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An iron–sulfur–tin cluster with amino-ligands and its reactions with thiols

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Abstract

The dinuclear complex $\text{Fe}_2(\mu_2\text{-}\eta^2\text{-S}_2)(\text{CO})_6$ (**1**) has been reacted with the bis(amino)stannylene $\text{Sn}(\mu\text{-N}t\text{-Bu})_2\text{SiMe}_2$ (**2**) to form the new 1:1 complex $\text{Me}_2\text{Si}(\mu\text{-N}t\text{-Bu})_2\text{SnFe}_2(\mu_3\text{-S})_2(\text{CO})_6$ (**4**). The ‘double-star’ shape of its $\text{Fe}_2\text{S}_2\text{Sn}$ central core (X-ray structure analysis, multinuclear NMR) contains a tetracoordinated tin atom, which provides a spirocyclic connection between the Fe_2S_2 butterfly and the four-membered SnN_2Si cycle. The reaction can thus be described as an insertion of the divalent tin into the sulphur–sulphur bond of the $\text{Fe}_2(\mu_2\text{-}\eta^2\text{-S}_2)(\text{CO})_6$ precursor. All distances and angles in **4** are in accordance with tin being in the formal oxidation state +4. The Sn–N bonds in this cluster can serve as excellent targets for the subsequent addition of thiols (sulphanes). Indeed, these bonds are highly reactive and when $\text{HS}(\text{CH}_2)_2\text{SH}$ is allowed to react with **4**, the cluster is destroyed and the spiro-cyclic tin sulphide $\text{Sn}[\text{S}_2(\text{CH}_2)_2]_2$ is the only isolable reaction product. If $\text{HS}(\text{CH}_2)_2\text{SH}$ is replaced by $\text{Me}_3\text{Si}(\text{CH}_2)_2\text{SH}$, the 1:1 adduct $\text{Me}_2\text{Si}(\mu\text{-N}t\text{-Bu})[\mu\text{-N}(\text{H})t\text{-Bu}]\text{Sn}\{\text{S}(\text{CH}_2)_2\text{SiMe}_3\}(\mu_3\text{-S})_2\text{Fe}_2(\text{CO})_6$ (**6a**) is isolated. This new cluster contains a five-coordinate tin atom (three S and two N donors) and has several functional groups (X-ray structure analysis, NMR). The proton of the thiol reagent $\text{Me}_3\text{Si}(\text{CH}_2)_2\text{SH}$ has migrated to one of the nitrogen atoms as a result of selective S–H addition across an Sn–N bond, while the $\text{Fe}_2\text{S}_2\text{Sn}$ core remains intact. To the best of our knowledge, no other tin compound displaying two nitrogen and three sulphur ligands has been structurally described before. *To cite this article: M. Veith et al., C. R. Chimie 8 (2005).*

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Résumé

Le complexe dinucléaire $\text{Fe}_2(\mu_2\text{-}\eta^2\text{-S}_2)(\text{CO})_6$ (**1**) réagit avec le bis(amino)stannylène $\text{Sn}(\mu\text{-N}t\text{-Bu})_2\text{SiMe}_2$ (**2**) pour donner le nouveau complexe 1:1 $\text{Me}_2\text{Si}(\mu\text{-N}t\text{-Bu})_2\text{SnFe}_2(\mu_3\text{-S})_2(\text{CO})_6$ (**4**). La forme en « double étoile » du cœur central $\text{Fe}_2\text{S}_2\text{Sn}$ (analyse structurale par diffraction des rayons X, RMN multinoyaux) contient un atome d’étain tétracoordiné, qui joue le rôle d’une jonction spirocyclique entre le papillon Fe_2S_2 et le cycle à quatre chaînons SnN_2Si . Cette réaction peut donc être décrite comme l’insertion d’un étain divalent dans la liaison S–S du précurseur $\text{Fe}_2(\mu_2\text{-}\eta^2\text{-S}_2)(\text{CO})_6$. Les distances et angles dans **4** sont en

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accord avec un étain au degré d'oxydation formel +4. Les liaisons Sn–N dans ce cluster peuvent donner lieu à des réactions d'addition ultérieures avec les thiols (sulfanes). Ces liaisons sont en effet très réactives et la réaction de HS(CH₂)₂SH avec **4** conduit à la destruction de ce dernier, le complexe Sn[S₂(CH₂)₂]₂ étant le seul produit isolé. En revanche, lorsque HS(CH₂)₂SH est remplacé par Me₃Si(CH₂)₂SH, le produit d'addition 1:1 Me₂Si(μ-N*t*-Bu)[μ-N(H)*t*-Bu]Sn{S(CH₂)₂SiMe₃}(μ₃-S)₂Fe₂(CO)₆ (**6a**) a pu être isolé. Ce nouveau cluster contient un atome d'étain pentacoordiné (trois S et deux N) et plusieurs groupes fonctionnels (étude structurale par diffraction des rayons X et RMN). À la suite de l'addition sélective de la liaison S–H de Me₃Si(CH₂)₂SH sur une liaison Sn–N de **4**, le proton a migré sur l'un des atomes d'azote, alors que le cœur Fe₂S₂Sn reste intact. À notre connaissance, aucun autre complexe de l'étain porteur de deux ligands azotés et de trois ligands soufrés n'avait été caractérisé auparavant. **Pour citer cet article** : M. Veith et al., C. R. Chimie 8 (2005).

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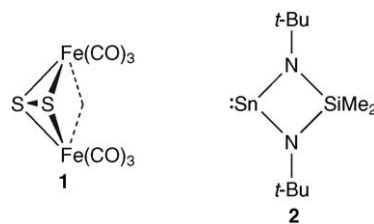
Keywords: Iron–tin–sulfur clusters; Functionalization of clusters; Reactivity of sulphanes (thiols); Stannylenes

Mots clés : Clusters fer–étain–soufre ; Fonctionnalisation de clusters métalliques ; Réactivité des thiols ; Stannyliènes

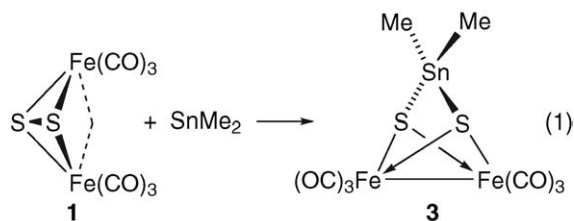
1. Introduction

The synthesis and characterization of various multinary sulphide tin-based semiconductors have recently attracted considerable attention [1–6]. Also the grafting and incorporation of metallic clusters with appropriate ligands on polymer or ceramic surfaces has been widely applied to intermetallics or bimetallic complexes [7–9]. We have focused our interest on the synthesis of sulphur-containing tin–iron heterobimetallic complexes and their functionalisation by tin–nitrogen bonds. Here, we present our results on the synthesis of several Fe₂S_nSn complexes that contain reactive tin–nitrogen bonds.

In the early eighties, Seyferth and co-workers developed the chemistry of Fe₂(μ₂-η²-S₂)(CO)₆ (**1**) [10]. This complex has been independently used by different groups as a precursor for the synthesis of various heteropolymetallic complexes and clusters, obtained by reaction with [CpNi(μ-CO)]₂ [11], [CpCr(CO)₃]₂ [12], [CpMo(CO)₃]₂ [13], [Mn₂(CO)₁₀] [14], Co₂(CO)₈ [15] or, more recently, Cp₂MoH₂ [16]. However, sulphur-containing tin–iron compounds are rare, and clusters with reactive tin–nitrogen bonds have proved to be very versatile [17]. To gain further insight into the reactivity of functionalised iron–tin–sulphur clusters, we have attempted to synthesize a new iron–tin–sulphur cluster by reacting **1** with the bis(amino)stannylyene Sn(μ-N*t*-Bu)₂SiMe₂ (**2**).



Since **1** can be viewed as an inorganic compound that mimics the organic disulphides owing to the behaviour of its sulphur–sulphur bond [10b], and since stannylenes are known to react with organic disulphides or with sulphur to give tetravalent Sn(IV) species [18], it is not surprising that the reaction of **1** with SnMe₂ has afforded the heterometallic complex **3** (equation (1)) [10e].



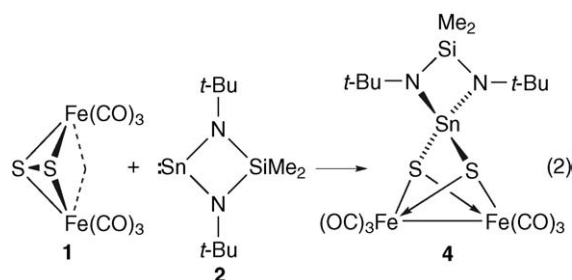
Therefore, the idea to react **1** with **2** seemed a straightforward approach to the desired target. Furthermore, the Sn–N bonds could provide reactive sites for the addition of thiols. In this paper we describe the synthesis of the new heterometallic complex Me₂Si(μ-N*t*-

$\text{Bu}_2\text{SnFe}_2(\mu_3\text{-S})_2(\text{CO})_6$ (**4**) and its reactions with the thiols $\text{HSCH}_2\text{CH}_2\text{SH}$ and $\text{HSCH}_2\text{CH}_2\text{SiMe}_3$.

2. Results and discussion

2.1. Synthesis and structure of the sulphur-containing tin–iron heterodimetallic cluster **4**

The reaction of $\text{Fe}_2(\mu_2\text{-}\eta^2\text{-S}_2)(\text{CO})_6$ (**1**) with one equivalent of the bis(amino)stannylene $\text{Sn}(\mu\text{-N}t\text{-Bu})_2\text{SiMe}_2$ (**2**) in hexane was almost quantitative and afforded a brown complex **4** in 64% isolated yield (equation (2)). This new cluster has been fully characterized by single crystal X-ray diffraction, IR, and NMR spectroscopic methods, and elemental analysis.



Cluster **4** is very soluble in most common organic solvents (hexane, C_6H_6 , THF), and can be isolated as solvent-free crystals. In a reaction similar to the one that led to **3**, the tin atom has inserted itself into the sulphur–sulphur bond of **1** and its oxidation state has increased from +2 to +4. This can also be deduced from the $^{119}\text{Sn}\{^1\text{H}\}$ NMR chemical shift of $\delta -24.73$, which corresponds to an upfield shift of 701 ppm with respect to the stannylene **2**, in which the tin atom is divalent. The nature of the reaction product is again consistent with the sulphur–sulphur anti-bonding character of the LUMO of **1**. Similar upfield shifts have already been observed in tin-alkoxides when changing the tin oxidation state from +2 to +4 and are attributed to an increase in the coordination number of the tin atom [19]. The ^1H and ^{13}C NMR spectra are in accord with a $C_{2v}(mm2)$ symmetry for molecule **4** (one signal for each one of the methyl and *tert*-butyl groups in the ^1H NMR spectrum and four signals for the carbon atoms in ^{13}C NMR, all carbonyl groups being equivalent). The $\nu(\text{CO})$ region

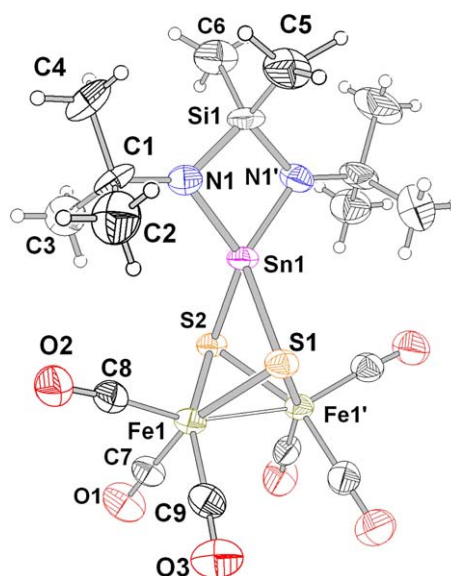


Fig. 1. Ball and stick view (with 50% thermal ellipsoids) of the molecular structure of **4** [31]; the small circles designate the locations of the hydrogen atoms.

in the infrared spectrum is consistent with the NMR findings and compared to **1**, the number (always 3) and intensity of the absorptions in **4** is unchanged, which is in accordance with a reaction of the stannylene **2** at the S–S edge of **1**.

The molecular structure of **4** has been determined from single crystal X-ray data. The compound crystallizes in the monoclinic space group $P2_1/m$ with two molecules per unit cell and has a crystallographic mirror plane containing the atoms S(1), S(2), Sn(1), Si(1), C(5) and C(6) (Fig. 1 and Table 1). A closer look at the distances and angles within **4** reveals (Table 1) that the distortion away from C_{2v} symmetry is only small. The Fe_2S_2 quasi-tetrahedral arrangement in **1** becomes a butterfly-type geometry in **4**, since the tin atom has inserted itself into the S–S bond and the S–S distance increases from 2.021(4) Å in **1** [20a] (typical σ -bonding distance for sulphur–sulphur bonds, see for example 3,3,6,6-tert-amethyl-*S*-tetrathiane [21]) to 3.046(4) Å in **4**. The $\text{Fe}_2\text{S}_2\text{Sn}$ cage part of the molecule and the four-membered SnN_2Si cycle share a common apex. The cage part of **4** is reminiscent of the structural features found in other $\text{Fe}_2\text{S}_2\text{M}$ clusters (where M = Pd, Mo, Ti, Ni) [10b, 10d, 10e, 16].

The small distortions away from C_{2v} symmetry in **1** to C_m in **4** can be exemplified by the pairs of distances

Table 1
Selected bond lengths (Å) and angles (°) for **4**

Bond distances			
Sn(1)–S(1)	2.447(3)	Fe(1)–S(1)	2.309(3)
Sn(1)–S(2)	2.455(3)	Fe(1)–S(2)	2.324(3)
Sn(1)–N(1)	2.042(7)	Si(1)–N(1)	1.747(7)
Fe(1)–Fe(1')	2.489(2)	Si(1)–C(5,6) mean	1.867(9)
Fe(1)–C(7,8,9) mean	1.78(1)	C(7,8,9)–O(1,2,3) mean	1.15(1)
Bond angles			
N(1)–Sn(1)–S(1)	126.7(2)	Fe(1')–S(1)–Fe(1)	65.2(1)
N(1)–Sn(1)–S(2)	129.2(2)	Fe(1)–S(2)–Fe(1')	64.7(1)
N(1')–Sn(1)–N(1)	76.5(4)	S(1)–Fe(1)–S(2)	82.3(1)
S(1)–Sn(1)–S(2)	76.9(1)		
Torsion angles			
N(1')–Sn(1)–N(1)–Si	6.37(1)	Fe(1)–S(1)–Fe(1')–S(2)	53.18(1)

Fe(1)–S(1)/Fe(1)–S(2) (difference 0.015 Å) or Sn–S(1)/Sn–S(2) (difference 0.008 Å). Since the structural data of **1** and **2** are known [20,22], a comparative analysis of the molecular structure of **4** is possible.

The sulphur atoms have become μ_3 -bonded and the Sn–S distances (mean: 2.450(6) Å) are in the range of normal Sn(IV)–S distances in molecules with tin bonded simultaneously to nitrogen and sulphur (the mean Sn–S bond length in [(Me₃Si)₂N]₂Sn(μ -S)]₂ is 2.417(8) Å [23]. The insertion of the tin atom in the S–S bond in **1** is accompanied by its formal oxidation and consequently, the Sn–N distances shrink as compared to the starting molecule **2** (from 2.092(4) to 2.042(7) Å in **4**), because the atomic radius of Sn(IV) is smaller than that of Sn(II) [24], and the N–Sn–N angle in the four-membered ring N(1)–Si(1)–N(1')–Sn(1) of **4** (76.5(4)°) is enlarged compared to that in **2** (73.2°). The opening of this angle can be understood in terms of a change in hybridisation of the tin atom, which in the stannylene **2** uses only p orbitals for bonding (the non-bonding electrons in a first approximation are in the s orbital), whereas it is approximately sp³ in **4**. The angle deformation at tin away from the idealized situation is 16.8° (90–73.2°) in **2** and 33° (109.5–76.5°) in **4**. The mean Sn–N distances in **4** compare well with bond lengths in molecules such as [SeSn(μ -N*t*-Bu)₂SiMe₂]₂ and [TeSn(μ -N*t*-Bu)₂SiMe₂]₂ (2.023(8) and 2.030(9) Å) [25], and the S₂Sn(μ -N*t*-Bu)₂SiMe₂ part of the cluster is identical to the corresponding subunit in [SSn(μ -N*t*-Bu)₂SiMe₂]₂ synthesized several years ago [26].

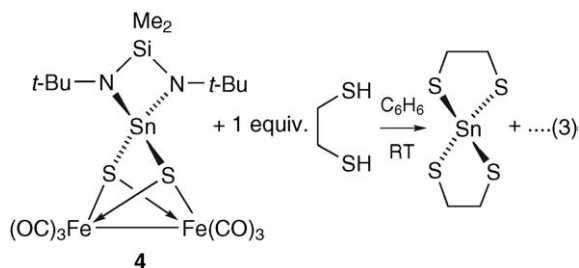
The Fe₂S₂(CO)₆ part of **4** also reveals some further information when compared to the structure of **1**. Inser-

tion of tin in the S–S bond results in an elongation of the Fe–S bonds (from Fe–S_{mean} = 2.235(7) in **1** to 2.317(7) Å in **4**) and a shrinkage of the Fe–Fe bond length (2.556(2) to 2.489(2) Å) [20]. This is in accordance with expectations: the separation of the two sulphur atoms in **4** makes the Fe₂S₂ bisphenoid flatter and therefore more flexible, allowing a tighter Fe–Fe bond. The withdrawal of electron density due to the Sn–S bonds from sulphur should elongate the adjacent bonds. The spirocyclic tin atom occupies the centre of a strained tetrahedron with acute N–Sn–N and S–Sn–S angles of 76.5(4) and 76.9(1)°.

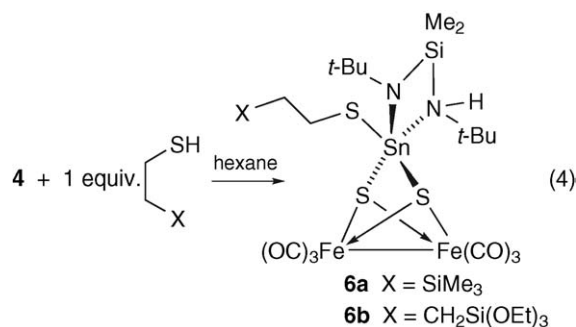
In summary, the structure of the new heterodimetallic cluster **4** is reminiscent of those found in other Fe₂S₂M clusters [10b, 10d, 10e,16] with the peculiarity of having two acute angles at tin and therefore a certain strain. We were therefore interested to examine whether the SnN₂ or the SnS₂ part of the molecule would be more reactive towards thiols and looked at the reaction of **4** with either HSCH₂CH₂SH or HSCH₂CH₂SiMe₃.

2.2. Reactions of the heterodimetallic cluster **4** with thiols and dithiols

The reaction of tin–iron–sulphur complex **4** with the dithiol HSCH₂CH₂SH in a 1:1 molar ratio led to cluster degradation. We were not able to separate and isolate all the products, but could recrystallise the Sn(IV) thiolate **5** after dissolution of the brown precipitate in a THF/hexane (1:1) mixture (equation (3)). It was fully characterized by X-ray structure analysis and compared with the data of the published structure [27].



Since it appears that the thiol attacks both the SnS_2 and SnN_2 moieties of complex **4**, we blocked one end of the thiol by a trimethylsilyl group to reduce its reactivity. The reaction of **4** with 1 equiv of $\text{Me}_3\text{Si}(\text{CH}_2)_2\text{SH}$ is shown in equation (4). It can also be run with $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{SH}$ (in place of $\text{Me}_3\text{Si}(\text{CH}_2)_2\text{SH}$) in a similar way (^1H NMR, IR evidence), but so far no complete characterization of the product **6b** has been possible¹.



The new cluster **6a** was isolated as the only product in 51% yield and this adduct between the two molecular precursors has been fully characterized by single crystal X-ray diffraction, IR, ^1H , ^{13}C , ^{119}Sn NMR and elemental analysis.

Compared to **4**, cluster **6a** has a lower molecular symmetry. This can already be seen from the IR spectrum in the CO region (five absorptions) in contrast to the C_{2v} symmetry molecules **1** and **4**, which show only three absorption bands. The dimethylsilyl group gives

¹ Selected data for **6b**: ^{13}C (^1H)NMR (C_6D_6) $\delta = -1.8$ (s, SiCH_3), 1.3 (s, SiCH_3), 15.5 (s, $\text{SiOCH}_2\text{CH}_3$), 21.9 (s, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{S}$), 25.7 (s, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{S}$), 31.9 (s, CCH_3), 33.8 (s, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{S}$), 35.2 (s, CCH_3), 54.4 (s, CCH_3), 54.6 (s, CCH_3), 65.8 (s, $\text{SiOCH}_2\text{CH}_3$), 210.2 (br s, CO).

rise to two singlets in ^1H and ^{13}C NMR spectroscopy and the two tert-butyl groups appear as two signals. The splitting of one of these signals in the ^{13}C NMR spectrum indicates some hindered rotation of the tert-butyl-N(H) group around the C–N bond; we assume that this rotation is more hindered than that of the other tert-butyl group owing to the tetrahedral coordination geometry of the nitrogen atom (atom N(2) in Fig. 2). Although there are two stereogenic centres in the molecule (tin and nitrogen atom N(2)), which are (from a dynamical point of view) fixed in the crystal structure (see below), there is clear indication that these stereogenic centres convert to the mirror image on the NMR timescale in solution. The resonance of the tin atom in the ^{119}Sn NMR is shifted from $\delta = -24.7$ (molecule **4**) to $\delta = -152.8$ in **6a**, which is consistent with an expansion of the coordination sphere.

A ball and stick view with thermal ellipsoids of $\text{Me}_2\text{Si}(\mu\text{-N}t\text{-Bu})[\mu\text{-N}(\text{H})t\text{-Bu}]\text{Sn}\{\text{S}(\text{CH}_2)_2\text{SiMe}_3\}(\mu_3\text{-S})_2\text{Fe}_2(\text{CO})_6$ (**6a**), obtained by X-ray diffraction methods, is shown in Fig. 2. The atoms Sn(1) and N(2) are stereogenic centres and two (of the four possible) diastereomers are present in the unit cell. The $\text{Fe}_2\text{S}_2(\text{CO})_6$ butterfly moiety of **6a** is almost unchanged compared to **4**, with all carbonyl groups being terminal. The most obvious difference between the structures of **4** and **6a** is the environment of the tin atom, which in **6a** has a distorted trigonal bipyramidal coordination sphere constituted by three sulphur and two nitrogen atoms. To

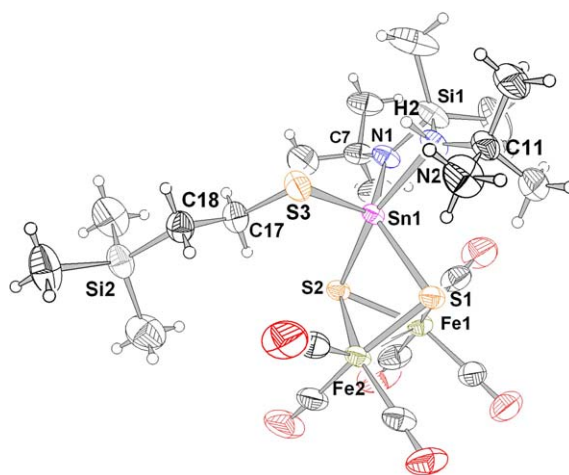


Fig. 2. Ball and stick view (with 50% thermal ellipsoids) of the molecular structure of **6a** [31]; the small circles designate the locations of the hydrogen atoms. The unlabelled atoms are either carbon or oxygen atoms (please refer to Fig. 1).

Table 2
Selected bond lengths (Å) and angles (°) for **6a**

Bond distances			
Sn(1)–S(1)	2.510(1)	Fe(1)–S(1)	2.273(1)
Sn(1)–S(2)	2.506(1)	Fe(1)–S(2)	2.310(1)
Sn(1)–S(3)	2.420(1)	Fe(1)–Fe(2)	2.494(1)
Sn(1)–N(1)	2.077(4)	Fe(2)–S(1)	2.284(1)
Sn(1)–N(2)	2.368(4)	Fe(2)–S(2)	2.298(1)
Si(1)–N(1)	1.694(4)	Si(1)–C(15,16) mean	1.860(7)
Si(1)–N(2)	1.816(4)	Si(2)–C(18–21) mean	1.873(6)
Bond angles			
N(1)–Sn(1)–N(2)	69.8(1)	S(3)–Sn(1)–N(2)	89.6(1)
S(2)–Sn(1)–S(1)	73.64(4)	S(2)–Sn(1)–N(2)	163.5(1)
N(2)–Sn(1)–S(1)	96.2(1)	S(1)–Sn(1)–N(1)	131.1(1)
N(1)–Sn(1)–S(2)	106.8(1)	S(1)–Fe(1)–S(2)	81.98(5)
S(3)–Sn(1)–S(1)	115.25(5)	S(1)–Fe(2)–S(2)	82.00(5)
S(3)–Sn(1)–S(2)	106.42(5)	Fe(1)–S(1)–Fe(2)	66.36(4)
S(3)–Sn(1)–N(1)	111.4(1)	Fe(1)–S(2)–Fe(2)	85.53(4)

the best of our knowledge, no other tin compound displaying two nitrogen and three sulphur ligands has been structurally described before.

From a chemical point of view, the sulphane (thiol) has added across one of the Sn–N bonds in **4** (the S(3)⋯H separation is only 2.88(1) Å). A related addition of an N–H bond across a Sn–N bond of **2** (or stannylene insertion into a N–H bond) has been reported recently [28]. As a consequence of this addition reaction, the sum of the bond angles around N(2) amounts to 349.2° (neglecting the hydrogen atom), compared to the sum of the bond angles around N(1), which retains its almost trigonal planar coordination geometry (359.7°). The addition of the hydrogen atom also leads to an elongation of the Sn–N(2) bond length compared to Sn–N(1) by 0.291 Å (Table 2). The equatorial ligands around tin are S(1), N(1), and S(3), while N(2) and S(2) are in axial positions. An alternative description of the coordination geometry around tin would be that of a distorted square pyramid with S(3) in the apical position. This would neglect the very wide S(2)–Sn(1)–N(2) angle of 163.5(1)°, but could account for the similar Sn–S(1,2) bond lengths and the shorter Sn(1)–S(3) distance, although this difference is also due to the λ^2/λ^3 nature of the sulphur atoms (Table 2) (see also [29]). The expansion of the tin coordination sphere in **6a** compared to **4** has almost no effect on the Fe(1)–Fe(2) distance, but is reflected in smaller Fe–S distances in **6a** (Fe–S_{mean}: 2.29(1) Å) compared to **4** (Fe–S_{mean}: 2.32(1) Å). The latter effect is due to less tight bonding

of the tin atom to the Fe₂S₂(CO)₆ butterfly moiety in **6a** because of its involvement in bonding to three electronegative ligands instead of two.

3. Experimental section

The syntheses of the dinuclear complex Fe₂(μ₂-η²-S₂)(CO)₆ (**1**) [20] and of the bis(amino)stannylene Sn(μ-Nt-Bu)₂SiMe₂ (**2**) [22] were carried out following the established procedures. All experimental manipulations were performed in a modified Schlenk-type apparatus taking stringent precautions against atmospheric moisture. Solvents were purified by standard methods and stored over appropriate desiccating agents. The single crystal X-ray diffraction study was performed on a IPDS instrument of STOE (Darmstadt, Germany), using the Mo Kα radiation (Table 3). The structures were solved by direct methods and refined with anisotropic temperature factors for all non-hydrogen atoms [30]. The hydrogen atoms were refined as idealized rigid groups [30]. The infrared spectra were recorded as KBr discs on a BioRad FT-IR-165 spectrometer. NMR spectra were measured on a Bruker (Karlsruhe) 200-MHz apparatus (ACF) with 5% deuterio-benzene in benzene as a solvent. The C,H-analyses were obtained with a LECOTM apparatus (St. Joseph, MI, USA).

3.1. Me₂Si(μ-Nt-Bu)₂SnFe₂(μ₃-S)₂(CO)₆ (**4**)

In a 250 ml flask were placed together **1** (3.56 g, 13.2 mmol) and **2** (4.20 g, 13.2 mmol) in hexane

Table 3
Crystallographic data for **4** and **6a**

Compound	4	6a
Formula	C ₁₆ H ₂₄ Fe ₂ N ₂ O ₆ S ₂ SiSn	C ₂₉ H ₃₇ Fe ₂ N ₂ O ₆ S ₃ Si ₂ Sn
<i>M_r</i>	662.97	797.28
Crystal group	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>C</i> 2/ <i>c</i>
<i>F</i> (000)	660	3232
<i>A</i> (Å)	6.470(1)	17.781(4)
<i>b</i> (Å)	17.418(3)	18.354(4)
<i>c</i> (Å)	11.903(2)	21.555(4)
<i>β</i> (°)	104.91(3)	95.83(3)
<i>V</i> (Å ³)	1296.2(4)	6998(3)
<i>Z</i>	2	8
Abs. coeff. (Mo Kα) (mm ⁻¹)	2.299	1.807
Theta range (°)	1.77–24.20	1.80–24.04
Indep. reflections	2008	5399
Parameters	159	338
<i>R</i> -value [<i>I</i> > 2 σ(<i>I</i>)]	0.0546	0.0399
<i>wR</i> 2	0.0993	0.0971
Largest peak/hole (e Å ⁻³)	1.008/–1.374	1.303/–0.919

(100 ml) at 0 °C. The solution was stirred for 1 h and then warmed up to room temperature. From the solution held at –20 °C in hexane, red-brown needles of **4** crystallized (5.50 g, 8.3 mmol, yield: 64%). Selected IR data (C₆H₆) : ν(CO) 2067 (s), 2030 (s), 1999 (w) cm⁻¹. ¹H NMR (C₆D₆) δ: 0.23 (s, 6H, SiMe), 1.24 (s, 18H, *t*-Bu). ¹³C{¹H} (C₆D₆) δ: 6.7 (s, SiCH₃), 36.6 (s, CCH₃), 54.0 (s, CCH₃), 208.67 (s, CO). ¹¹⁹Sn{¹H} (C₆D₆) δ: –24.73. Anal. calcd for C₁₆H₂₄Fe₂N₂O₆S₂SiSn (663.00): C, 28.99; H, 3.65; N, 4.23. Found: C, 27.77; H, 3.62; N, 4.17.

3.2. Me₂Si(μ-*Nt*-Bu)[μ-*N(H)t*-Bu]Sn{S(CH₂)₂SiMe₃}- (μ₃-S)₂Fe₂(CO)₆ (**6a**)

In a 100-ml flask, 0.550 g of **4** (0.83 mmol) was dissolved in 20 ml of hexane. To this solution was slowly added a solution of HSCH₂CH₂SiMe₃ (0.111 g, 0.83 mmol) in hexane (2 ml). The solution turned brown within a few minutes; it was stirred overnight and separated from solid residues. The filtrate was concentrated and cooled to –20 °C upon which brown, parallelepipedic crystals of **6a** were formed (0.340 g, 0.43 mmol, 51%). Selected IR data (hexane): ν(CO) 2068 (s), 2030 (s), 1999 (s) 1988 (m) 1975 (m) cm⁻¹. ¹H NMR (C₆D₆) δ: 0.02 (s, 9H, SiMe₃), 0.16 (s, 3H, NHSiMe), 0.24 (s, 3H, NSiMe), 1.04 (s, 9H, NH*t*-Bu), 1.14 (m, 2H,

CH₂SiMe₃), 1.33 (s, 9H, *Nt*-Bu), 1.81 (s br, 1H, NH), 3.10 (m, 2H, CH₂SSn). ¹³C{¹H} (C₆D₆) δ: –0.2 (s, SiCH₃), 5.5 (s, SiCH₃), 6.2 (s, Si(CH₃)₃), 21.4 (s, CH₂SiMe₃), 25.2 (s, CH₂SSn), 31.4 (s, CCH₃), 34.5 (s, CCH₃), 34.9 (s, CCH₃), 53.9 (s, CCH₃), 54.1 (s, CCH₃), 209.7 (br s, CO). ¹¹⁹Sn{¹H} (C₆D₆) δ: –152.8. ¹¹⁹Sn (C₆D₆) δ: –152.8 (pseudo t, ³*J*_{Sn-H} = 40 Hz, Sn–SCH₂). Calcd for C₂₉H₃₇Fe₂N₂O₆S₃Si₂Sn (797.32): C, 31.64; H, 4.80; N, 3.51; Found C, 30.30; H, 4.96; N, 3.37%.

The most relevant crystallographic data for compound **4** and **6a** are assembled in Table 3. Further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ (UK) on quoting the depository numbers CCDC-250612 and 250613.

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