Reactions of *N*-(2-thienylmethylidene)-2-thienylmethylamine derivatives with diiron nonacarbonyl: characterization and structures of cyclometallated diiron complexes Fe$_2$(CO)$_6$(R–C$_4$HS–CH$_2$NCH$_2$–C$_4$H$_3$S) and linear tetrairon clusters Fe$_4$(CO)$_{10}$(R–C$_4$HS–CH= NCH$_2$–C$_4$H$_3$S)$_2$

Yu-Fun Tzeng [a], Chih-Yu Wu [a], Wen-Shu Hwang [a],[*], Chen-Hsiung Hung [b]

[a] *Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 947, Taiwan, ROC*
[b] *Department of Chemistry, National Changhua University of Education, Chunghua, Taiwan, ROC*

Abstract

The reaction of *N*-(2-thienylmethylidene)-2-thienylmethylamine (**1**) with Fe$_2$(CO)$_9$ under mild conditions in anhydrous benzene yields the iron carbonyl products **2**, **3**, and **4**. Complex **2** is a cyclometallated complex Fe$_2$(CO)$_6$(R–C$_4$HS–CH$_2$NCH$_2$–C$_4$H$_3$S), in which the organic ligand is (μ-η^1:η^2-thienyl β-C, α, β-C=C; η^1:η^1-(N))-coordinated to the diiron center. Complexes **3** and **4** are novel linear tetrairon complex isomers Fe$_4$(CO)$_8$(μ-CO)$_2$(R–C$_4$HS–CH=NCH$_2$–C$_4$H$_3$S)$_2$, in which the two organic ligands are (μ-η^1-thienyl β-C: η^1-N;η^2-thienylα, β-C=C:η^2-C=N)-coordinated to two diiron centers, respectively. These complexes were well characterized spectrally. The molecular structures of **1a**, **2a**, **2b**, **3a**, and **3b** have been determined by means of X-ray diffraction. The linear arrangement of the four iron atoms in the 66e clusters **3** and **4** is consistent with the closed valance molecular orbital (CVMO) theory. Complexes **3** and **4** may be viewed as consisting of a central Fe$_2$(CO)$_2$(μ-CO)$_2$ core to which two η^5-azaferracyclopentadieny fragments are coordinated; hence **3** and **4** are isolobally-related analogues of [CpFe(CO)(μ-CO)]$_2$. Thermal reaction of **3** or **4** in hexane, benzene, or acetonitrile leads to the decomposition of the complex. No interconversion between isomers **3** and **4** has been observed.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Diiron nonacarbonyl; Cyclometallated diiron complexes; Linear tetrairon clusters

1. Introduction

One of the most prominent challenges in organometallic chemistry in recent decades has been the transition-metal mediated activation of C–H bond. Cyclometallation has been one of the most prevalent methods used in activating the C–H bonds existing in hetero-substituted organic molecules [1]. It is well known that N-donor ligands have a strong tendency to produce five-membered metallacycle [2] and that Schiff base ligands have traditionally been the compound of choice employed in the study of cyclometalla-

tion reactions due to their strong tendency to produce *endo* cyclometallated derivatives [3]. In recent years, C–H activation reactions of Schiff bases have been used to develop catalytic C–C coupling reactions with CO and/or olefins [4]. It has also been shown that Schiff bases react with diiron nonacarbonyl to produce cyclometallated hexacarbonyldiiron complexes in which an *endo* orthometallation accompanies the transformation of β-hydrogen to imine carbon to form a methylene group [5].

Although it is a well-established fact that 1-azadiene ligands react with diiron nonacarbonyl to create mononuclear complexes of the type (η^4-azadiene)Fe(CO)$_3$ [6], there are only a few structurally characterized iron carbonyl complexes in which an aromatic π-system is

---

* Corresponding author. Fax: +886-3-8662527.
E-mail address: hws@ndhu.edu.tw (W.-S. Hwang).

involved in the η^4-coordination mode including anthracene, naphthalene, indene, and benzene [7]. To the present time, only a few examples of metal carbonyl complexes having linear M_4 geometries have been reported in the literature. Interestingly enough, the central two metal atoms in these complexes are second- or third-row metals.

The present paper reports on the authors' investigations into the action of diiron nonacarbonyl on N-(2-thienylmethylidene)-2-thienylmethylamine derivatives (1). In the course of reactions, a diiron hexacarbonyl complex (2) and two linear tetrairon decacarbonyl diastereomers (3 and 4) were isolated and fully characterized. Complex 2 was produced resulting from *endo* cyclometallation followed by an intermolecular 1,3-hydrogen shift. The resulting organic ligand shows a unique 6e-[μ-η^1:η^2-(thienyl); η^1:η^1-(N)] binding mode in that the β-carbon and a α,β-C=C π bond of the bridging thiophene and the azomethine nitrogen atom all are coordinated to the diiron (Fe–Fe) unit. *Endo* cyclometallation of the organic ligands were also observed in the linear tetrairon complexes 3 and 4. Each of the two thienyl Schiff bases in the complex serves as a di-bridging ligand to one of the two Fe–Fe centers via a novel 7e-[μ-η^1-(thienyl β-C): η^1-N; η^4-(thienyl α, β-C=C, C=N)] binding mode.

2. Experimental

Diiron nonacarbonyl was prepared through the photolysis of iron pentacarbonyl (Aldrich) in glacial AcOH [8]. Solvents were dried (sodium/benzophenone, P_4O_{10}) and distilled under nitrogen prior to use. 2-Formylthiophene, 2-thienylmethylamine (Aldrich) and 5-methyl-2-formylthiophene (Fluka) were distilled by a Kugelrohr distillation apparatus under reduced pressure (0.1 mmHg) prior to use. All other chemicals were reagent grade and used without further purification. The NMR spectra were recorded on a Bruker DX-300 NMR spectrometer (^{1}H, 299.95 MHz; ^{13}C, 75.43 MHz). Chemical shifts were referenced to Me$_4$Si and deuterated acetone (Janssen) was used as a solvent and as a secondary reference. Mass spectra were obtained from a Micromass Platform II spectrometer. IR spectra were recorded employing a Mattson Genesis FTIR spectrophotometer. Elemental analyses were performed using a Perkin–Elmer 2400, 2400II elemental analyzer. Crystals for X-ray diffraction were obtained from acetone. A single crystal was mounted on a glass fiber and the X-ray diffraction intensity data were measured either on a Rigaku AFC7S diffractometer (2a) or a Bruker Smart 1000 CCD XRD (1a, 2b, 3a, and 3b).

2.1. Synthesis of thienyl Schiff bases N-(2-thienylmethylidene)-2-thienylmethylamine (1a) and N-(5-methyl-2-thienylmethylidene)-2-thienylmethylamine (1b)

The synthesis of Schiff base employed the usual approach of condensation in either an ether (1a) or a MeOH (1b) solution [9]. Equimolar quantities of 2-formylthiophene or 5-methyl-2-formylthiophene (10 mmol) and 2-thienylmethylamine (10 mmol) were heated at reflux in 200 ml of anhyd ether (E. Merck) or MeOH (J. T. Baker) for 24 h. The solvent was removed in vacuo overnight to give pure yellow product 1a in 96% yield (9.6 mmole) or 1b in 97% yield (9.7 mmole).

Compound 1a: m.p. 54.6–55.0 °C. Anal. Calc. for $C_{10}H_9NS_2$: C, 57.97; H, 4.35; N, 6.76; S, 30.92. Found: C, 58.18; H, 4.49; N, 6.75; S, 30.86%. ^{13}C-NMR: δ 155.5, 155.2, 143.0, 142.6, 131.5, 129.5, 127.7, 127.0, 124.8, 58.3 ppm.

Compound 1b: Anal. Calc. for $C_{11}H_{11}NS_2$: C, 59.73; H, 4.98; N, 6.33; S, 28.96. Found: C, 59.91; H, 5.03; N, 6.33; S, 28.93%. ^{13}C-NMR: δ 155.4, 144.2, 142.9, 140.6, 131.7, 126.7, 126.0, 124.6, 124.4, 58.3, 14.8 ppm.

Other spectral data for compounds 1a and 1b were tabulated in Table 1.

2.2. Reaction of 1a/1b with Fe$_2$(CO)$_9$ in benzene to yield [μ-N-(((2,3-η^1:η^2)-2-thienyl)methyl)-η^1:η^1 (N)-2-thienylmethylamino]hexacarbonyldiiron (2a)/[μ-N-(((2,3-η^1:η^2)-5-methyl-2-thienyl)methyl)-η^1:η^1 (N)-2-thienylmethylamino]hexacarbonyldiiron (2b), di-μ-[(((2,3-η^1:η^2)-2-thienyl)methylidene)-η^1:η^2 (C, N)-2-thienylmethylamino]di-μ-carbonyloctacarbonyltetrairon (3a)/di-μ-[(((2,3-η^1:η^2)-5-methyl-2-thienyl)methylidene)-η^1:η^2 (C, N)-2-thienylmethylamino]di-μ-carbonyloctacarbonyltetrairon (3b), and 4a/4b

3.00 mmol of compound 1a/1b and 9.00 mmol of Fe$_2$(CO)$_9$ were stirred in 50 ml of anhydrous benzene in the dark under nitrogen for 24 h at room temperature (r.t.). The reaction mixture was filtered through Celite 545 and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column with n-hexane/CH$_2$Cl$_2$ (20/1) as eluent to separate the resulting reddish orange product 2a/2b and a brown band. The collected brown band was further treated by column chromatography with n-hexane/benzene (3/5) as eluent to remove the trace amount of yellow starting material 1a/1b. Pure brown products 3a/3b and 4a/4b were finally obtained from thin layer chromatograph with n-hexane/EtOAc (10/1) as eluent.

Compound 2a: 0.763 g (1.568 mmol), 52.3% yield. M.p. 95.6–96.0 °C. Anal. Calc. for $C_{16}H_9Fe_2NO_6S_2$: C, 39.42; H, 1.85; N, 2.88; S, 13.14. Found: C, 39.52; H,

Table 1
^{1}H-NMR (δ, ppm), IR (v, cm^{-1}), and mass data for compounds **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **4a**, and **4b**

	1a	1b	2a	2b	3a	3b	4a	4b
^{1}H-NMR								
Thienyl proton	7.59 (d)^a, H$_4$	7.32 (d)^a, H$_{10}$	7.70 (d)^a, H$_4$	7.48 (d)^a, H$_4$	7.94 (d, 2H)^a, H$_4$	7.47 (d, 2H)^a, H$_{10}$	7.77 (d, 2H)^a, H$_4$	7.46 (d, 2H)^a, H$_{10}$
Thienyl proton	7.46 (d)^b, H$_2$	7.23 (d)^b, H$_2$	7.48 (d)^a, H$_3$	7.12 (d)^b, H$_8$	7.46 (d, 2H)^a, H$_3$	7.13 (d, 2H)^b, H$_8$	7.46 (d, 2H)^a, H$_3$	7.18 (d, 2H)^b, H$_8$
Thienyl proton	7.34 (d)^a, H$_{10}$	6.98 (d, 2H)^b, H$_3$, H$_8$	7.39 (d)^a, H$_{10}$	7.05 (s), H$_3$	7.42 (d, 2H)^a, H$_{10}$	7.09 (s, 2H), H$_3$	7.32 (d, 2H)^a, H$_{10}$	7.03 (dd, 2H)^c, H$_9$
Thienyl proton	7.13 (dd)^c, H$_3$	6.80 (dd)^c, H$_9$	7.15 (dd)^c, H$_9$	7.01 (dd)^c, H$_9$	7.13 (d, 2H)^b, H$_8$	7.02 (dd, 2H)^c, H$_9$	7.20 (d, 2H)^b, H$_8$	6.92 (s, 2H), H$_3$
Thienyl proton	6.99 (m), H$_8$, H$_9$		7.13 (d)^b, H$_8$		7.02 (dd, 2H)^c, H$_9$		7.03 (dd, 2H)^c, H$_9$	
−C(H)=N−	8.57 (s, 1H)	8.43 (s, 1H)			7.39 (s, 2H)	7.21 (s, 2H)	7.56 (s, 2H)	7.36 (s, 2H)
−CH$_2$−	4.92 (s, 2H)	4.88 (s, 2H)	4.19 (s, 2H)	4.16 (s, 2H)	4.85 (d, 2H)^d	4.85 (d, 2H)^d	5.25 (d, 2H)^d	5.23 (d, 2H)^d
					4.67 (d, 2H)^d	4.68 (d, 2H)^d	5.05 (d, 2H)^d	5.01 (d, 2H)^d
−CH$_2$−			3.96 (s, 2H)	3.88 (s, 2H)				
−CH$_3$		2.47 (s, 3H)		2.45 (s, 3H)		2.59 (s, 6H)		2.52 (s, 6H)
IR (KBr film)								
CN	1623	1630			1637	1637	1637	1639
Terminal CO			2060, 2022, 1989	2063, 2022, 1988	2053, 2030, 1987	2051, 2026, 1986	2052, 2028, 1986	2051, 2028, 1987
Terminal CO					1958	1955	1956	1952
Bridging CO					1764	1771	1760	1752
Mass (*m/z*)	208 (M$^+$)	221 (M$^+$)	487 (M$^+$)	501 (M$^+$)	916 (M$^+$)	944 (M$^+$)	916 (M$^+$)	944 (M$^+$)
			459 (M$^+$−CO)	473 (M$^+$−CO)	888 (M$^+$−CO)	916 (M$^+$−CO)	888 (M$^+$−CO)	916 (M$^+$−CO)
			431 (M$^+$−2CO)	445 (M$^+$−2CO)	860 (M$^+$−2CO)	888 (M$^+$−2CO)	860 (M$^+$−2CO)	888 (M$^+$−2CO)
			403 (M$^+$−3CO)	417 (M$^+$−3CO)	832 (M$^+$−3CO)	860 (M$^+$−3CO)	832 (M$^+$−3CO)	860 (M$^+$−3CO)
			375 (M$^+$−4CO)	389 (M$^+$−4CO)	804 (M$^+$−4CO)	832 (M$^+$−4CO)	804 (M$^+$−4CO)	832 (M$^+$−4CO)
			347 (M$^+$−5CO)	361 (M$^+$−5CO)	776 (M$^+$−5CO)	804 (M$^+$−5CO)	776 (M$^+$−5CO)	804 (M$^+$−5CO)
			319 (M$^+$−6CO)	333 (M$^+$−6CO)	748 (M$^+$−6CO)	776 (M$^+$−6CO)	748 (M$^+$−6CO)	776 (M$^+$−6CO)
			207 (L)	221 (L)	720 (M$^+$−7CO)	748 (M$^+$−7CO)	720 (M$^+$−7CO)	748 (M$^+$−7CO)
					692 (M$^+$−8CO)	720 (M$^+$−8CO)	692 (M$^+$−8CO)	720 (M$^+$−8CO)
					664 (M$^+$−9CO)	692 (M$^+$−9CO)	664 (M$^+$−9CO)	692 (M$^+$−9CO)
					636 (M$^+$−10CO)	664 (M$^+$−10CO)	636 (M$^+$−10CO)	664 (M$^+$−10CO)
					486 (M$^+$/2+CO)	500 (M$^+$/2+CO)	486 (M$^+$/2+CO)	500 (M$^+$/2+CO)
					458 (M$^+$/2)	472 (M$^+$/2)	458 (M$^+$/2)	472 (M$^+$/2)
					430 (M$^+$/2−CO)	444 (M$^+$/2−1CO)	430 (M$^+$/2−CO)	444 (M$^+$/2−1CO)
					402 (M$^+$/2−2CO)	416 (M$^+$/2−2CO)	402 (M$^+$/2−2CO)	416 (M$^+$/2−2CO)
					374 (M$^+$/2−3CO)	388 (M$^+$/2−3CO)	374 (M$^+$/2−3CO)	388 (M$^+$/2−3CO)
					346 (M$^+$/2−4CO)	221 (L)	346 (M$^+$/2−4CO)	332 (M$^+$/2−5CO)
					207 (L)		207 (L)	221 (L)

^{a} $J_{H-H} = 5.1$ Hz.
^{b} $J_{H-H} = 3.6$ Hz.
^{c} $J_{H-H} = 5.1, 3.6$ Hz.
^{d} Two well-separated doublet with $J_{H-H} = 14.4$ Hz.

1.95; N, 2.93; S, 13.06%. ^{13}C-NMR: δ 210.4, 154.7, 139.4, 131.7, 128.6, 126.6, 126.3, 117.5, 65.5, 63.8 ppm. Compound **3a**: 0.174 g (0.190 mmol), 12.7% yield. M.p. 141.0–141.8 °C. Anal. Calc. for $C_{30}H_{16}Fe_4N_2O_{10}S_4$: C, 39.30; H, 1.75; N, 3.06; S, 13.97. Found: C, 39.42; H, 1.78; N, 2.99; S, 13.86%. ^{13}C-NMR: δ 213.9, 212.1, 168.2, 142.0, 136.7, 133.1, 127.2, 127.0, 126.6, 114.6, 114.3, 65.6 ppm. Compound **4a**: 0.157 g (0.172 mmol), 11.4% yield. M.p. 140.5–141.0 °C. Anal. Calc. for $C_{30}H_{16}Fe_4N_2O_{10}S_4$: C, 39.30; H, 1.75; N, 3.06; S, 13.97. Found: C, 39.44; H, 1.70; N, 3.09; S, 14.11%. ^{13}C-NMR: δ 214.0, 212.2, 166.5, 144.6, 142.5, 135.7, 133.2, 127.3, 126.6, 124.2, 113.8, 61.8 ppm.

Compound **2b**: 0.828 g (1.653 mmol), 55.1% yield. M.p. 131.0–131.5 °C. Anal. Calc. for $C_{17}H_{11}Fe_2NO_6S_2$: C, 40.71; H, 2.20; N, 2.80; S, 12.78. Found: C, 40.89; H, 2.12; N, 2.873; S, 13.04%. ^{13}C-NMR: δ 210.4, 153.8, 147.8, 147.4, 139.7, 139.0, 132.2, 131.7, 118.4, 67.6, 66.8, 20.6 ppm. Compound **3b**: 0.175 g (0.172 mmol), 11.5% yield. M.p. 162.5–163.0 °C. Anal. Calc. for $C_{32}H_{20}Fe_4$-$N_2O_{10}S_4$: C, 40.68; H, 2.12; N, 2.96; S, 13.56. Found: C, 40.71; H, 2.20; N, 2.93; S, 13.80%. ^{13}C-NMR: δ 219.8, 217.9, 153.8, 147.8, 139.7, 139.0, 132.2, 131.7, 119.4, 118.4, 113.8, 67.6, 20.6 ppm. Compound **4b**: 0.156 g (0.0.167 mmol), 11.1% yield. M.p. 161.5–162.0 °C. Anal. Calc. for $C_{32}H_{20}Fe_4N_2O_{10}S_4$: C, 40.68; H, 2.12; N, 2.96; S, 13.56. Found: C, 40.82; H, 2.08; N, 2.98; S, 13.68%. ^{13}C-NMR: δ 219.4, 217.5, 148.2, 142.6, 137.8, 133.8, 127.2, 127.0, 126.5, 113.8, 113.2, 61.6, 15.4 ppm.

Other spectral data for these products were summarized in Table 1.

3. Results and discussion

The thienyl Schiff base **1a/1b** was prepared by condensation of 2-formylthiophene/5-methyl-2-formylthiophene and 2-thienylmethylamine in anhydrous ether/methanol. These compounds were fully characterized spectrally as described in the experimental section. The structure of compound **1a** was further confirmed by single-crystal X-ray analysis. The ORTEP drawing of **1a** is shown in Fig. 1. Crystal and data collection parameters are shown in Table 2. Selected bond lengths and bond angles are tabulated in Table 3. The unit cell has two crystallographically independent molecules. The dihedral angles between two thiophene rings in each of these two independent molecules are 76.43(30)° and 43.26(37)°, respectively. There exists a hydrogen bonding between N(2) of one molecule and H(2) (on C(2)) of another molecule.

The thienyl Schiff base **1** reacts with diiron nonacarbonyl under mild conditions in anhydrous benzene to give off one diiron hexacarbonyl complex and two linear tetrairon decacarbonyl clusters, which we formulate as the major products **2**, **3**, and **4** (Scheme 1). In all cases, a
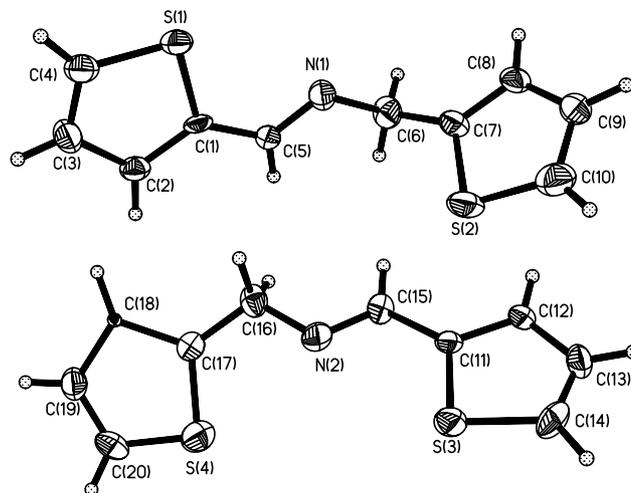

Fig. 1. ORTEP diagrams of compound **1a** at the 50% probability level.

C–H activation is observed at the β-carbon of the thienyl ring of the thienylmethylidene moiety to form a five-membered *endo* metallacycle. The formation of **2** proceeds further through an intramolecular 1,3-hydrogen shift of the hydrogen originating from the β-carbon toward the former imine group, thus producing a new methylene group. In the formations of **3** and **4**, no hydrogen shift is observed after the C–H activation. Complexes **3** and **4** are diastereomers. Complexes **2**, **3** and **4** are stable in their solid state at room temperature. Prolonged stirring of **2**, **3** or **4** in *n*-hexane, benzene, or acetonitrile at room temperature for several days leads to the decomposition of the complex. Decomposition of the complex in the aforementioned solvent takes place within 15 h at refluxing temperature.

3.1. Molecular structures of **2a**, **2b**, **3a**, and **3b**

The molecular structures of **2a**, **2b**, **3a**, and **3b**, as determined through single-crystal X-ray diffraction analysis, are shown in Figs. 2–5, respectively. Their crystal and data collection parameters are tabulated in Table 2 and selected bond lengths and bond angles are summarized in Tables 3 and 4.

Regarding compound **2a**, it is evident in Fig. 2 that the β-carbon, C(2), of a thienyl ring is σ bonded to Fe(1) with a bond distance of 1.970(2) Å. C(1) and C(2) are π bonded to Fe(2) with bond distances of 2.304(2) and 2.149(2) Å, respectively, and the bond distance between C(1) and C(2) is 1.393(4) Å, which is about the same as that in the free ligand **1a**. The thienyl ring of the thienylmethylidene moiety acts as a three-electron donor and, thereby, bridges the two iron centers. The bond distances from N(1) to C(5) is lengthened to 1.473(3) Å, which is in the single bond range and which is comparable to that of N(1)–C(6) single bond distance (1.478(3) Å). The nitrogen atom serves as an another three-electron bridge and the bond distances to Fe(1)

Table 2
Crystal and data collection parameters for compounds **1a**, **2a**, **2b**, **3a**, and **3b**

	1a	2a	2b	3a	3b
Empirical formula	$C_{20}H_{18}N_2S_4$	$C_{16}H_9Fe_2NO_6S_2$	$C_{17}H_{11}Fe_2NO_6S_2$	$C_{60}H_{32}Fe_8N_4O_{20}S_8$	$C_{35}H_{26}Fe_4N_2O_{11}S_4$
Formula weight	414.60	487.06	501. 09	1832.18	1002.22
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$Pna2(1)$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.1365(10)	7.9718(7)	10.4063(6)	12.1639(7)	11.1383(8)
b (Å)	11.3317(16)	10.677(1)	13.9769(8)	15.6354(9)	12.0675(10)
c (Å)	21.629(3)	11.280(1)	14.0883(9)	18.4215(10)	16.6474(12)
α (°)	90.00	101.306(7)	90.00	85.6990(10)	74.680(2)
β (°)	90.00	94.373(7)	109.8840(10)	71.3590(10)	88.0070(10)
γ (°)	90.00	97.314(7)	90.00	83.1140(10)	64.4030(10)
V (Å^3)	1994.2(5)	928.7(2)	1927.0(2)	3293.3(3)	1938.2(2)
Z	4	2	4	2	2
D_{calc} (g cm^{-3})	1.381	1.742	1.727	1.847	1.717
Crystal size (mm)	$0.20 \times 0.15 \times 0.12$	$0.80 \times 0.60 \times 0.50$	$0.58 \times 0.49 \times 0.25$	$0.39 \times 0.28 \times 0.22$	$0.34 \times 0.20 \times 0.08$
Temperature (K)	150(2)	298	150(2)	150(2)	150(2)
θ Range (°)	1.88–27.49	52.0 ($2\theta_{max}$)	2.12–27.50	1.17–27.53	1.27–27.54
Reflections measured	6581	3839	6772	21 133	12 470
No. data collected	2730	3636	3915	14 695	8616
Number of reflections ($I > 2.00\sigma(I)$)	1632	3107 ($I > 3.00\sigma(I)$)	3477	8484	4727
Number of parameters	235	244	254	886	507
$F(000)$	864	488.00	1008	1830	1012
Goodness-of-fit	0.982	1.24	1.023	0.924	0.860
R_1	0.0722	0.0336	0.0276	0.0481	0.0443
wR_2	0.1957	0.0523	0.0710	0.1244	0.0944

Table 3
Selected bond lengths (Å) and angles (°) of compounds **1a**, **2a**, and **2b**

	1a	2a	2b
Bond lengths			
C(5)–N(1)	1.287(12)	1.473(3)	1.482(2)
C(6)–N(1)	1.422(13)	1.478(3)	1.482(2)
C(1)–C(2)	1.396(13)	1.393(4)	1.394(3)
C(1)–C(5)	1.422(14)	1.494(4)	1.497(3)
Fe(1)–Fe(2)	2.4477(4)	2.4345(4)	
Fe(1)–C(2)	1.970(2)	1.9667(19)	
Fe(1)–N(1)	1.991(2)	1.9898(15)	
Fe(2)–C(1)	2.304(2)	2.2849(17)	
Fe(2)–C(2)	2,149(2)	2.1608(16)	
Fe(2)–N(1)	1.965(2)	1.9648(16)	
Bond angles			
C(1)–C(5)–N(1)	119.6(10)	99.1(2)	98.19(14)
C(5)–N(1)–C(6)	117.5(9)	112.5(2)	111.67(14)
Fe(1)–C(2)–Fe(2)	72.76(8)	72.12(6)	
Fe(1)–N(1)–Fe(2)	76.43(7)	75.99(6)	
C(1)–Fe(2)–C(2)	36.26(9)	36.40(7)	
C(1)–Fe(2)–Fe(1)	72.77(6)	73.24(5)	
C(1)–Fe(2)–N(1)	63.27(9)	63.46(6)	
C(2)–Fe(2)–Fe(1)	50.23(7)	50.25(5)	
C(2)–Fe(2)–N(1)	74.62(9)	74.53(6)	
Fe(1)–Fe(2)–N(1)	52.26(5)	52.47(4)	
C(2)–Fe(1)–N(1)	78.22(9)	78.49(7)	
Fe(2)–Fe(1)–N(1)	51.31(5)	51.54(5)	
Fe(2)–Fe(1)–C(2)	57.01(7)	57.64(5)	
C(5)–C(1)–Fe(2)	86.0(1)	86.49(10)	
C(1)–C(2)–Fe(2)	77.9(2)	76.65(10)	
C(2)–C(1)–Fe(2)	65.81(9)	66.95(9)	
C(5)–N(1)–Fe(2)	100.2(1)	99.77(11)	
C(1)–C(2)–Fe(1)	112.9(2)	112.86(13)	

and Fe(2) are 1.991(2) and 1.965(2) Å, respectively. An iron–iron distance of 2.4477(4) Å is shorter than usual for diiron complexes [10] but is in accordance with that of other nitrogen bridged diiron complexes [5,11]. The deviation of the bond angles of C(1)–C(5)–N(1) (99.1(2)°), C(5)–N(1)–C(6) (112.5(2)°), Fe(1)–C(2)–Fe(2) (72.76(8)°), and Fe(1)–N(1)–Fe(2) (76.43(7)°) from the tetrahedral value is a result of the ligand constraint of double bridging, which also bring about the shorter metal–metal distance. As demonstrated above, the structure and bonding feature of compound **2b**, as shown in Fig. 3 and Table 2, closely resembles that of compound **2a**.

The molecular geometry of **3a** alone with the adopted numbering scheme is shown in Fig. 4. Two enantiomers are co-crystallized and presented in a 1:1 ratio in the unit cell. Each enantiomer exhibits noncrystallographic C_2 symmetry, with the 2-fold axis running through the midpoint of the central Fe(2)–Fe(3)/Fe(6)–Fe(7) bond and perpendicular to the plane defined by Fe(2), C(25), Fe(3), C(26)/ Fe(6), C(55), Fe(7), C(56). The linear arrangement of the four iron atoms in **3a** is by far the most exciting feature of the structure. The three Fe–Fe bond distances are Fe(1)–F(2) = 2.5152(10) Å, Fe(2)–Fe(3) = 2.5659(10) Å, and Fe(3)–Fe(4) = 2.4958(10) Å, while the Fe(1)–Fe(2)–Fe(3) and Fe(2)–Fe(3)–Fe(4) bond angles are 173.06(4)° and 167.63(4)°, respectively. The terminal Fe–Fe distance in **3a** is longer than that of **2** and than those found in nitrogen-bridged diiron complexes [5,11]; however, it is in accordance with other
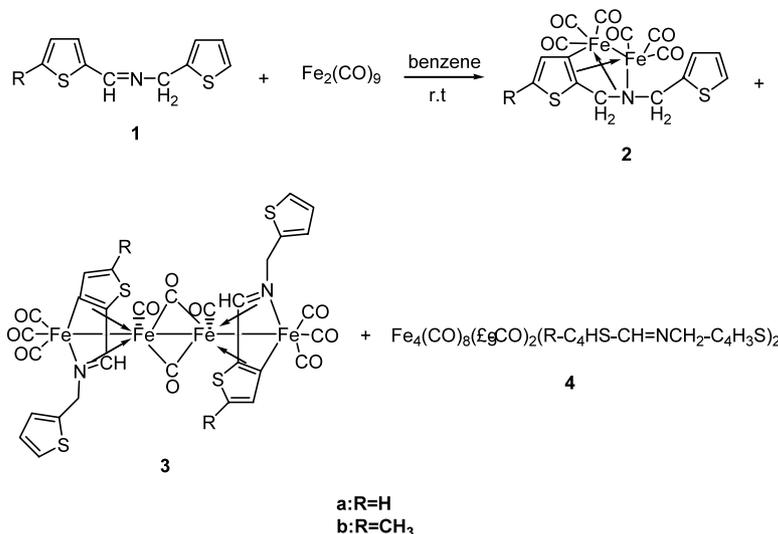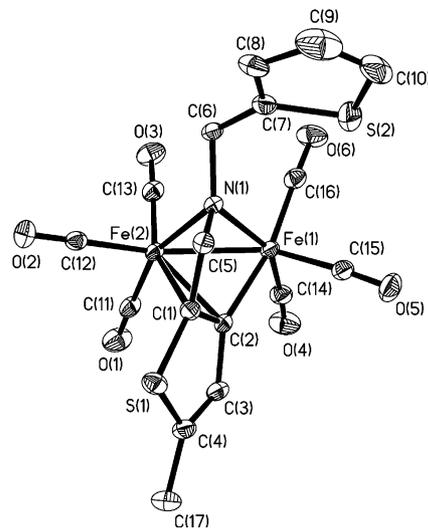
Scheme 1.
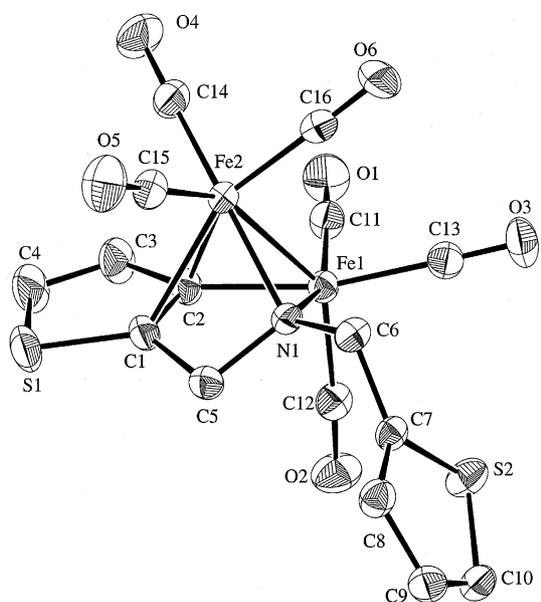
Fig. 2. ORTEP diagram of compound **2a** at the 50% probability level.

Fig. 3. ORTEP diagram of compound **2b** at the 50% probability level.

single Fe–Fe bond diiron complexes [10]. The central Fe–Fe distance, which is normal for a CO-bridged Fe–Fe bond length [12], is about 0.05 Å longer than that of a terminal Fe–Fe bond. Each of the outmost Fe atom bears three terminal CO ligands, while the inner two Fe atoms each have one terminal CO and share two bridging COs. The isolated Fe_2C_2 rhombohedron is planar. The two terminal CO ligands of the inner two Fe atoms are in mutual *cis* position and are about perpendicular with the plane defined by Fe(2), C(25), Fe(3), and C(26).

Two thienyl Schiff bases are involved in molecule **3a**, and each serves as a di-bridging ligand to two iron centers. The ligand is three-electron, σ-N and σ-C,

bonded to Fe(1) via the imine nitrogen, N(1), and the β-carbon of the thienyl ring of the thienylmethylidene moiety, C(2), with bond lengths of 1.989(4) Å and 1.937(6) Å. The N(1)–Fe(1)–C(2) bond angle is 80.7(2)°. The imine group C=N and the C=C group of the α,β-carbon of the thienyl ring are further coordinated to Fe(2) via their π systems with the bond lengths of 2.083(4) Å, 2.133(5) Å, 2.208(5) Å, and 2.244(5) Å for Fe(2)–N(1), Fe(2)–C(5), Fe(2)–C(1), and Fe(2)–C(2), respectively. The bond angles N(1)–Fe(2)–C(2) and C(1)–Fe(2)–C(5) are 71.81(19)° and 37.54(19)°. The plane defined by N(1), C(5), C(1), and C(2), which is almost coplanar to the S(1)–thiophene ring, is almost perpendicular (82.89(23)°) to the plane defined by C(24), Fe(2), Fe(3), and C(27) and has a dihedral angle of 47.50(20)° to the plane defined by Fe(2), C(25), Fe(3), and C(26). The bond lengths of C(5)–N(1) and C(1)–
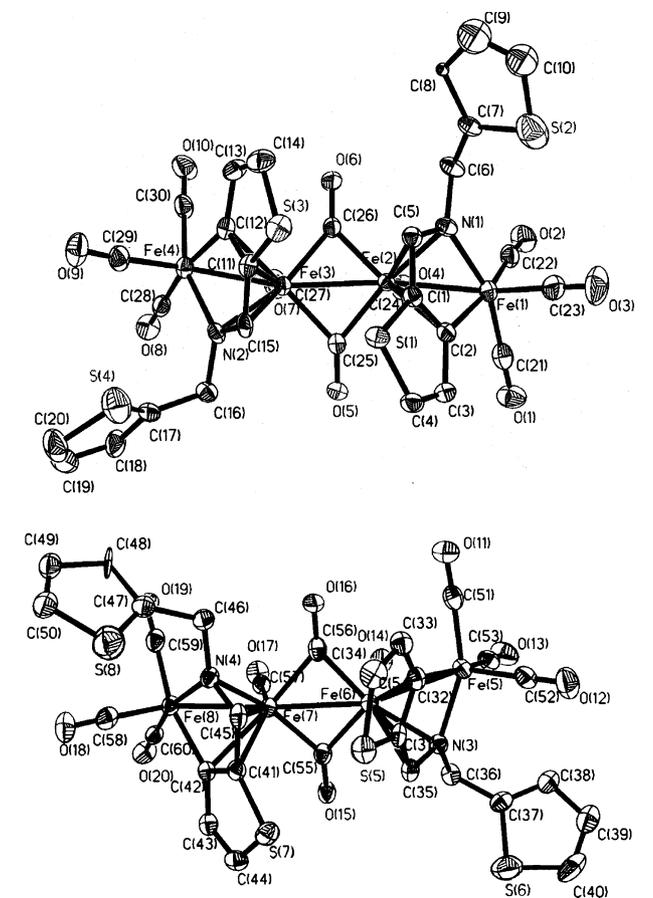
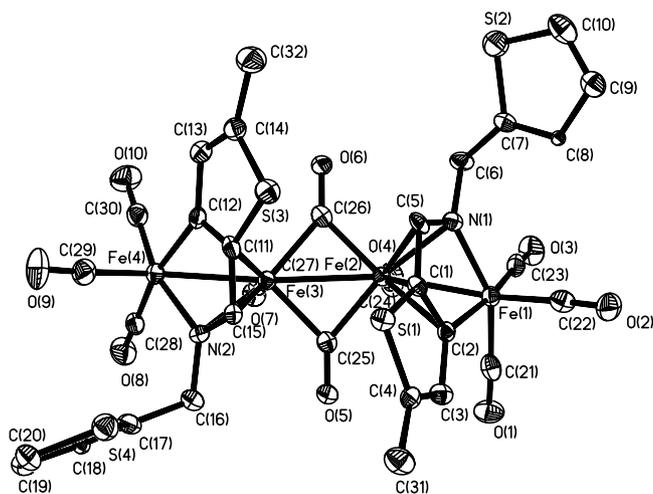Fig. 4. ORTEP diagram of compound **3a** at the 50% probability level.

Fig. 5. ORTEP diagram of compound **3b** at the 50% probability level.

C(2) double bonds are lengthened to 1.364(6) Å and 1.421(7) Å, while the central C(1)–C(5) bond length is shortened to 1.398(7) Å. The C(2)–C(1)–C(5), N(1)–C(5)–C(1) and C(5)–N(1)–(6) bond angles have been adjusted, from their sp² configurations, to 116.4(5)°, 112.0(5)° and 115.7(4)°, respectively. These geometries correspond very well with the 7e-bond (3e η¹-N; η¹-C

and 4e η⁴-C=N–C=C) description and also indicate that the LUMO of the ligand is extensively occupied, thereby lengthening the imine and the α, β-C=C bonds and shortening the central C(1)–C(5) bond. There are only a few structurally characterized iron carbonyl complexes in which an aromatic π-system is involved in the η⁴-coordination mode including anthracene, naphthalene, indene, and benzene [6]. Complex **3a** is the first example of a η⁴-coordinated iron carbonyl complex in which the C=C double bond is part of a thiophene.

The tetranuclear cluster Fe₄(CO)₁₀(R–C₄HS–CH= NCH₂–C₄H₃S)₂, **3a**, containing two *ortho*-cyclometal-lated thienylmethylidene thienylmethylamine ligands represents a rare example of a cluster consisting of a linear array of four transition-metal atoms. The 66-electron complex may be viewed as a symmetrical dimmer, consisting of two linked 33-electron Fe₂(CO)₅(R–C₄HS–CH=NCH₂–C₄H₃S) fragments, in which the ligands form 7 e bridges between the Fe(CO)₃ and the Fe(CO)₂ moieties. The plane containing N(1), C(5), C(1), and C(2) also contains to a good approximation the Fe(1) atom with a root-mean-square deviation of 0.0529. The sum of the enclosed angles amounts to 539.6°, a value that is extremely close to the theoretical 540° for a pentagon confined to one plane. Therefore the ligand can be viewed as part of an η⁵-coordinated azaferracyclopentadienyl ring, which is isolobally related to an η⁵-coordinated cyclopentadinyl ring. The coordination of two such heterocycles to a central [Fe(CO)(μ-CO)]₂ core let us to the conclusion that **3a** is an isolobal analogue of [CpFe(CO)(μ-CO)]₂ [13]. To date, only a few examples of complexes containing linear M₄ geometries have been reported [14]. Interestingly, the central two metal atoms in all complexes are second- or third-row metals, and the ligands used are mostly derivatives of 1,4-diaza-1,3-butadiene or 1-aza-1,3-butadiene. The only linear tetra-iron carbonyl cluster of the same structure type that has been reported in the literature is the one that has been derived from *N*-α-naphthylidene cyclohexylamine [7i]. In that case, two terminal CO ligands on the inner two Fe atoms are in mutual *trans* position, and the three Fe–Fe bond lengths are 2.521(2)Å, 2.580(1), and 2.520(1) Å, while the two Fe–Fe–Fe bond angles are bent to 154.16(6)° and 154.48(5)°, respectively.

The structure and bonding feature of compound **3b**, as shown in Fig. 5 and Table 4, closely resembles that of compound **3a**, as explained above. However it is important to note that no co-crystallization of enantio-mers was observed.

3.2. ¹H-NMR spectroscopy

The ¹H-NMR data of the free ligands (**1a** and **1b**), diiron complexes (**2a** and **2b**) and tetrairon clusters (**3a**,

Table 4
Selected bond lengths (Å) and bond angles (°) of compounds **3a** and **3b**

	3a	3b		3a	3b
Fe(1)−Fe(2)	2.5152(10)	2.4999(10)	Fe(3)−Fe(4)	2.4958(10)	2.5245(10)
Fe(2)−Fe(3)	2.5659(10)	2.5728(10)			
Fe(1)−C(2)	1.937(6)	1.942(4)	Fe(4)−C(12)	1.955(6)	1.932(5)
Fe(1)−N(1)	1.989(4)	1.987(4)	Fe(4)−N(2)	1.966(4)	1.966(4)
Fe(2)−N(1)	2.083(4)	2.043(4)	Fe(3)−N(2)	2.055(4)	2.056(4)
Fe(2)−C(5)	2.133(5)	2.119(5)	Fe(3)−C(15)	2.132(5)	2.119(5)
Fe(2)−C(1)	2.208(5)	2.213(5)	Fe(3)−C(11)	2.230(5)	2.206(5)
Fe(2)−C(2)	2.244(5)	2.236(5)	Fe(3)−C(12)	2.214(5)	2.244(5)
Fe(2)−C(25)	1.943(6)	1.925(5)	Fe(3)−C(25)	1.941(5)	1.938(5)
Fe(2)−C(26)	1.936(5)	1.930(5)	Fe(3)−C(26)	1.906(6)	1.919(5)
C(1)−C(2)	1.421(7)	1.415(6)	C(11)−C(12)	1.409(7)	1.433(7)
C(1)−C(5)	1.398(7)	1.411(6)	C(11)−C(15)	1.408(8)	1.403(6)
C(5)−N(1)	1.364(6)	1.359(6)	C(15)−N(2)	1.341(6)	1.367(6)
C(6)−N(1)	1.488(7)	1.481(5)	C(16)−N(2)	1.508(7)	1.446(6)
The metal carbonyl part					
Fe(1)−Fe(2)−Fe(3)	173.06(4)	167.62(4)	Fe(2)−Fe(3)−Fe(4)	167.63(4)	174.19(4)
Fe(2)−C(25)−O(5)	140.1(4)	139.8(4)	Fe(3)−C(25)−O(5)	137.1(4)	136.7(4)
Fe(2)−C(26)−O(6)	136.7(4)	136.0(4)	Fe(3)−C(26)−O(6)	139.5(4)	140.0(4)
Fe−C−O (terminal)	176.7(6)				
Around Fe(1), Fe(4)					
Fe(2)−Fe(1)−C(2)	58.83(16)	58.87(14)	Fe(3)−Fe(4)−C(12)	58.146(15)	58.68(14)
Fe(2)−Fe(1)−N(1)	53.56(13)	52.68(11)	Fe(3)−Fe(4)−N(2)	53.27(12)	52.73(11)
N(1)−Fe(1)−C(2)	80.7(2)	80.77(17)	N(2)−Fe(4)−C(12)	80.8(2)	81.58(18)
Around Fe(2), Fe(3)					
Fe(1)−Fe(2)−C(2)	47.61(14)	48.01(12)	Fe(4)−Fe(3)−C(12)	48.61(14)	47.34(12)
Fe(1)−Fe(2)−N(1)	50.18(12)	50.65(11)	Fe(4)−Fe(3)−N(2)	50.04(12)	49.54(14)
Fe(1)−Fe(2)−C(1)	73.17(14)	73.20(12)	Fe(4)−Fe(3)−C(11)	72.79(14)	72.85(13)
Fe(1)−Fe(2)−C(5)	75.90(14)	76.39(13)	Fe(4)−Fe(3)−C(15)	75.24(14)	75.14(13)
N(1)−Fe(2)−C(1)	64.42(18)	65.00(15)	N(2)−Fe(3)−C(11)	64.29(19)	65.32(16)
N(1)−Fe(2)−C(2)	71.81(19)	72.85(16)	N(2)−Fe(3)−C(12)	72.95(19)	72.47(16)
N(1)−Fe(2)−C(5)	37.72(17)	38.07(15)	N(2)−Fe(3)−C(15)	37.30(18)	38.17(16)
C(1)−Fe(2)−C(2)	37.21(19)	37.09(16)	C(11)−Fe(3)−C(12)	36.97(18)	37.55(17)
C(1)−Fe(2)−C(5)	37.54(19)	37.94(16)	C(11)−Fe(3)−C(15)	37.6(2)	37.79(16)
C(2)−Fe(2)−C(5)	66.3(2)	67.95(17)	C(12)−Fe(3)−C(15)	66.7(2)	66.65(17)
Fe(3)−Fe(2)−C(25)	48.61(15)	48.46(15)	Fe(2)−Fe(3)−C(25)	48.68(16)	48.04(15)
Fe(3)−Fe(2)−C(26)	47.61(17)	47.86(14)	Fe(2)−Fe(3)−C(26)	48.60(16)	48.25(15)
Fe(1)−Fe(2)−C(24)	79.85(17)	79.87(17)	Fe(4)−Fe(3)−C(27)	78.94(17)	78.79(16)
Fe(3)−Fe(2)−C(24)	99.95(18)	98.20(16)	Fe(2)−Fe(3)−C(27)	99.53(18)	99.70(16)
The ligand part					
Fe(1)−C(2)−Fe(2)	73.56(18)	73.11(15)	Fe(3)−C(12)−Fe(4)	73.26(18)	73.98(16)
Fe(1)−N(1)−Fe(2)	76.27(15)	76.67(13)	Fe(3)−N(2)−Fe(4)	76.70(15)	77.72(13)
Fe(1)−N(1)−C(5)	116.8(3)	117.0(3)	Fe(4)−N(2)−C(15)	117.1(4)	116.4(3)
Fe(1)−C(2)−C(1)	113.7(4)	113.3(3)	Fe(4)−C(12)−C(11)	112.4(4)	113.1(3)
Fe(2)−C(5)−C(1)	74.1(3)	74.7(3)	Fe(3)−C(15)−C(11)	75.0(3)	74.5(3)
Fe(2)−C(1)−C(5)	68.3(3)	67.4(3)	Fe(3)−C(11)−C(15)	67.4(3)	67.8(3)
Fe(2)−C(1)−C(2)	72.8(3)	72.4(3)	Fe(3)−C(11)−C(12)	70.9(3)	72.7(3)
Fe(2)−C(2)−C(1)	70.0(3)	70.6(3)	Fe(3)−C(12)−C(11)	72.2(3)	69.8(3)
Fe(2)−N(1)−C(5)	73.1(3)	74.0(3)	Fe(3)−N(2)−C(15)	74.5(3)	73.4(3)
Fe(2)−C(5)−N(1)	69.1(3)	68.0(2)	Fe(3)−C(15)−N(2)	67.4(3)	67.8(3)
N(1)−C(5)−C(1)	112.0(5)	111.6(4)	N(2)−C(15)−C(11)	112.5(5)	112.5(4)
C(5)−C(1)−C(2)	116.4(5)	116.6(4)	C(15)−C(11)−C(12)	116.0(5)	115.6(4)
C(5)−N(1)−C(6)	115.7(4)	115.3(4)	C(15)−N(2)−C(16)	116.9(4)	117.9(4)

3b, **4a**, and **4b**) are summarized in Table 1. The thienyl proton in each compound can be easily assigned according to its specific position and the characteristic coupling constant. The free ligand **1** is identified by the presence of a singlet imine proton at δ 8.57 (**1a**) or 8.43

ppm (**1b**) and another singlet methylene resonance at δ 4.92 (**1a**) and 4.88 ppm (**1b**).

The most significant feature of the ^{1}H-NMR spectrum of **2** is the absence of imine proton resonance and of one β-thienyl proton relative to the free ligand.

Signals for the thienyl protons were found to be down-field shifted due to the cyclometallation of a thienyl ring. However, a pair of singlet resonance representing the methylene groups appears at δ 419 and 3.96 ppm for **2a** and at δ 4.16 and 3.88 ppm for **2b**, indicating the formation of the second methylene group in **2**. The lack of diastereotopicity of the methylene protons in the azametallacycle of **2** indicates that a fluxional process, the so-called "windshield-wiper type oscillation", of the ligand might occur in this complex [14h]. The ^{1}H-NMR spectrum of **2** shows properties that closely resemble those of dinuclear iron carbonyl complexes derived from other thienyl Schiff base derivatives [5].

The ^{1}H-NMR spectra of **3** and **4** also show the missing of one β-thienyl proton relative to the free ligand. The same C–H activation as that in **2** has occurred at the β-carbon of the thienyl ring next to the imine group; however, no hydrogen transformation is found. The imine protons are found to have substantially up-field shifted to δ 7.39 (**3a**), 7.21 (**3b**), 7.56 (**4a**), and 7.36 ppm (**4b**). This phenomenon is attributed to the π-coordination and back-π accepting of the C=N group. There exists only one set of methylene resonance consisting of two well-separated doublets, a typical AB spin pattern, with a coupling constant of $J_{H-H} = 14.4$ Hz. This set of signal is much more down-field shifted relative to **2** but close to that of **1**. The observation of diastereotopicity at the methylene group indicates the rigidity of the thienylmethylamine moiety to the bulky coordination core of the two inner iron centers.

3.3. IR spectroscopy

The IR $\nu(CO)$ frequencies of carbonyls on terminal iron centers, $Fe(CO)_3$, that appear in the range of 2063–1986 cm^{-1} are characteristic for all six complexes [5] (Table 1). For **3a**, the $Fe(CO)_3$ unit evinces local C_s symmetry and the $\nu(CO)$ frequencies at 2053, 2030, and 1988 cm^{-1} can be ascribed to the A′ and A′+A″ vibrations in the $Fe(CO)_3$ group. The $\nu(CO)$ frequency of the terminal carbonyl on inner iron is observed at a lower frequency (1958 cm^{-1}) as might be expected for a CO with lower bond order. The even lower absorption band (1764 cm^{-1}) is found in the stretching range of bridging COs and is, therefore, assigned to the antisymmetric stretching mode of the $Fe_2(\mu\text{-}CO)_2$ entity. A similar pattern is observed in **3b**, **4a**, or **4b**. Complexes **3** and **4** also show a characteristic C=N stretching absorption at 1637 cm^{-1}, which is comparable to that of free ligand due to the long conjugate chain of ligand [15].

3.4. Mass spectrometry

The molecular formula of each complex has been confirmed by the observation of a signal for the molecular ion peak and absorption peaks corresponding to the fragments with sequential loss of CO from the molecule (Table 1).

While no direct structural evidence is available for **4a** and **4b**, we are able to deduce their structures to be the diastereomers of **3a** and **3b**, respectively, from their NMR, IR, and mass spectra, as well as elemental analysis. There are four possible stereoisomers [14g] of **3**, as shown in Fig. 6. Both **3a** and **3b** are isolated as the pure Z_{Fe},E_N form, although **3a** exists in 1:1 enantiomers. The structure of **4** is believed to be one of the other three stereoisomers other than the Z_{Fe},E_N form. No evidence of interconversion between **3** and **4** isomers has ever been found during the course of thermal reaction studies of **3** or **4**.

Tetranuclear transition-metal clusters may exhibit several geometric configurations, depending on the number of valance electrons provided by the metal atoms and the ligands that are involved in coordination [14e]. **3** and **4** clusters contain three metal–metal bonds, two ligands, each with the σ-N, σ-C, η^2-C=N, and η^2-C=C (a total of 7e) coordination mode, bridge to two diiron centers, and ten carbonyls, in agreement with the presence of 66 closed valence electrons (CVE) [16], indicating that the molecule is electron-precise.

Among the authors' previous studies of iron carbonyl complexes from a series of thienylmethylidene amine derivatives, Th–CH=N–R where R = –Ph, –CH$_2$Ph, or –CH(Me)Ph, the results reported in the current paper represent the first time that they were able to produce and isolate the linear tetrairon complexes, **3** and **4**, with R = –CH$_2$–Th. At present, however, this deviating reactivity is not yet fully understood. Since a molecular structure of **3** reveals that different R groups do not make much difference structurally and inductively, more research is needed that attempts to answer this question. An attractive alternative perception of **3** is that it is a structural analogue of $[CpFe(CO)(\mu\text{-}CO)]_2$. In this view, the azametallacycle, which contains the outer iron and is almost planar, can be imagined to be a diheterocyclopentadienyl fragment and is η^5-coordinated to inner iron. Whether the chemical behavior of this complex resembles that of $[CpFe(CO)(\mu\text{-}CO)]_2$ remains open to question and will be the subject of further studies.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Center, CCDC nos. 211922–211926 for compounds **1a**, **2a**, **2b**, **3a**, and **3b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).
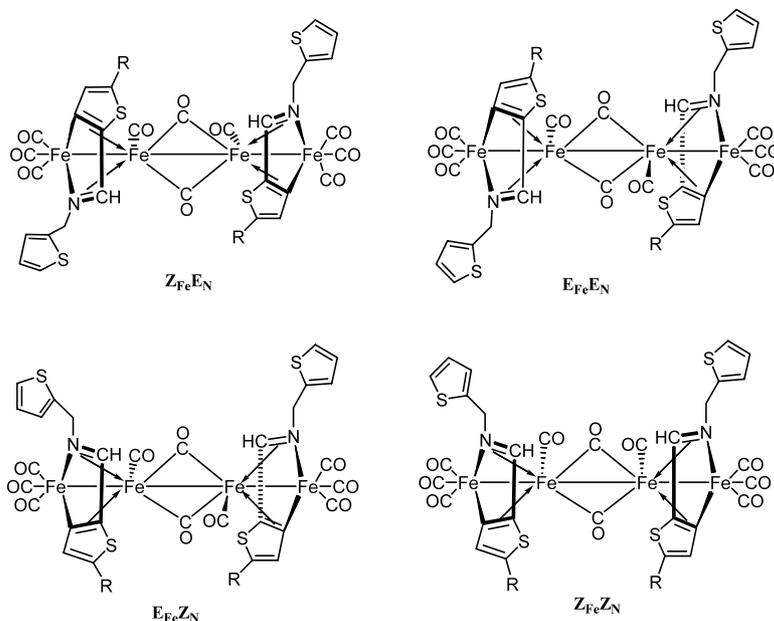
Fig. 6. Geometric isomers of **3**.

Acknowledgements

References

[1] (a) G.W. Parshall, Acc. Chem. Res. 3 (1970) 139;
(b) H. Alper, A.S.K. Chan, J. Am. Chem. Soc. 95 (1973) 4905;
(c) H. Alper, W.G. Root, J. Am. Chem. Soc. 97 (1975) 4251;
(d) M.I. Bruce, Angew. Chem. Int. Ed. Engl. 16 (1977) 73;
(e) G.R. Newkome, W.E. Puckett, W.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451;
(f) P.W. Clark, S.F. Dyke, G. Smit, C.H.L. Kennard, J. Organomet. Chem. 330 (1987) 427;
(g) I. Omae, Coord. Chem. Rev. 83 (1988) 137;
(h) A.D. Ryabov, Chem. Rev. 90 (1990) 403;
(i) J. Albert, J. Barro, J. Granell, J. Organomet. Chem. 408 (1991) 115;
(j) J. Alber, R.M. Ceder, M. Gómez, J. Granell, J. Sales, Organometallics 11 (1992) 1536;
(k) J. Alber, J. Granell, R. Moragas, J. Sales, M. Font-Bardía, X. Solans, J. Organomet. Chem. 494 (1995) 95;
(l) K.A. Azam, R. Dilshad, S.E. Kabir, M.A. Mottalib, M.B. Hursthouse, K.M.A. Malik, Polyhedron 19 (2000) 1081.
[2] (a) A.C. Cope, E.C. Friedrich, J. Am. Chem. Soc. 90 (1968) 909;
(b) A.J. Deeming, J.P. Rothwell, J. Organomet. Chem. 205 (1981) 117;
(c) A.J. Klaus, P. Rys, Helv. Chim. Acta 64 (1981) 1452;
(d) K. Gehring, M. Fugentobler, A.J. Klaus, P. Rys, Inorg. Chem. 21 (1982) 2493.
[3] (a) J. Albert, J. Granell, J. Sales, J. Organomet. Chem. 272 (1984) 393;
(b) J. Albert, J. Gómez, J. Granell, J. Sales, M. Solans, Organometallics 9 (1990) 1405.

[4] (a) F. Kakiuchi, F. Yamauchi, N. Chatani, S. Murai, Chem. Lett. (1996) 111;
(b) T. Fukuyama, N. Chatani, F. Kakiuchi, S. Murai, J. Org. Chem. 62 (1997) 5647;
(c) T. Fukuyama, N. Chatani, J. Tatsumi, F. Kakiuchi, S. Murai, J. Am. Chem. Soc. 120 (1998) 11522;
(d) W.S. Hwang, D.L. Wang, M.Y. Chiang, J. Organomet. Chem. 613 (2000) 231.
[5] (a) P.E. Baikei, O.S. Mill, Chem. Commun. (1966) 707;
(b) M.M. Bagga, W.T. Flannigan, G.R. Knox, P.L. Pauson, F.J. Preston, R.I. Reed, J. Chem. Soc. C (1968) 36;
(c) D.L. Wang, W.S. Hwang, L.C. Liang, L.Y. Wang, L. Lee, M.Y. Chiang, Organometallics 16 (1997) 3109;
(d) W. Imhof, A. Göbel, D. Ohlmann, J. Flemming, H. Fritzsche, J. Organomet. Chem. 584 (1999) 33;
(e) D.L. Wang, W.S. Hwang, L. Lee, M.Y. Chiang, J. Organomet. Chem. 579 (1999) 211;
(f) W. Imhof, Organometallics 18 (1999) 4845;
(g) C.J. Lin, W.S. Hwang, M.Y. Chiang, J. Organomet. Chem. 640 (2000) 85;
(h) W.S. Hwang, T.S. Tzeng, D.L. Wang, M.Y. Chiang, Polyhedron 20 (2001) 353.
[6] (a) S. Otsuka, T. Yoshida, A. Nakamura, Inorg. Chem. 6 (1967) 20;
(b) A.M. Brodie, B.F.G. Johnson, P.L. Josty, J. Lewis, J. Chem. Soc. Dalton Trans. (1972) 2031;
(c) M.F. Semmelhack, C.H. Cheng, J. Organomet. Chem. 393 (1990) 237;
(d) H.-J. Knölker, G. Baum, N. Foitzik, H. Goesmann, P. Gonser, P.G. Jones, H. Röttele, Eur. J. Inorg. Chem. (1998) 993 (and references cited therein).
[7] (a) A. Bond, M. Bottrill, M. Green, A. Welch, J. Chem. Soc. Dalton Trans. (1977) 2372;
(b) F.H. Herbstein, M.G. Reisner, Acta Crystallogr. Sec. B 33 (1977) 3304;
(c) H. Schaufele, D. Hu, H. Pritzkow, U. Zenneck, Organometallics 8 (1989) 396;
(d) C. Brodt, S. Niu, H. Pritzkow, M. Stephan, U. Zenneck, J. Organomet. Chem. 459 (1993) 283;
(e) H. Schulz, H. Pritzkow, W. Siebert, Chem. Ber. 124 (1991) 2203;

(f) H. Schulz, H. Pritzkow, W. Siebert, Chem. Ber. 125 (1992) 987;
(g) T.A. Petrel, J.M. Stephan, K.F. McDaniel, M.C. McMills, A.L. Rheingold, G.P.A. Yao, J. Org. Chem. 61 (1996) 4188;
(h) M.A. Bennett, Z. Lu, X. Wang, M. Brown, D.C.R. Hockless, J. Am. Chem. Soc. 120 (1998) 10409;
(i) W. Imhof, Organometallics 18 (1999) 4845.

[8] D.F. Shriver, K.H. Whitmire, in: G. Wilkinson, F.A.G. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chenistry, vol. 4 (Chapter 31.1), Pergamon, Oxford, 1982, p. 1982 (Chapter 31.1).

[9] P. Guerrieor, E. Bullita, P.A. Vigato, B. Pelli, P. Traldi, J. Heterocyclic Chem. 25 (1988) 145.

[10] A.E. Ogilvy, M. Draganjac, T.B. Rauchfuss, S.R. Wilson, Organometallics 7 (1988) 1171.

[11] A. DeCain, R. Weiss, Y. Chauvin, D. Commereuc, D. Hugo, J. Chem. Soc. Chem. Commun. (1976) 249.

[12] (a) J. Keijsper, L.H. Polm, G. van Koten, K. Vrieze, G. Abbel, C.H. Stam, Inorg. Chem. 23 (1984) 2142;
(b) J. Keijsper, L.H. Polm, G. van Koten, K. Vrieze, C.H. Stam, J.-D. Schagen, Inorg. Chim. Acta 103 (1985) 137.

[13] (a) D.L. Thorn, R. Hoffmann, Inorg. Chem. 17 (1978) 126;
(b) R. Hoffmann, Angew. Chem. 94 (1982) 725.

[14] (a) J.R. Moss, W.A.G. Graham, Inorg. Chem. 16 (1977) 75;
(b) D.A. Bohling, T.P. Gill, K.R. Mann, Inorg. Chem. 20 (1981) 194;
(c) R.I. Haines, N.D.C.T. Steen, R.B. English, J. Chem. Soc. Dalton Trans. (1983) 1607;
(d) P. Braunstein, D. Matt, O. Bars, M. Loeur, D. Grandjean, J. Fisher, A. Mitschler, J. Organomet. Chem. 213 (1981) 79;
(e) K. Keijsper, L.H. Polm, G. van Koten, K. Vrieze, E. Nieisen, C.H. Stam, Organometallics 4 (1985) 2006;
(f) P.M. Shulman, E.D. Burkhardt, E.C. Laudquist, R.S. Pilato, G.L. Geoffroy, Organometallics 6 (1987) 101;
(g) L.H. Polm, W.P. Mul, C.J. Elsevier, K. Vrieze, M.J.N. Christophersen, C.H. Stam, Organometallics 7 (1988) 423;
(h) W.P. Mul, C.J. Elsevier, M. van Leijen, K. Vrieze, A. Spek, Organometallics 10 (1991) 533;
(i) W.P. Mul, C.J. Elsevier, L.H. Polm, K. Vrieze, M.C. Zoutberg, D. Heijdenrijk, C.H. Stam, Organometallics 10 (1991) 2247;
(j) W.P. Mul, C.J. Elsevier, K. Vrieze, W.J.J. Smeets, A. Spek, Organometallics 11 (1992) 1891;
(k) M. Terada, M. Akita, Organometallics 22 (2003) 355.

[15] A. Grag, J.P. Tandon, Transition Met. Chem. 13 (1988) 395.

[16] J.W. Lauther, J. Organomet. Chem. 213 (1981) 25.