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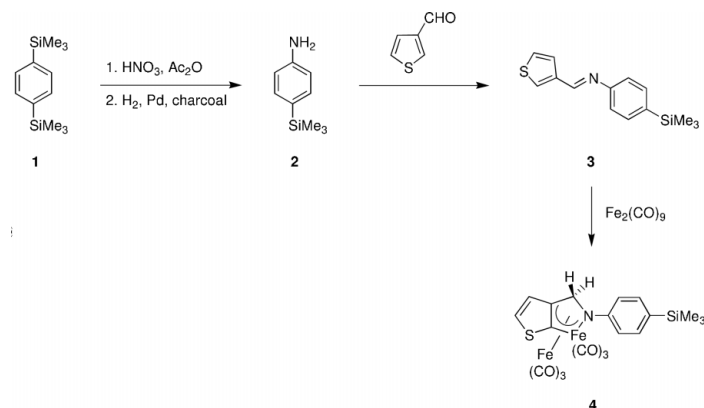
## Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$   
 $R$  factor = 0.038  
 $wR$  factor = 0.108  
Data-to-parameter ratio = 11.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Hexacarbonyl[ $\mu_2$ - $\eta^3$ - $N$ -(3-thienylmethylidene)-4-(trimethylsilyl)aniline]diiron

The title compound,  $[\text{Fe}_2(\text{C}_{14}\text{H}_{17}\text{NSSi})(\text{CO})_6]$ , was produced by the reaction of  $N$ -(3-thienylmethylidene)-4-(trimethylsilyl)aniline and  $\text{Fe}_2(\text{CO})_9$  via a reaction sequence involving a C–H activation step, followed by an intramolecular hydrogen transfer to the former imine C atom. The crystal structure analysis clearly proves that the reaction takes place regioselectively at the 2-position of the thiophene moiety. The structure of the title compound consists of an azaferrocyclopentadiene ring to which another  $\text{Fe}(\text{CO})_3$  moiety is apically coordinated. There are two independent molecules per asymmetric unit, which differ slightly in their bond lengths and angles.

## Comment

The reaction of heterocyclic aromatic imines with  $\text{Fe}_2(\text{CO})_9$  yields dinuclear iron carbonyl complexes (Imhof, 1997, 1998; Tzeng *et al.*, 2003). For analogous reactions with benzaldehyde derivatives, it has been shown that this reaction proceeds by strictly intramolecular C–H activation in the *ortho*-position with respect to the exocyclic imine function. This is followed by a 1,3-hydrogen shift to the former imine C atom, thus producing a methylene group instead (Imhof *et al.*, 1999).



The formation of such iron carbonyl complexes may be viewed as a model for C–C bond-forming reactions catalyzed by ruthenium or rhodium compounds, in which a C–H activation step initiates the catalytic cycle. These catalytic reactions have been shown to take place with the same regioselectivity as the C–H activations induced stoichiometrically with  $\text{Fe}_2(\text{CO})_9$  (Murai *et al.*, 1993, 1998; Pfeffer *et al.*, 2002; Imhof & Berger, 1999; Imhof & Dönnecke, 2003). Heterocyclic imines with two H atoms in the *ortho*-position with respect to the imine substituent have very rarely been investigated with respect to the preferred regioselectivity of C–H activation reactions, either stoichiometrically or cata-

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lytically. Against this background, we present here the structure of the title compound, (4).

In the crystal structure of (4) there are two independent molecules (*A* involving atom Fe1 and *B* involving atom Fe3) in the asymmetric unit, which differ slightly in their bond lengths and angles. Selected geometric parameters are given in Table 1. The molecular structure of molecule *A* is shown in Fig. 1. It can clearly be seen that the C–H activation reaction takes place regioselectively at the 2-position of the thiophene system (C4). The structure consists of an azaferracyclopentadiene ring (C3/C4/C5/N1/Fe2) to which another Fe(CO)<sub>3</sub> moiety is apically coordinated.

The Fe–C bond lengths of the thiophene double bond, C3=C4 to atom Fe1 (molecule *A*) and C23=C24 to atom Fe3 (molecule *B*), are not identical. The bond directed towards the C atom where C–H activation occurred (C4 and C24, respectively) is significantly shorter. The differences between these two Fe–C bonds are 0.153 and 0.117 Å in molecules *A* and *B*, respectively. The other bond lengths and angles are as expected, as can be seen in Table 1.

The aromatic substituent at the N atom shows a nearly perpendicular arrangement with respect to the plane of the azaferracyclopentadiene system [102.1 (2)° in molecule *A* and 105.7 (2)° in molecule *B*].

The crystal packing of (4) is shown in Fig. 2. The shortest intermolecular distances represent quite weak hydrogen bonds between the O atoms of the CO ligands and the H atoms of the SiMe<sub>3</sub> substituents; details are given in Table 2.

## Experimental

4-Trimethylsilylaniline, (2), was prepared by a procedure published previously by Felix *et al.* (1979). The reaction of (2) (2.2 g) with thiophene-3-carbaldehyde (1.5 g) and distillation of the oily brown crude product yielded the corresponding imine, (3), in 75% yield (2.6 g), as a pale-yellow liquid, which crystallized upon standing at room temperature (m.p. 325 K; b.p. 388 K at  $5 \times 10^{-5}$  Torr; 1 Torr = 133.322 Pa). Imine (3) (520 mg) was stirred together with Fe<sub>2</sub>(CO)<sub>9</sub> (730 mg) in *n*-heptane (50 ml) at 323 K for 2 h. The solution turned red as the ligand and Fe<sub>2</sub>(CO)<sub>9</sub> dissolved. After evaporation of all volatile material, the crude product was chromatographed on silica gel. Use of light petroleum as the eluent yielded (4) as a red solution (450 mg, 42%). Crystals of (4) were obtained at 253 K from a concentrated solution in light petroleum (b.p. 313–333 K).

### Crystal data

[Fe<sub>2</sub>(C<sub>14</sub>H<sub>17</sub>NSSi)(CO)<sub>6</sub>]  
*M<sub>r</sub>* = 539.20  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 25.4591 (11) Å  
*b* = 14.1058 (7) Å  
*c* = 13.2386 (6) Å  
 $\beta$  = 99.223 (3)°  
*V* = 4692.8 (4) Å<sup>3</sup>  
*Z* = 8

*D<sub>x</sub>* = 1.526 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 5103 reflections  
 $\theta$  = 3.4–23.4°  
 $\mu$  = 1.41 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Block, red  
 0.34 × 0.30 × 0.25 mm

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\omega$  scans  
 6680 measured reflections  
 6680 independent reflections

5103 reflections with *I* > 2σ(*I*)  
 $\theta_{\max}$  = 23.3°  
*h* = –28 → 27  
*k* = –15 → 0

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.038  
*wR*(*F*<sup>2</sup>) = 0.108  
*S* = 1.00  
 6680 reflections  
 566 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.7589P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.006$   
 $\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0046 (4)

**Table 1**

Selected geometric parameters (Å, °).

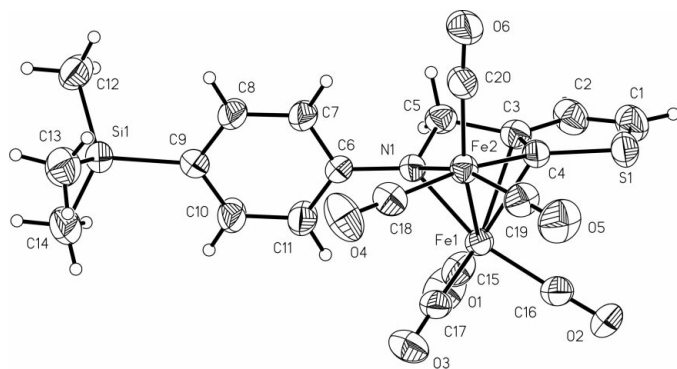
Fe1–N1	1.968 (3)	Fe3–N2	1.987 (3)
Fe1–C4	2.169 (3)	Fe3–C24	2.154 (3)
Fe1–C3	2.322 (4)	Fe3–C23	2.271 (4)
Fe1–Fe2	2.4538 (7)	Fe3–Fe4	2.4570 (7)
Fe2–C4	1.939 (4)	Fe4–C24	1.938 (4)
Fe2–N1	1.991 (3)	Fe4–N2	2.008 (3)
S1–C1	1.717 (5)	S2–C21	1.715 (4)
S1–C4	1.743 (3)	S2–C24	1.756 (3)
C1–C2	1.348 (6)	C21–C22	1.345 (5)
C2–C3	1.429 (5)	C22–C23	1.430 (5)
C3–C4	1.412 (5)	C23–C24	1.406 (5)
C3–C5	1.497 (5)	C23–C25	1.498 (4)
C5–N1	1.486 (4)	C25–N2	1.495 (4)
N1–C6	1.447 (4)	N2–C26	1.446 (4)
N1–Fe1–C4	73.16 (12)	N2–Fe3–C24	73.42 (12)
N1–Fe1–C3	64.07 (12)	N2–Fe3–C23	64.82 (11)
C4–Fe1–C3	36.45 (13)	C24–Fe3–C23	36.92 (13)
N1–Fe1–Fe2	52.11 (8)	C23–Fe3–Fe4	74.51 (9)
C4–Fe1–Fe2	49.11 (9)	C24–Fe4–N2	77.85 (13)
C3–Fe1–Fe2	73.64 (9)	C24–Fe4–Fe3	57.25 (10)
C4–Fe2–N1	77.90 (13)	N2–Fe4–Fe3	51.68 (8)
C4–Fe2–Fe1	57.76 (10)	C24–Fe4–C23	25.88 (12)
N1–Fe2–Fe1	51.28 (8)	C21–S2–C24	92.49 (18)
C1–S1–C4	92.5 (2)	C22–C21–S2	113.4 (3)
C2–C1–S1	113.5 (3)	C21–C22–C23	111.6 (4)
C1–C2–C3	111.4 (4)	C24–C23–C22	114.4 (3)
C4–C3–C2	114.2 (3)	C24–C23–C25	113.6 (3)
C4–C3–C5	113.6 (3)	C22–C23–C25	129.6 (3)
C2–C3–C5	130.2 (4)	C24–C23–Fe3	67.0 (2)
C4–C3–Fe1	65.9 (2)	C23–C24–S2	108.0 (3)
C3–C4–S1	108.4 (3)	C23–C24–Fe4	117.1 (3)
C3–C4–Fe2	116.6 (3)	S2–C24–Fe4	134.6 (2)
C3–C4–Fe1	77.7 (2)	C23–C24–Fe3	76.1 (2)
Fe2–C4–Fe1	73.13 (12)	Fe4–C24–Fe3	73.59 (12)
N1–C5–C3	100.6 (3)	N2–C25–C23	100.1 (3)
C6–N1–C5	110.5 (3)	C26–N2–C25	112.6 (2)
C6–N1–Fe2	122.9 (2)	C26–N2–Fe4	120.6 (2)
C5–N1–Fe2	112.9 (2)	C25–N2–Fe4	112.5 (2)
Fe1–N1–Fe2	76.61 (10)	Fe3–N2–Fe4	75.90 (9)

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C12–H12A...O1 <sup>i</sup>	0.96	2.80	3.668 (5)	151
C33–H33B...O4 <sup>ii</sup>	0.96	2.78	3.376 (6)	121
C33–H33A...O7 <sup>iii</sup>	0.95	2.74	3.567 (6)	145
C25–H25B...O9 <sup>iv</sup>	0.97	2.77	3.458 (5)	129
C34–H34C...O11 <sup>v</sup>	0.96	2.77	3.521 (6)	136

Symmetry codes: (i) 1 – *x*, *y* –  $\frac{1}{2}$ ,  $\frac{1}{2}$  – *z*; (ii) *x*,  $-\frac{1}{2}$  – *y*, *z* –  $\frac{1}{2}$ ; (iii) –*x*, *y* –  $\frac{1}{2}$ ,  $-\frac{1}{2}$  – *z*; (iv) *x*,  $\frac{1}{2}$  – *y*, *z* –  $\frac{1}{2}$ ; (v) *x*,  $-\frac{1}{2}$  – *y*,  $\frac{1}{2}$  + *z*.



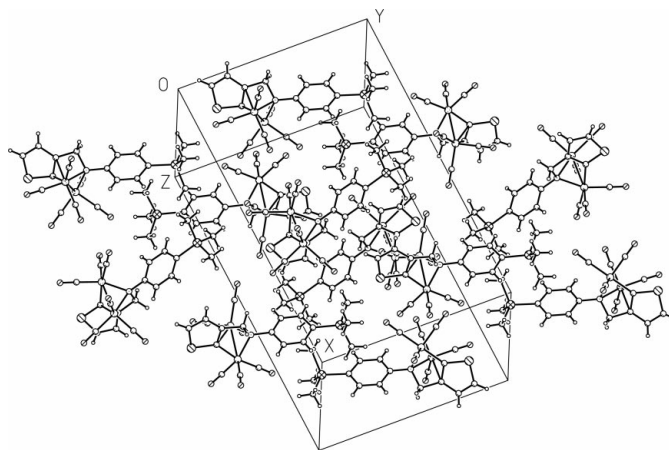
**Figure 1**  
The molecular structure of one independent molecule of (4), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

All H atoms were constrained in idealized positions during the refinement, with the methyl groups being allowed to rotate around their C—C bond and with  $U_{\text{iso}}(\text{H})$  values fixed at  $0.08 \text{ \AA}^2$ .

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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**Figure 2**  
A packing diagram of (4).

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