Trimethylsilyl-functionalised bis(indenyl)iron(II) complexes: solid-state structure of $[\eta^5\text{-}1,3\text{-}(SiMe_3)_2C_9H_5]_2Fe$

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Abstract

The synthesis of the bis(η^5-indenyl)iron sandwich complexes (η^5-1-SiMe$_3$–C$_9$H$_6$)$_2$Fe (**3a**), (η^5-2-SiMe$_3$–C$_9$H$_6$)$_2$Fe (**3b**), [η^5-1,2-(SiMe$_3$)$_2$C$_9$H$_5$]$_2$Fe (**4a**) and [η^5-1,3-(SiMe$_3$)$_2$C$_9$H$_5$]$_2$Fe (**4b**), by the reaction of the appropriate lithium indenide salts [prepared from 1-SiMe$_3$–C$_9$H$_7$ (**2a**), 2-SiMe$_3$–C$_9$H$_7$ (**2b**), 1,2-(SiMe$_3$)$_2$C$_9$H$_6$ (**2c**) or 1,3-(SiMe$_3$)$_2$C$_9$H$_6$ (**2d**)] with ferrous chloride (**1**) in a 2:1 molar ratio is discussed. The solid-state structure of **4b** was determined by single-crystal X-ray diffractometry. Complex **4b** exists in a *gauche* conformation, showing that the indenyl ligands are sterically imposed by the bulk of the Me$_3$Si substituents. The average Fe–C distance is 2.091(3) Å. Cyclovoltammetric studies indicate that **3** and **4** are redox-active with one-electron oxidations [$E^{1/2} = -270$ to -360 mV versus Fc/Fc$^+$, Fc = (η^5-C$_5$H$_5$)$_2$Fe].
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1. Introduction

Cyclopentadienyl and indenyl ligands are two of the most commonly used classes of building blocks in organometallic chemistry, because they are straightforward to tune and can also be readily functionalised [1–4]. Depending on the nature of the substituents at the π-annulene, complexes containing such ligands are of particular interest, for example, as catalytic species in homogeneous catalysis [1], and in the preparation of multimetallic complexes in which the metal atoms may exhibit synergistic and co-operative effects. While the coordination chemistry of cyclopentadienyls with transition metals is well studied, investigations of their indenyl counterparts are not as extensive, which is

attributed to, for example, the enhanced reactivity of the transition metal indenyl complexes, when compared with their cyclopentadienyl analogues [1–4]. This can be explained by the relative ease of the slippage of the indenyl building block from $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ [4c].

In this paper, we report on the synthesis and characterisation of a variety of Me$_3$Si-substituted bis(indenyl)iron sandwich complexes.

2. Results and discussion

The synthesis of the Me$_3$Si-substituted indenes 1-SiMe$_3$–C$_9$H$_7$ (**2a**), 2-SiMe$_3$–C$_9$H$_7$ (**2b**), 1,2-(SiMe$_3$)$_2$ C$_9$H$_6$ (**2c**) and 1,3-(SiMe$_3$)$_2$C$_9$H$_6$ (**2d**) have been reported [5]. These species can easily be lithiated by the addition of equimolar amounts of *n*-BuLi at low-temperature in tetrahydrofuran. The lithium salts thus obtained can be reacted further with ferrous chloride (**1**) to produce the bis(indenyl)iron complexes **3** and **4** (Eq. 1) (Table 1).

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$$2a - 2d \xrightarrow[\text{2. FeCl}_2\ (1)]{\text{1. }^n\text{BuLi}} 3, 4 \qquad (1)$$
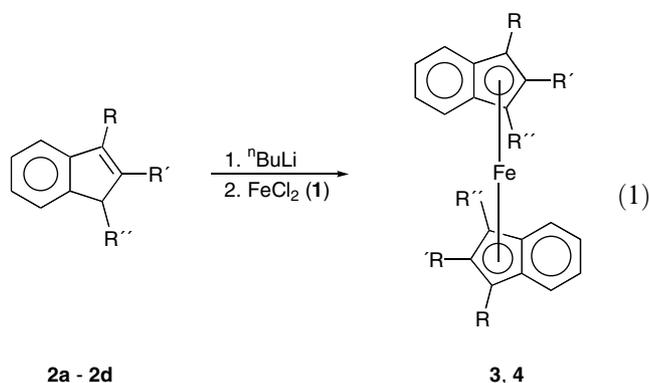
Filtration through Celite and removal of all volatile materials provides **3** and **4** in yields of 35–75% (Table 1) as green (**3a**), green-blue (**3b**) oils, or green solids (**4a** and **4b**), which are only stable under inert gas atmosphere.

Compounds **3** and **4** have been characterised by IR-, UV–Vis-, ^{1}H- and ^{13}C$\{^1$H$\}$ NMR spectroscopy, microanalysis, cyclovoltammetry and mass spectrometry [6]. The X-ray structure analysis of **4b** is also reported.

The infrared spectra of **3** and **4** are not very enlightening, since only distinctive vibrations for the C=C, CH and C–Si entities are found. More informative is NMR spectroscopy. Thus, in the ^{1}H NMR spectra of **3** and **4**, typical resonance signals for the Me$_3$Si groups are observed between 0.0 and 0.5 ppm. The indenyl ring protons appear in the range of 3.2–8.0 ppm of which the benzo protons resonate at somewhat lower field than the respective cyclopentadienyl ring protons. Nevertheless, the hydrogen atoms of the latter ring show a very characteristic pattern. In **3a**, two sets of two resonance signals are observed at 3.24 and 4.68 ppm as well as 3.99 and 4.94 ppm, which can be assigned to the protons in positions 2 and 3 (high-field and low-field, respectively). This indicates that **3a** is obtained as a mixture of two isomers, the *rac* and *meso* diastereomers, in a 1.6:1 ratio. This is also evidenced by ^{13}C$\{^1$H$\}$ NMR spectroscopic studies, since two sets of resonance signals are found. For **3b**, due to the symmetric arrangement of the Me$_3$Si group in position 2, only one signal for the cyclopentadienyl ring protons is observed at 3.86 ppm. The proton present in **4b** shows its resonance signal at 4.46 ppm, whereas in **4a**, for the proton in position 3, two signals (3.75 and 5.1 ppm) are observed in the ratio of

1:1.2, indicating again that two isomers are present (vide supra).

In the ^{13}C$\{^1$H$\}$ NMR spectra of **3** and **4**, well-resolved signals are found, of which the signals for the cyclopentadienyl ring carbon atoms appear at higher field (62–90 ppm) than the ones for the benzo group (124–131 ppm). The assignment of the Me$_3$Si resonance signals are readily made based on their chemical shift (0.3–1.5 ppm).

Reversible one-electron oxidations were observed for each of the bis(indenyl)iron complexes using cyclic voltammetry, with dichloromethane as a solvent (Fig. 1).
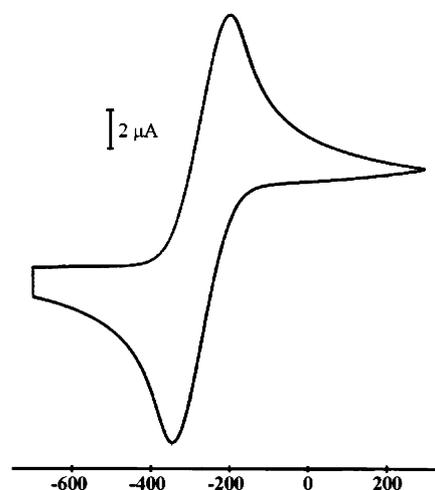

Fig. 1. Cyclic voltammogram of **3b** in dichloromethane, 0.1 M [^{n}Bu$_4$N]PF$_6$, scan rate = 200 mV s^{-1}; potential in V vs. FcH/FcH$^+$ [Fc = [η^5-C$_5$H$_5$]$_2$Fe].

Table 1
Synthesis of complexes **3** and **4**

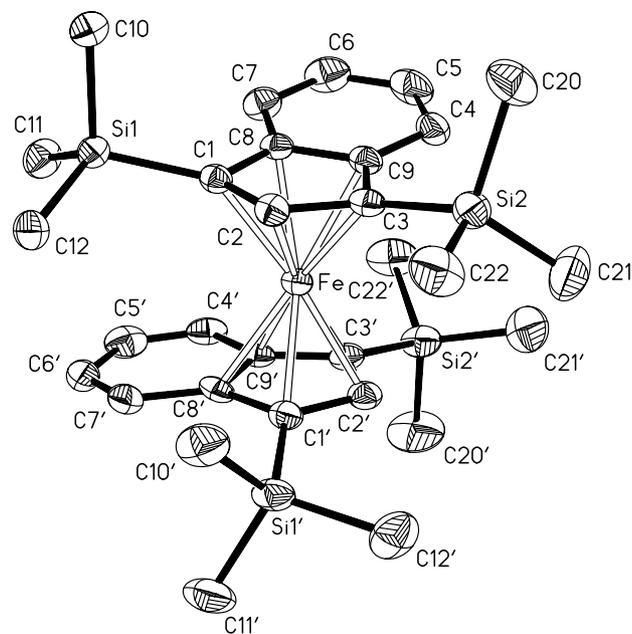| Compound	R	R′	R″	Yield (%)[a]
3a	SiMe$_3$	H	H	74
3b	H	SiMe$_3$	H	63
4a	SiMe$_3$	SiMe$_3$	H	35
4b	SiMe$_3$	H	SiMe$_3$	39

[a] Based on **1**.

Fig. 2. XP-plot (drawing at 50% probability level) of the molecular structure and adopted atom-numbering scheme of **4b**.

Table 2
Selected interatomic distances (Å) and angles (°) of complex 4b[a]

Bond distances (Å)

Fe–C(1)	2.075(3)	C(1)–C(2)	1.435(5)
Fe–C(1′)	2.074(3)	C(1)–C(2′)	1.431(5)
Fe–C(2)	2.043(3)	C(2)–C(3)	1.424(5)
Fe–C(2′)	2.045(3)	C(2′)–C(3′)	1.436(5)
Fe–C(3)	2.080(3)	C(3)–C(9)	1.458(5)
Fe–C(3′)	2.091(3)	C(3′)–C(9′)	1.439(5)
Fe–C(8)	2.130(3)	C(8)–C(9)	1.434(5)
Fe–C(8′)	2.123(3)	C(8′)–C(9′)	1.438(5)
Fe–C(9)	2.125(3)	C(1)–C(8)	1.449(5)
Fe–C(9′)	2.121(3)	C(1′)–C(8′)	1.462(5)
Si(1)–C(1)	1.859(4)	Ind–Fe[b]	1.695
Si(1′)–C(1′)	1.863(4)	Fe–Ind′	1.694
Si(2)–C(3)	1.867(4)		
Si(2′)–C(3′)	1.860(4)		

Bond angles (°)

Si(1)–C(1)–C(2)	125.1(2)	C(1)–C(2)–C(3)	112.2(3)
Si(1′)–C(1′)–C(2′)	126.3(3)	C(1′)–C(2′)–C(3′)	112.3(3)
Si(1)–C(1)–C(8)	126.7(3)	C(2)–C(3)–C(9)	105.0(3)
Si(1′)–C(1′)–C(8′)	126.3(3)	C(2′)–C(3′)–C(9′)	105.0(3)
Si(2)–C(3)–C(2)	125.9(3)	C(9)–C(8)–C(1)	108.9(3)
Si(2′)–C(3′)–C(2′)	125.5(3)	C(9′)–C(8′)–C(1′)	108.4(3)
Si(2)–C(3)–C(9)	126.1(3)	C(8)–C(1)–C(2)	105.1(3)
Si(2′)–C(3′)–C(9′)	127.9(3)	C(8′)–C(1′)–C(2′)	104.7(3)
Si(1)–C(1)–Fe	139.2(2)	Ind–Fe–Ind′[b]	178.0
Si(1′)–C(1′-Fe	138.3(2)		
Si(2)–C(3)–Fe	139.3(2)		
Si(2′)–C(3′)–Fe	136.2(2)		

[a] The estimated standard deviations of the last significant digits are shown in parantheses.
[b] Midpoint of the cyclopentadienyl groups of the indenyl ligand.

The potentials [versus Fc/Fc+, Fc = (η5-C5H5)2Fe] for these oxidations are $E^{1/2} = -275$ mV ($E = 125$ mV, 3a), $E^{1/2} = -270$ mV ($\Delta E = 145$ mV, 3b), $E^{1/2} = -291$ mV ($\Delta E = 112$ mV, 4a) and $E^{1/2} = -358$ mV ($\Delta E = 70$ mV, 4b). These data indicate that the ease of oxidation increases when one goes from ferrocene to bis(indenyl)iron sandwich complexes {e.g. (η5-C5H5)2Fe: 0.0 V; [7] (η5-C9H7)2Fe, −278 mV [8]}.

High-resolution mass spectrometric studies confirm the composition of 3 and 4.

Single crystals of 4b could be obtained by slowly cooling a petroleum solution containing 4b to −20 °C. The molecular structure of 4b is depicted in Fig. 2. Selected interatomic bond distances (Å) and angles (°) are listed in Table 2 and crystal data and structure refinement parameters are given in Table 3 (Section 4).

Compound 4b crystallises in the monoclinic space group P2₁/c. The molecular structure of 4b shows the iron atom Fe coordinated linearly by the centroids of the indenyl five-membered rings (Fig. 2). The two indenyl ligands are orientated almost parallel to each other (5.8°); the Ind–Fe–Ind′ angle (Ind = centroid of the five-membered ring) is 178.0°. Due to the steric congestion of the four Me3Si units, the indenyl rings are twisted by 94.3° [C(1)–Ind–Ind′–C(1′); C(3)–Ind–Ind′–C(3′)] with respect to each other to give a *gauche* conformation. The average bond distance of the 5-

Table 3
Crystal data and structure refinement parameters for complex 4b

Formula weight	574.88
Chemical formula	C30H46FeSi4
Crystal system	Monoclinic
Space group	P2₁/c
a (Å)	19.56(1)
b (Å)	10.238(5)
c (Å)	18.634(9)
V (Å³)	3283(3)
β (°)	118.361(7)
δcalc (g cm−3)	1.163
F(000)	1232
Crystal dimensions (mm³)	0.43×0.30×0.03
Z	4
Radiation, μ (Å)	0.71073
Maximum and minimum transmission	1.000000 and 0.901477
Total reflections	41 643
Unique reflections	6712
Observed reflections [$I \geqslant 2\sigma(I)$]	3897
Refined parameters	316
R_1[a], wR_2[b] [$I \geqslant 2\sigma(I)$]	0.0387, 0.1107
R_1[a], wR_2[b] (all data)	0.0936, 0.1515
R_{int}	0.0921
Maximum and minimum peak (e Å−3)	0.311 and −0.285
Goodness-of-fit on F^2	0.580

$P = [F_o^2 + 2F_c^2]/3c$; $S = \left[\sum w(F_o^2 - F_c^2)^2\right] \Big/ (n-p)^{1/2}$; n is number of reflections, p is parameters used; $w = 1 \Big/ \left[\sum{}^2(F_o^2) + (aP)^2 + bP\right]$.
[a] $R_1 = [\sum(||F_o| - |F_c|/\sum|F_o|)]$.
[b] $wR_2 = \left[\sum(w(F_o^2 - F_c^2)^2) \Big/ \sum(wF_o^4)\right]^{1/2}$.

membered ring centroids (Ind) to the iron atom is 1.695 Å (Table 2), which is in agreement with such sandwich complexes [for example: $[(\eta^5\text{-}C_9H_7)_2Fe$, 1.665 Å; $(\eta^5\text{-}C_9Me_7)_2Fe$, 1.677 Å] [9]]. The bond distances Fe –C(1), –C(2), –C(3), –C(8), –C(9) and Fe–C(1′), –C(2′), –C(3′), –C(8′), –C(9′) are 2.043(3) [Fe–C(2)], 2.075(3)/ 2.080(3) [Fe–C(1)/Fe–C(3)] and 2.125(3)/2.130(3) Å [Fe–C(9)/Fe–C(8)]. They point to the fact that the five-membered ring of the indenyl group is somewhat unsymmetrically bound to iron. This asymmetry can also be found in the different C–C bond lengths in the 5-membered indenyl ring. The C–C distances in the allylic sub-unit [C(1) to C(3)] are 0.023 Å shorter than the distances to the aromatic benzene structure [C(1)–C(8); C(3)–C(9)].

3. Conclusion

We have isolated and characterised the Me_3Si-functionalised bis(indenyl)iron sandwiches $[1\text{-}SiMe_3\text{-}C_9H_6]_2$-Fe (**3a**), $[2\text{-}SiMe_3\text{-}C_9H_6]_2Fe$ (**3b**), $[1,2\text{-}(SiMe_3)_2C_9H_5]_2Fe$ (**4a**) and $(1,3)\text{-}(SiMe_3)_2C_9H_5]_2Fe$ (**4b**). Complexes **3a** and **4a** exist in two isomeric forms: a *rac* form with C_2 symmetry and a *meso* form with C_s symmetry. Cyclovoltammetric studies show no influence of the position, 1 or 2, of the Me_3Si group on the oxidation potential of **3a** and **3b** in comparison with $(\eta^5\text{-}C_9H_7)_2Fe$. However, sandwiches **4a** and **4b** possess different potentials, depending on the position of the Me_3Si groups.

4. Experimental

4.1. General methods

All reactions were carried out in an atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were purified by distillation; petroleum ether and dichloromethane: calcium hydride; tetrahydrofuran, diethyl ether: sodium/benzophenone ketyl. FT-IR spectra were obtained on a Perkin–Elmer FT-IR 1000 spectrometer as KBr pressings. NMR spectra were recorded on a Bruker Avance 250 spectrometer, operating in the Fourier transform mode. ^1H NMR spectra were recorded at 250.130 MHz (internal standard relative to C_6D_6, $\delta = 7.24$ or $CDCl_3$, $\delta = 7.27$). $^{13}C\{^1H\}$ NMR spectra were recorded at 62.860 MHz (internal standard relative to $CDCl_3$, $\delta = 77.0$). Chemical shifts are reported in δ units (ppm) downfield from $SiMe_4$ with the solvent as reference signal. Melting points were determined using analytically pure samples, sealed off in nitrogen-purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Electrochemical measurements were carried out by cyclic voltammetry

with a platinum disc electrode (0.125 cm^2, EDI 101 T, Radiometer), a platinum wire counter electrode and a saturated calomel electrode filled with methylenedichloride as solvent of the electrolyte solution at 25 °C, using a standard three-electrode cell in a Radiometer Copenhagen DEA 101 Digital Electrochemical Analyser with a IMT 102 (Radiometer) Electrochemical Interface. Experiments were run with VOLTALAB-3.1 software (V.2.0) at a scan rate $dE/dt = 200$ mV s^{-1}. All potentials were referenced to the ferrocene/ferrocenium [ferrocene $= (\eta^5\text{-}C_5H_5)_2Fe$] couple, which was used as an internal standard with $E_0 = 0.00$ V. Electrolyte solutions were prepared from $[^nBu_4N][PF_6]$ (Fluka, dried in an oil pump vacuum at 120 °C), 0.1 M in methylenedichloride with 5.0 mg of the complex in 5.0 ml of methylenedichloride. Microanalysis of **4a** was performed by the Organic Department, Chemnitz, Technical University.

4.2. General remarks

Indenes **2a**–**2d** were prepared by published procedures [5]. All other chemicals were purchased by commercial suppliers and were used as received.

4.3. Preparation of bis[1-(trimethylsilyl)indenyl]iron(II) (3a)

To a solution of 1-(trimethylsilyl)indene (1.208 g, 6.41 mmol) in tetrahydrofuran (50 ml) is added *n*-BuLi (4.00 ml, 1.6 M, 6.41 mmol) at −80 °C. After stirring the reaction mixture at ambient temperature for 2 h, $FeCl_2$ (**1**) (0.410 g, 3.21 mmol) is added and the reaction mixture is stirred for further 3 h at ambient temperature. Afterwards, the solvent is removed by oil-pump vacuum to leave a dark green oily residue, which is dissolved in diethyl ether and filtered through Celite. Removal of the solvent by oil-pump vacuum yielded 1.03 g (2.40 mmol, 74% based on **1**) of **3a** as a dark-green oily residue. The product obtained is a mixture of *rac* and *meso* diastereomers in a 1.6:1 ratio.

Major isomer. ^1H NMR $(CDCl_3)$: 0.49 (s, 18H, $SiMe_3$), 3.99 (s, 2H, H2), 4.94 (s, 2H, H3), 6.51–7.60 (m, 8H, H4–7). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 0.35 ($SiMe_3$), 62.92 (C1), 65.19 (C3), 74.07 (C2), 90.20, 90.41 [C8(9)], 122.19, 122.35 [C5(6)], 124.36, 127.02 [C4(7)].

Minor isomer. ^1H NMR $(CDCl_3)$: δ 0.39 (s, 18H, $SiMe_3$), 3.24 (s, 2H, H2), 4.68 (s, 2H, H3), 6.51–7.60 (m, 8H, H4–7). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 0.44 ($SiMe_3$), 62.79 (C1), 65.60 (C3), 78.04 (C2), 89.96, 90.09 [C8(9)], 123.94, 124.27 [C5(6)], 129.73, 130.55 [C4(7)].

EI-MS: [m/z (%)]: 430 (33, M$^+$), 241 [25, C_9H_4 $(SiMe_3)Fe^+$], 187 (45, $C_9H_6SiMe_3^+$), 112 (46, $C_9H_4^+$), 73 (100, $SiMe_3^+$). HR-MS: M$^+$, Calc., 430.12345; Found: 430.12247. CV (CH_2Cl_2): $E^{1/2} = -275$ mV, $\Delta E_p = 125$ mV.

4.4. Preparation of bis[2-(trimethylsilyl)indenyl]iron(II) (3b)

To a solution of 2-(trimethylsilyl)indene (1.266 g, 6.72 mmol) in tetrahydrofuran (50 ml) is added *n*-BuLi (4.20 ml, 1.6 M, 6.72 mmol) at −80 °C. After stirring the reaction mixture at ambient temperature for 6 h, FeCl$_2$ (1) (0.852 g, 3.36 mmol) is added and the reaction mixture is stirred a further 16 h at ambient temperature. The solvent is removed by oil-pump vacuum to leave a dark-green oily residue, which is dissolved in petroleum ether and filtered through Celite. Removal of solvent by oil-pump vacuum yields 0.92 g (2.14 mmol, 63% based on 1) of 1 as a dark blue oily residue.

^{1}H NMR (C$_6$D$_6$): δ 0.36 (s, 18H, SiMe$_3$), 3.86 [s, 4H, H1(3)], 7.00 [AA′BB′, 4H, H5(6)], 7.41 [AA′BB′, 4H, H4(7)]; H4–7 exhibit an AA′BB′ pattern with $^3J_{H4H5} = 3$ Hz, $^4J_{H4H6} = 9$ Hz and $^3J_{H5H6} = 3$ Hz. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 0.35 (SiMe$_3$), 66.76 [C1(3)], 77.21 (C2), 90.88 [C8(9)], 124.05 [C5(6)], 129.86 [C4(7)]. EI-MS: [m/z (%)]: 430 (100, M$^+$), 358 (26, HM$^+$–SiMe$_3$), 172 (14, C$_9$H$_6$SiMe$_2^+$), 115 (25, C$_9$H$_7^+$), 73 (47, SiMe$_3^+$). HR-MS: M$^+$, Calc., 430.12345; Found: 430.12257. CV (CH$_2$Cl$_2$): $E^{1/2} = -270$ mV, $\Delta E_p = 145$ mV.

4.5. Preparation of bis[1,2-bis(trimethylsilyl)indenyl]iron(II) (4a)

To 1,2-bis(trimethylsilyl)indene (1.00 g, 3.84 mmol) in tetrahydrofuran (50 ml), *n*-BuLi (1.54 ml, 3.84 mmol, 2.5 M in hexane) is added at −78 °C. After stirring the reaction mixture at ambient temperature for 12 h, FeCl$_2$ (1) (0.245 g, 1.92 mmol) is added, and the reaction mixture is stirred for another 6 h. Afterwards, the solvent is removed in oil-pump vacuum to leave a green-blue oily residue. The remaining oil is purified by column chromatography (column size: 20×2.5 cm, petroleum ether, silica gel). After the solvent is removed from the eluate by oil-pump vacuum, 0.39 g (0.68 mmol, 35% based on 1) of 4b as a mixture of *rac* and *meso* isomers can be obtained in a 1.2:1 ratio as a green solid.

^{1}H NMR (CDCl$_3$): δ 0.00 (s, 9H, SiMe$_3$), 0.03 (s, 9H, SiMe$_3$), 0.12 (s, 9 H, SiMe$_3$), 0.31 (s, 9H, SiMe$_3$), 3.75 (m, 1H, C$_9$H$_6$), 5.1 (m, 1H, C$_9$H$_6$), 7.25 (m, 4H, C$_9$H$_6$), 7.5 (m, 2H, C$_9$H$_6$), 7.9 (m, 2H, C$_9$H$_6$). IR (KBr, cm^{-1}): 3054(w), 2985(m), 2685(m), 2410(w), 2305(w), 1422(s), 1264(s). Anal. Calc. for C$_{30}$H$_{46}$Fe$_2$Si$_4$: C, 62.68; H: 8.07. Found: C, 63.05; H, 7.95%. CV (CH$_2$Cl$_2$): $E^{1/2} = -291$ mV, $\Delta E_p = 112$ mV.

4.6. Preparation of bis[1,3-bis(trimethylsilyl)indenyl]iron(II) (4b)

To a solution of 1,3-bis(trimethylsilyl)indene (1.055 g, 4.05 mmol) in tetrahydrofuran (50 ml), *n*-BuLi (2.53 ml, 1.6 M, 4.05 mmol) is added at −80 °C. After stirring the

reaction mixture at ambient temperature for 12 h, FeCl$_2$ (1) (0.260 g, 2.03 mmol) is added, and the reaction mixture is stirred for a further 6 h at ambient temperature. The solvent is removed by oil-pump vacuum to leave a green/blue oily residue. Chromatography on silica gel (25 °C) with petroleum ether gives green 4b, which is crystallised from petroleum ether at −20 °C to afford 0.45 g (0.78 mmol, 39% based on 1) of 4b.

^{1}H NMR (C$_6$D$_6$): δ 0.37 (s, 36H, SiMe$_3$), 4.46 (s, 2H, H2), 7.03 [AA′BB′, 4H, H5(6)], 7.57 [AA′BB′, 4H, H4(7)]; H4–7 exhibit an AA′BB′ pattern with $^3J_{H4H5} = 3$ Hz, $^4J_{H4H6} = 9$ Hz and $^3J_{H5H6} = 3$ Hz. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 0.94 (SiMe$_3$), 64.92 [C1(3)], 82.21 (C2), 95.78 [C8(9)], 124.87 [C5(6)], 130.94 [C4(7)]. EI-MS: [m/z (%)]: 574 (83, M$^+$), 501 (7, M$^+$–SiMe$_3$) 259 [17, C$_9$H$_5$(SiMe$_3$)$_2^+$], 244 [17, C$_9$H$_5$(SiMe$_3$)(SiMe$_2$)$^+$], 229 [24, C$_9$H$_5$(SiMe$_2$)$_2^+$], 187 (38, C$_9$H$_6$SiMe$_3^+$), 172 (100, C$_9$H$_5$SiMe$_2^+$), 73 (65, SiMe$_3^+$). HR-MS: M$^+$ Calc., 574.20260; Found: 574.20464. CV (CH$_2$Cl$_2$): $E^{1/2} = -358$ mV, $\Delta E_p = 70$ mV. Anal. Calc. for C$_{30}$H$_{46}$FeSi$_4$: C, 62.68; H, 8.07. Found: C, 63.01; H, 7.93%.

4.7. X-ray structure determination of 4b

The solid-state structure of the title compound was determined by single-crystal X-ray diffraction. Data collection was performed on a Siemens P4 Smart CCD area detector using Mo Kα radiation. Crystallographic data of 4b is listed in Table 3.

The structure was solved by direct methods (G.M. Sheldrick, SHELX-97; University of Göttingen: Göttingen, Germany, 1997). An empirical absorption correction was applied. The structure was refined by the least squares method based on F^2 with all reflections. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were placed in calculated positions. The picture was drawn using XP in SHELXTL.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 210352 for complex 4b. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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