic core (see Scheme 4). The spiro[5.5]octaferrocenylpentasiloxane **4** is indeed a very interesting macromolecule, with two cyclosiloxane rings, bearing ferrocenyl units linked in pairs to silicon atoms. To the best of our knowledge, species **4** is the first example of a molecular spirocyclic silicate with electroactive organometallic units. Unfortunately, all attempts to accurately separate the pure spirocyclic **4** from hexaferrocenylcyclotrisiloxane **3**, either by column chromatography or precipitation, have been unsuccessful so far. Only a reasonable amount of pure **4** was obtained, allowing its characterization by MALDI-TOF mass spectrometry (Figure S1 in Supplementary Material), elemental analysis, and single crystal X-ray diffraction (see Section 3.2).

The formation of the spirocyclic silicate **4** is far from being obvious and only becomes understandable when looking at the reactions explained above for the formation of siloxane **3**. A tentative path for the formation of such a Si-centered spirocyclic species **4** from triferrocenylsilanol **2** is outlined in Scheme 4. Most likely, under forced reaction conditions, in the presence of DMF, $\text{Mo}(\text{CO})_6$, and heat, the generated triferrocenylsilanol **2** can decompose, losing not only one ferrocene as commented for the formation of **3**, but even up to all three ferrocenyl units, causing the formation of tetrahydroxysilane (orthosilicic acid) **C**. This silanol $\text{Si}(\text{OH})_4$ is extremely reactive and would be able to condense with four molecules of **A** to form **4**. A second possible pathway to spirocyclic **4** would involve the condensation reaction of $\text{Si}(\text{OH})_4$ and two molecules of the tetrametallic disiloxane **B**. Again, these processes are facilitated by the high tendency of silanol compounds, in this case, di- and tetra-silanol, to self-condense.

Therefore, we believe that the presence of DMF, as an oxygen-donor solvent; of $\text{Mo}(\text{CO})_6$ as a catalyst; and the high temperatures achieved in the $\text{Fc}_3\text{Si-H}$ (**1**) \rightarrow $\text{Fc}_3\text{Si-OH}$ (**2**) transformation attempts were enough to: (1) decompose triferrocenylsilanol **3**, via Si-Fc bond break and formation of pure ferrocene; (2) generate initially unexpected silanols **A**, **B**,

and C; (3) favor intermolecular condensations of silanols A–C, less sterically hindered than silanol 2, to form cyclic 3 and spirocyclic 4 macromolecules.



Scheme 4. Suggested route for the formation of Si-centered spiro[5.5]octaferrocenylpentasiloxane 4.

A further alternative would be to admit the presence of a small amount of silica (SiO_2) in the reaction flask, which would react with silanols A and/or B, under the reaction conditions already mentioned, to form spirocyclic 4. A well-known route to organic spirosilicates implies the reaction of glycol derivatives with SiO_2 , at very high temperatures and with or without KOH [40,41]. In some cases, it was observed that triethylenetetramine (TETA), used as a solvent, acted in turn as an accelerator to dissolve silica [41].

3.2. Single Crystal X-ray Diffraction

Compound 4 was characterized by single crystal X-ray diffraction, after manually isolating the orange needle-shaped crystals. It was found to crystallize as a solvate with a sum formula $(\text{C}_{80}\text{H}_{72}\text{Fe}_8\text{O}_6\text{Si}_5) \cdot 2(\text{CH}_2\text{Cl}_2)$ in the tetragonal $P4_2/n$ space group. The asymmetric unit contains a quarter of the spiro[5.5]octaferrocenylpentasiloxane and half of a highly disordered dichloromethane molecule, as both moieties are coincident with symmetry elements (a fourfold rotoinversion axis, in the case of compound 4, with the inversion center located at Si1; and a 4_2 axis intersecting at the carbon atom C21, in the case of CH_2Cl_2).

Compound 4 displays an extremely unusual core with two perpendicular flat six-membered siloxane rings. This disposition had only been reported previously in the octamethyl spiro-5,5-pentasiloxane published by Roth et al. (CSD code OMSSIO, [42]). Siloxane core structures with a spiral disposition of two cyclic units can also be found in the structures with CSD codes MIWKIP [43] and TMPSIX [44], although in those cases the siloxane rings are not planar.

Regarding the ferrocene moieties, the minimum distance between iron atoms (Fe1-Fe2, from ferrocenes bonded to the same silicon atom) is 6.066(1) Å, while the largest one is 11.242(2) Å, between Fe1 atoms located in opposite sides of the molecule (namely Fe1-Fe1ⁱⁱ and Fe1-Fe1ⁱⁱⁱ) as can be seen in Figure 2. Finally, the packing of the molecules of 4 is achieved by weak C-H \cdots π interactions.

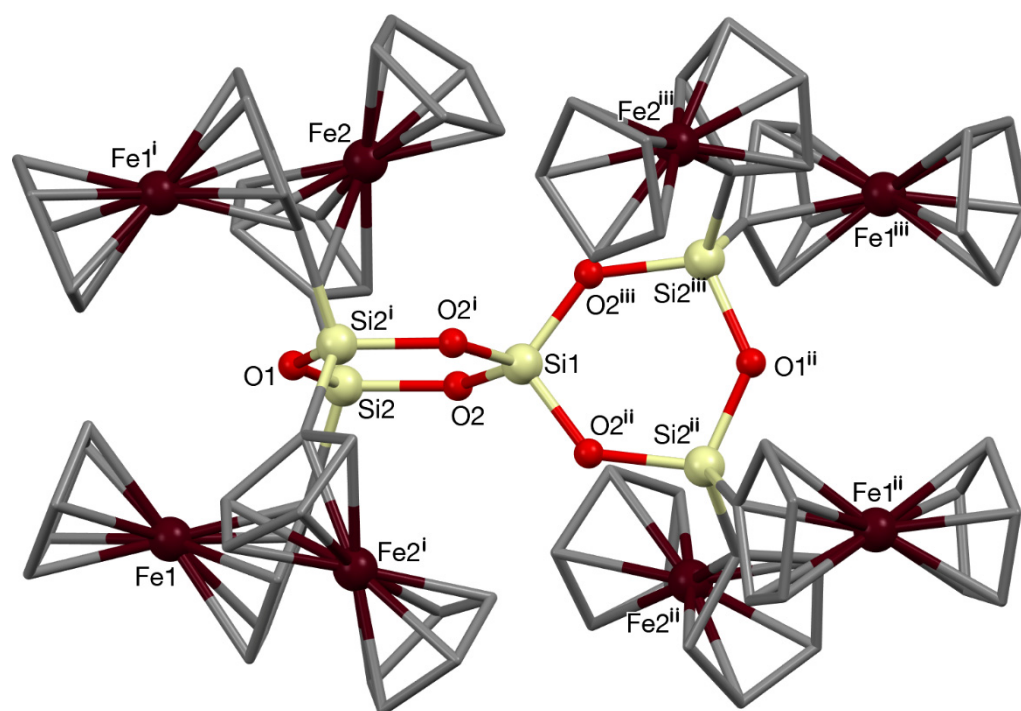


Figure 2. Molecular plot of the crystal structure of compound **4** with selected atoms labeled (symmetry operations: (i) $-x + 1/2, -y + 1/2, z$; (ii) $y, -x + 1/2, -z + 3/2$; (iii) $-y + 1/2, x, -z + 3/2$). Hydrogen atoms and the solvent molecule have been omitted for clarity.

4. Conclusions

In summary, the several attempts to transform the silicon hydride functionality within triferrocenyilsilane **1** into a silanol Si–OH group, using different metallic catalysts (with Pt(0) or Mo(0)) and different solvents (DMF or DMSO) as oxygen-donor agents, gave the triferrocenyilsilanol **2** as the major product; however, these reactions were accompanied by different secondary processes, mainly facilitated by the high tendency of the silanol group to experiment intermolecular condensation reactions. Intriguingly, when $\text{Mo}(\text{CO})_6$ is used as a catalyst, DMF as the oxygen-donor solvent, and the reaction is heated at 90°C for 72 h, intermediate species such as $\text{Fc}_2\text{Si}(\text{OH})_2$ (**A**) and $\text{Fc}_2(\text{OH})\text{Si}-\text{O}-\text{Si}(\text{OH})\text{Fc}_2$ (**B**) seem to be formed, which, in turn, would condense to give the cyclic species hexaferrocenylcyclotrisiloxane **3**. Surprisingly, a molecular spirocyclic silicate that contains two ferrocenyl-functionalized cyclosiloxane rings, connected by one silicon atom was also obtained, the unexpected spiro[5.5]octaferrocenylpentasiloxane **4**. This molecule is the first example reported so far of a spirocyclic silicate with organometallic electroactive units, namely eight pendant ferrocenes. It is assumed that **4** is obtained from reactions of silanols **A** and **B** with either $\text{Si}(\text{OH})_4$ (**C**) or SiO_2 . The crystal structure of **4**, solved by single crystal X-ray diffraction, proves the unusual geometry of this compound.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst12081122/s1>, Figure S1: MALDI-TOF mass spectrometry of **4**; Figure S2: X-ray structure of **4**; Table S1: sample and crystal data for **4**; Table S2: data collection and structure refinement for **4**; Table S3: Si–O bond distances; Table S4: selected bond angles.

Author Contributions: Conceptualization, S.B. and I.C.; methodology, S.B. and J.P.; software, J.P.; formal analysis, S.B. and J.P.; investigation and data curation, S.B. and J.P.; writing—original draft preparation and—review and editing, S.B., I.C. and J.P.; supervision, S.B.; project administration and funding acquisition, I.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministerio de Ciencia e Innovación of Spain, grant number PGC2018-094644-B-C21.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Crystal structure of **4** has been deposited at the Cambridge Structural Database with deposit number CCDC 2182627.

Acknowledgments: In loving memory of our co-worker Ignacio Martínez Montero (1989–2020), the brightest person we knew.

Conflicts of Interest: The authors declare no conflict of interest.

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