



Synthesis of a distanna [2]ferrocenophane and reactivity of [2]ferrocenophanes towards elemental sulfur and selenium

H. Bera, H. Braunschweig*, A. Oechsner, F. Seeler, R. Sigritz

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

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ABSTRACT

Here we report the synthesis and crystal structure of a new [2]ferrocenophane $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\text{Sn}t\text{Bu}_2)_2]$ with a sterically demanding distannanediyl bridge. The reactivity of the title compound towards selected main group elements was examined and in addition, this reactivity pattern was established for the related diboranediyl bridged [2]ferrocenophane $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\text{BNMe}_2)_2]$.

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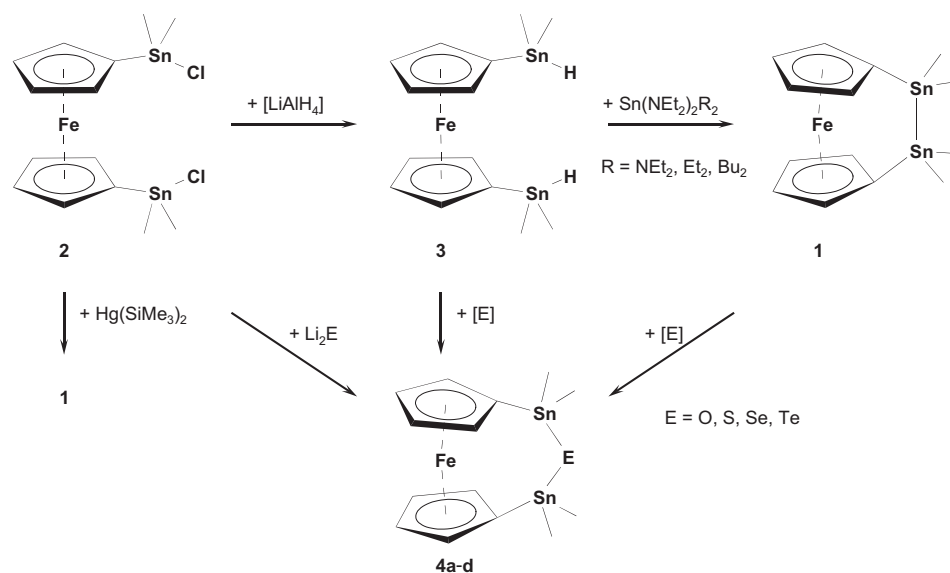
1. Introduction

The first 1,2-distanna [2]ferrocenophane (**1**) was reported more than one decade ago. Its synthesis was achieved *via* different multistep protocols, starting either from $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SnMe}_2\text{Cl})_2]$ (**2**), which was treated with $\text{Hg}(\text{SiMe}_3)_2$ or alternatively and in higher yields, by reacting **2** with $[\text{LiAlH}_4]$ to give $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SnMe}_2\text{H})_2]$ (**3**), followed by treatment with $\text{Sn}(\text{NEt}_2)_2\text{R}_2$ ($\text{R} = (\text{NEt}_2)_2, \text{Et}_2, \text{Bu}_2$) to generate **1** [1]. The reactivity of **1** towards transition metals was examined, showing that upon addition of suitable platinum phosphine complexes, an oxidative addition takes place with formation of 1,3-distanna-2-platina [3]ferrocenophanes that were structurally characterized [2,3]. Moreover, starting from these [3]ferrocenophanes, a reductive elimination was observed in the presence of stoichiometric amounts of alkynes and the corresponding 1,4-distanna [4]ferrocenophanes were formed. These compounds are also accessible by a Pt^0 catalyzed pathway starting from **1**, so that the platinum containing [3]ferrocenophanes must be considered as the catalytic active species [4]. In addition, the synthesis of 1,3-distanna-2-chalcogena [3]ferrocenophanes (**4a–d**) was established. This was accomplished by various synthetic routes, either *via* a salt elimination reaction on treating **2**

with Li_2E ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$) or directly, on reacting **1** or **3** with elemental oxygen, sulfur, selenium and tellurium, respectively [5]. Only recently, the insertion of chalcogens was intensely studied for corresponding distanna *ansa*-half-sandwich complexes of molybdenum and tungsten [6] (Scheme 1).

The 1,2-bis(dimethylamino)-1,2-dibora [2]ferrocenophane (**5**), which represents a diboron analogue of the aforementioned distanna [2]ferrocenophane, can also be obtained by various procedures. Originally it was synthesized from dilithiated ferrocene $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Li})_2 \cdot \text{tmeda}]$ (**6**) upon reaction with $\text{Cl}_2\text{B}_2(\text{NMe}_2)_2$ [7]. It is noteworthy, that the dilithiation of a large number of “non-iron” metallocenes and metalloarenes is well established by now and the aforementioned protocol for the synthesis of strained metallocenophanes and metalloarenophanes, respectively, is widely employed [8,9]. Subsequently, we reported an alternative synthesis of **5**, its crystal structure, and initiated reactivity studies of this compound, revealing distinct, and to some extent surprising reactivity patterns [10]. Thus, in the presence of either boranes or diboranes, the formation of 1,1'-diborylferrocenes was observed [11]. In addition, the reactivity towards multiple bond systems was examined and it was demonstrated that in the presence of the platinum phosphine complex $[\text{Pt}(\text{PET}_3)_3]$, the homogeneous transition metal catalyzed diboration of alkynes proceeded. The catalytically active species, a 1,3-dibora-2-platina [3]ferrocenophane, was isolated and structurally characterized [12]. This reactivity pattern was successfully transferred to other systems and for the

* Corresponding author. Tel.: +49 931 8885260; fax: +49 931 8884623.
E-mail address: h.braunschweig@uni-wuerzburg.de (H. Braunschweig).



Scheme 1. Synthesis of 1,3-distanna-2-chalcogena [3]ferrocenophanes **4a–d**.

first time, the diboration of the N–N double bond in azobenzene and the 1,1'-diboration of isocyanides was demonstrated [13,14]. It should be noted, that for the reaction of **4** with alkynes, an alternative heterogeneous catalyzed synthetic protocol was developed as well [12] (Scheme 2).

In this work, we present the synthesis and characterization of a new, sterically encumbered distanna [2]ferrocenophane and compare its reactivity towards selected group 16 elements with that of a corresponding dibora [2]ferrocenophane.

2. Results and discussion

The synthesis of 1,1,2,2-tetra-*tert*-butyl-1,2-distanna [2]ferrocenophane (**7**) was performed following the common synthetic route for [n]ferrocenophanes. A suspension of **6** in benzene was treated with equimolar amounts of $t\text{Bu}_4\text{Sn}_2\text{Cl}_2$ at rt. The reaction mixture was stirred for four hours during which the color changed from orange to red. After workup, **7** was obtained as orange crystals from a solution in pentane at -30°C in good yields of 74%. **7** is sensitive to moisture but can be stored under an atmosphere of argon at rt for several months without any signs of decomposition. The ^1H NMR spectra shows a characteristic set of signals for moderately strained ferrocenophanes with two multiplets at 4.41 and 4.32 ppm, respectively, and a singlet at 1.48 ppm ($^3J_{\text{H-Sn}} = 63/66$ Hz, $^4J_{\text{H-Sn}} = 6$ Hz), with an integration value of 4:4:36. The ^{119}Sn NMR spectrum shows one signal at 18.5 ppm ($^1J_{\text{Sn-Sn}} = 1698$ Hz) (Scheme 3).

Crystals suitable for X-ray diffraction were grown from hexane at -30°C . **7** crystallizes in the monoclinic space group $P2_1/n$. The compound is only slightly strained as shown by a small tilt angle α of 1.4° and a deformation angle δ of 178.8° . These structural data are in good agreement with the known distannanediyl bridged [2] ferrocenophane **1** ($\alpha = 0.7^\circ$, $\delta = 179.4^\circ$) [1], but in contrast to stanna [1]ferrocenophanes, such as $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{Sn}t\text{Bu}_2]$. The latter exhibits significant molecular strain, affirmed by the tilt angle $\alpha = 14.1^\circ$ [15] (Fig. 1).

The Sn–Sn bond length amounts to 2.8267(15) Å and thus, is in good agreement with that of the starting compound $\text{Cl}_2\text{Sn}_2t\text{Bu}_4$ (2.8299(5) Å) [16] and that of *ansa*-half-sandwich complexes of molybdenum or tungsten with values of 2.8200(12) Å and 2.8234 (4) Å, respectively, which also show the sterically demanding

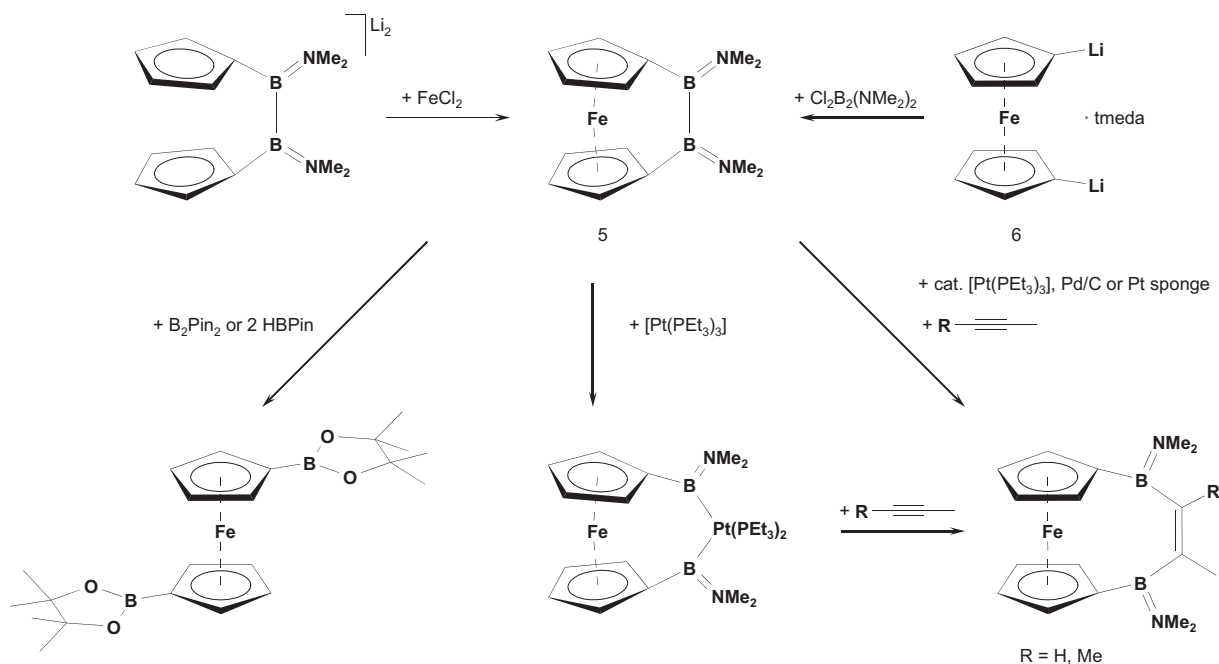
Sn_2tBu_4 -bridge [6]. However, the Sn–Sn bond length of **1** is significantly shorter (2.762(1) Å), obviously due to the presence of small methyl substituents [1].

In the following, the reactivity of **7** towards elemental sulfur and selenium was examined. The [2]ferrocenophane was mixed with an excess of elemental sulfur in C_6D_6 and the reaction mixture was kept at 80°C for five days. The multinuclear NMR spectra from monitoring the reaction gave no indication for the formation of a byproduct. After workup, the new 1,3-distanna-2-thia [3]ferrocenophane **8** was isolated in 84% yield. The ^1H NMR spectra show two high field shifted multiplets at 4.27 and 4.15 ppm, respectively, and a singlet at 1.42 ppm ($^3J_{\text{H-Sn}} = 74/77$ Hz), while the ^{119}Sn NMR spectrum shows one signal at 36.1 ppm ($^2J_{\text{Sn-Sn}} = 215$ Hz). The melting point of **8** was determined to be 109°C and the compound can be stored under an atmosphere of argon without any signs of decomposition.

Following the same procedure as described for the synthesis of **8**, the distanna [2]ferrocenophane **7** was reacted with elemental selenium, thus forming the 1,3-distanna-2-selena [3]ferrocenophane **9**, in 54% yield after workup. The ^1H NMR spectrum is very similar to that of **8**, showing two multiplets at 4.26 and 4.15 ppm and a singlet at 1.41 ppm ($^3J_{\text{H-Sn}} = 74/77$ Hz). The ^{119}Sn NMR spectrum shows one signal at 32.8 ppm (s, $^1J_{\text{Sn-Se}} = 1363$ Hz, $^2J_{\text{Sn-Sn}} = 194$ Hz) (Scheme 4).

Crystals of **8**, suitable for X-ray diffraction were grown from hexane at -30°C . The compound crystallizes in the monoclinic space group $P2_1/n$. **7** is slightly strained with values of $\alpha = 3.1^\circ$ and $\delta = 176.9^\circ$, but due to the lengthening of the bridging unit, the bending is on the opposite side of the bridge. All data are very close to those measured for the analogous compound **4b** ($\alpha = 3.3^\circ$, $\delta = 177.3^\circ$, Sn–S 2.409(1) Å and 2.410(1) Å, Sn–C_{Me/ips} 2.117–2.127 Å, Sn–S–Sn 104.2°) (Fig. 2).

The reactivity of elemental sulfur and selenium towards Sn–Sn bonds is well established and is transferred on 1,2-dibora [2]ferrocenophane **5**. By following the aforementioned procedure, **5** was mixed with elemental sulfur or red selenium, respectively, to give the sulfur or selenium containing compound **10** and **11**, respectively. It should be noted, that on the addition of grey selenium, no changes in the NMR spectra could be observed. After 24 h, the reaction was complete in each case and the color changed from red to orange (Scheme 5).



Scheme 2. Synthesis and reactivity of the 1,2-dibora [2]ferrocenophane **5**.

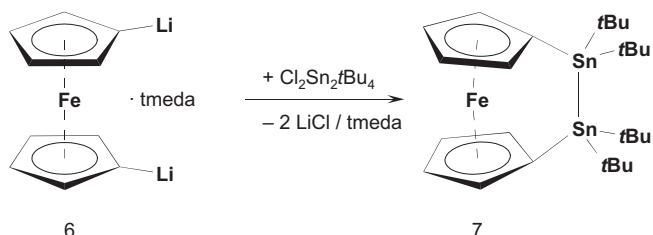
After workup, the 1,3-dibora-2-thia [3]ferrocenophane (**10**) and the 1,3-dibora-2-selena [3]ferrocenophane (**11**) were isolated in 63% and 65% yield, respectively, and their constitution in solution was confirmed by multinuclear NMR spectroscopy. Both compounds were initially synthesized *via* a ring-closure reaction, starting from 1,1'-bis[chloro(dimethylamino)boryl]ferrocene and reaction with either Li_2S or Li_2Se , respectively. All NMR spectroscopic data are identical to those previously published [17].

3. Summary

Here, we reported the synthesis and full characterization of a new, sterically encumbered 1,2-distanna [2]ferrocenophane **7**. Despite the presence of four *tert*-butyl substituents at the bridging distannediyl moiety, the tin–tin bond of **7** remains susceptible to insertion of elemental sulfur and selenium with formation of two new distanna [3]ferrocenophanes. Likewise, reaction of the diborane-bridged analogue **5** with elemental sulfur and selenium under somewhat harsher conditions, yielded the corresponding dibora [3]ferrocenophanes, with clean insertion of the group 16 element into the boron–boron bond. Access to the latter species was hitherto restricted to multistep salt elimination protocols.

4. Experimental

All manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques or in a glove box.



Scheme 3. Synthesis of **7**.

Solvents were dried according to standard procedures, freshly distilled prior to use, degassed and stored under argon over activated molecular sieves. Deuterated solvents were distilled from potassium. The starting materials $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{BNMe}_2)_2]$ (**5**) [7,10], $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Li})_2 \cdot \text{tmeda}]$ (**6**) [8], red selenium and $t\text{Bu}_4\text{Sn}_2\text{Cl}_2$ [16] were prepared according to published methods. The NMR spectra were recorded on a Bruker AV 500 (^1H , 500.13 MHz; ^{11}B , 160.46 MHz; ^{13}C , 125.75 MHz; ^{119}Sn , 186.50 MHz) FT-NMR spectrometer. ^1H and ^{13}C NMR spectra were referenced to external TMS *via* the residual protio solvent (^1H) or the solvent itself (^{13}C). ^{11}B NMR spectra were referenced to $\text{BF}_3 \cdot \text{OEt}_2$ and ^{119}Sn NMR spectra to Me_4Sn . Elemental analyses were performed on a Vario Micro Cube elemental analyzer. The melting points were measured on a Mettler Toledo DSC823^o.

[Fe($\eta^5\text{-C}_5\text{H}_4\text{Sn}t\text{Bu}_2$)₂] (7): 222 mg (0.041 mmol) of $t\text{Bu}_4\text{Sn}_2\text{Cl}_2$ were added under stirring to a suspension of 130 mg (0.41 mmol) of **6** in 80 mL benzene at rt. The reaction mixture was stirred for 4 h. All volatile components were removed *in vacuo*, the orange precipitate was extracted into pentane and all insoluble material

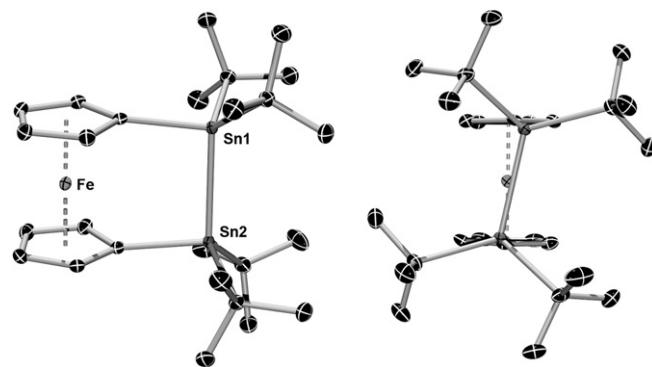
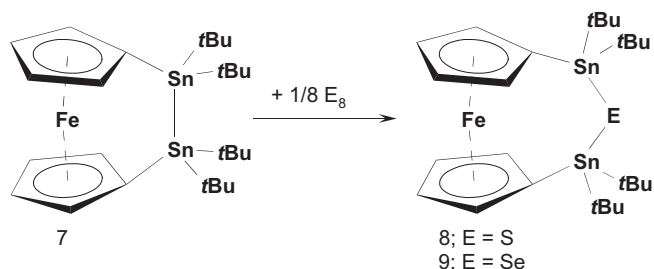


Fig. 1. Structure of **7** in the crystal (ellipsoid at 50% probability). Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–Sn2 2.8267(15), Sn1–C_{ipso} 2.1631(15), Sn2–C_{ipso} 2.1601(15), Sn–C_{tBu} 2.2054(16) and 2.2181(15), Sn2–C_{tBu} 2.2089(16) and 2.2091(16), C_{ipso}–Sn1–Sn2 96.35(4), C_{ipso}–Sn2–Sn1 95.93(4).

Scheme 4. Synthesis of **8** and **9**.

was filtered off. Orange colored crystals were obtained at -30°C from a concentrated solution. Yield: 199 mg (74%, 0.31 mmol). ^1H NMR (C_6D_6 , 297 K): $\delta = 4.41$ (m, 4H, C_5H_4), 4.32 (m, 4H, C_5H_4), 1.48 (s, 36H, tBu, $^3J_{\text{H-Sn}} = 65.9, 62.9$ Hz, $^4J_{\text{H-Sn}} = 5.6$ Hz) ppm. ^{13}C NMR (C_6D_6 , 297 K): $\delta = 76.7$ (C_{ipso}), 70.4, 68.9, 34.8 (C_q), 33.0 (C_{Me}) ppm. ^{119}Sn NMR (C_6D_6 , 297 K): $\delta = 18.54$ (s, $^1J_{\text{Sn-Sn}} = 1698.2$ Hz) ppm. Elemental analysis calcd (%) for $\text{C}_{26}\text{H}_{44}\text{FeSn}_2$: C 48.05 H 6.82; found: C 47.92 H 6.86.

[Fe($\eta^5\text{-C}_5\text{H}_4\text{Sn}(\text{tBu})_2$) $_2$ S] (8**):** 1 mg (0.31 mmol) of elemental sulfur was added to a solution of 13 mg (0.020 mmol) of **7** in 0.6 mL C_6D_6 in a NMR tube. The reaction mixture was heated to 100°C for 5 d. All volatile compounds were removed *in vacuo*, the orange colored precipitate was extracted with hexane and insoluble material was removed by filtration through celite. After removal of the solvent, 10.9 mg (84%, 0.016 mmol) of an orange solid was obtained. ^1H NMR (C_6D_6 , 293 K): $\delta = 4.27$ (m, 4H, C_5H_4), 4.15 (m, 4H, C_5H_4), 1.42 (s, 36H, tBu, $^3J_{\text{H-Sn}} = 77.31, 73.62$ Hz) ppm. ^{13}C NMR (C_6D_6 , 297 K): $\delta = 75.6$ (C_{ipso}), 71.3, 70.9, 32.3 (C_q), 31.3 (C_{Me}) ppm. ^{119}Sn NMR (C_6D_6 , 297 K): $\delta = 36.1$ (s, $^2J_{\text{Sn-Sn}} = 215.8$ Hz) ppm. Elemental analysis calcd (%) for $\text{C}_{26}\text{H}_{44}\text{FeSSn}_2$: C 45.80 H 6.50 S 4.70; found: C 45.34 H 6.42 S 5.59.

[Fe($\eta^5\text{-C}_5\text{H}_4\text{Sn}(\text{tBu})_2$) $_2$ Se] (9**):** A solution of 20 mg (0.068 mmol) of **7** in 0.7 mL C_6D_6 was treated with 5 mg (0.76 mmol) of red selenium for 5 d at 100°C . The workup was performed following the procedure as described for **8**. Yield: 22.3 mg (45%, 0.031 mmol). ^1H NMR (500.13 MHz, C_6D_6 , 293 K): $\delta = 4.26$ (m, 4H, C_5H_4), 4.15 (m, 4H, C_5H_4), 1.41 (s, 36H, tBu, $^3J_{\text{H-Sn}} = 77.31, 73.62$ Hz) ppm. ^{13}C NMR (125.75 MHz, C_6D_6 , 297 K): $\delta = 75.7$ (C_{ipso}), 71.2, 71.0, 36.7 (C_q), 30.1 (C_{Me}) ppm. ^{119}Sn NMR (187 MHz, C_6D_6 , 297 K): $\delta = 32.8$ (s, $^1J_{\text{Sn-Se}} = 1363$ Hz, $^2J_{\text{Sn-Sn}} = 194$ Hz) ppm. Elemental analysis calcd (%) for $\text{C}_{26}\text{H}_{44}\text{FeSeSn}_2$: C 42.85 H 6.08; found: C 42.74 H 6.03.

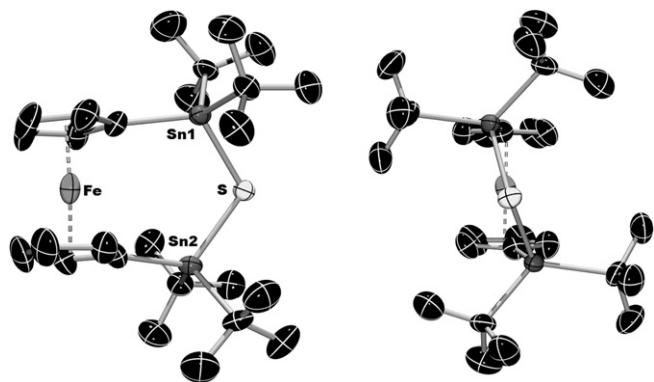
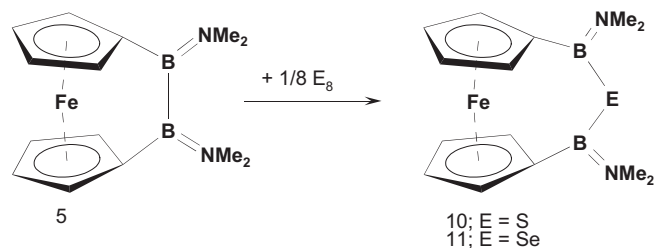


Fig. 2. Structure of **8** in the crystal (ellipsoid at 50% probability). Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn–S 2.4096(4), Sn–S 110.4, Sn– C_{ipso} 2.129(2), Sn– C_{tBu} 2.188(7) and 2.194(4), $\text{C}_{\text{ipso}}\text{–Sn–S}$ 115.76(6).

Scheme 5. Synthesis of **10** and **11**.

[Fe($\eta^5\text{-C}_5\text{H}_4\text{BNMe}_2$) $_2$ S] (10**):** 245 mg (0.86 mmol) of **5** dissolved in 10 mL toluene were treated with an excess of sulfur (100 mg, 3.12 mmol). After 24 h, the red solution brightened and all volatile compounds were removed *in vacuo*. The precipitate was dissolved in hexane and after filtration and removal of the solvent, an orange colored powder remained. Yield: 241 mg (63%, 0.54 mmol).

[Fe($\eta^5\text{-C}_5\text{H}_4\text{BNMe}_2$) $_2$ Se] (11**):** Following the same procedure as described above for **10**, 100 mg (0.34 mmol) of **5** were reacted with 30 mg (0.38 mmol) of red selenium in 10 mL of toluene. Yield: 85 mg (65%, 0.23 mmol).

5. Experimental details on the crystal structure determination

The crystal data of **6** and **7** were collected on a Bruker Apex diffractometer with a CCD area detector and graphite monochromated $\text{MoK}\alpha$ radiation. The structures were solved using direct methods, refined with the Shelx software package and expanded using Fourier techniques [18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealised positions and were included in structure factors calculations.

Crystal data for **7**: $\text{C}_{26}\text{H}_{44}\text{FeSn}_2$, $M_r = 649.84$, yellow plate, $0.18 \times 0.10 \times 0.03$ mm³, monoclinic space group $P2_1/n$, $a = 16.7792$ (3) Å, $b = 9.1918$ (2) Å, $c = 18.4377$ (3) Å, $\beta = 110.2950$ (10)°, $V = 2667.13$ (9) Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.618$ g cm⁻³, $\mu = 2.405$ mm⁻¹, $F(000) = 1304$, $T = 100$ (2) K, $R_1 = 0.0137$, $wR^2 = 0.0352$, 5262 independent reflections [$2\theta \leq 56.64^\circ$] and 262 parameters.

Crystal data for **8**: $\text{C}_{26}\text{H}_{44}\text{FeSSn}_2$, $M_r = 681.90$, yellow plate, $0.70 \times 0.34 \times 0.18$ mm³, monoclinic space group $P2_1/n$, $a = 12.1078$ (10) Å, $b = 9.5441$ (8) Å, $c = 13.0660$ (10) Å, $\beta = 105.6410$ (10)°, $V = 1454.0$ (2) Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.558$ g cm⁻³, $\mu = 2.279$ mm⁻¹, $F(000) = 684$, $T = 168$ (2) K, $R_1 = 0.0253$, $wR^2 = 0.0633$, 3630 independent reflections [$2\theta \leq 56.64^\circ$] and 179 parameters.

Appendix A. Supplementary material

CCDC 778787 (**7**) and 778788 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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