Double cyclopalladation of N,N,N',N'-tetramethylferrocene-1,1'-dicarbothioamide

Kyoko Hamamura, Masakazu Kita, Matsuo Nonoyama and Junnosuke Fujita

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464-01 (Japan)

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Abstract

A method was developed for one-pot synthesis of N,N,N',N'-tetramethylferrocene-1,1'-dicarbothioamide (H_2fdt); ferrocene was lithiated with n-butyl lithium and then treated with N,N-dimethylthiocarbamoyl chloride. The structure of H_2fdt was confirmed by X-ray analysis. The H_2fdt molecule had a twofold axis and the two thioamide groups were nearly stacked. The twist angle of two cyclopentadienyl rings was 22.5(2)°. H_2fdt was easily cyclopalladated with lithium tetrachloropalladate to give a mixture of isomers of the composition, Pd_2(fdt)Cl_2. The product reacted with bidentate ligands (L–L) to afford a mixture of *meso* and racemic isomers, Pd_2(fdt)(L–L)$_2$ (L–L ≡ acetylacetonate, dipivaloylmethanate, N,N-diethyldithiocarbamate and N,N-diisopropyldithiocarbamate (pdc) ions). The mixtures were separated into the two isomers by chromatography on a silica-gel column and the racemic isomer of Pd_2(fdt)(pdc)$_2$ was identified by X-ray analysis. In the complex, one Pd coordination subunit was placed nearly upon the other and the twist angle of two cyclopentadienyl rings was 19.1(8)°.

1. Introduction

The majority of examples of cyclometallated complexes are derived from planar benzene [1] and the chelates formed are in general not chiral. On the contrary, cyclometallated ferrocene derivatives are chiral; for example cyclopalladated N,N-dimethylaminomethylferrocene was resolved into optical isomers [2]. Mono-cyclopalladation of other monosubstituted ferrocenes has often been reported [1] but double cyclopalladation of 1,1'-disubstituted derivatives scarcely [3]. We have been interested in the cyclopalladation of ferrocene derivatives and in a previous paper [4] reported the reaction of N,N-dimethylferrocenecarbothioamide (Hfct). The study is now extended to N,N,N',N'-tetramethylferrocene-1,1'-dicarbothioamide (H_2fdt) (**I**) which upon double cyclopalladation forms two isomers: *meso* (having a plane of symmetry) (**II**) and racemic (having a twofold axis) (**III**). We have successfully separated the two isomers and identified their structures by X-ray analysis.

Correspondence to: Dr. M. Nonoyama.

2. Results and discussion

The ligand H_2fdt could be prepared with a yield of 14% by an assortment of known methods; ferrocene was first converted into ferrocene-1,1'-dicarboxylic acid, which was then transformed into N,N,N',N'-tetramethyldicarboxamide via the diacid chloride [5]. The carboxamide was treated with Lawesson's reagent to give H_2fdt [6]. We have obtained H_2fdt in a more convenient one-pot method; ferrocene is lithiated with n-butyl lithium, followed by treatment with N,N-dimethylthiocarbamoyl chloride to give H_2fdt with a yield of 29% (Table 1, I). H_2fdt was spectroscopically characterized (Tables 2 and 3) and the structure determined by X-ray analysis (see below).

The ^1H and $^{13}C\{^1H\}$ nuclear magnetic resonance (NMR) spectra (in $CDCl_3$ at room temperature and 90 MHz) of H_2fdt differ from those of Hfct in that the N-methyl signals of H_2fdt are not equivalent, while those of Hfct are equivalent under the same measurement conditions. These facts indicate that the rotational barrier of the $N(CH_3)_2$ group around the C–N bond of a thiocarbamoyl group is higher for H_2fdt than for Hfct. The barrier is lowered when a thiocarbamoyl

TABLE 1. Yields, analytical results and IR spectra of the thioamide and complexes

Compound [a]	Yield (%)	Analysis, found (calculated) (%)			IR, ν(C–N) [b] (cm^{-1})
		C	H	N	
H_2fdt	29	53.79(53.33)	5.72(5.59)	7.71(7.77)	1515
Pd_2(fdt)Cl_2	88	29.88(29.93)	2.95(2.83)	4.24(4.36)	1562
Pd_2(fdt)(acac)$_2$ (r)	19	40.59(40.61)	4.14(4.19)	3.60(3.64)	1570
(m)	15	41.00(40.61)	4.24(4.19)	3.14(3.64)	1579
Pd_2(fdt)(dpm)$_2$ (r)	57	48.68(48.67)	5.95(6.02)	2.89(2.99)	1562
(m)	68	48.66(48.67)	5.86(6.02)	2.84(2.99)	1560
Pd_2(fdt)(edc)$_2$ (r)	91	35.99(35.99)	4.47(4.41)	6.25(6.46)	1546
(m)	77	35.95(35.99)	4.15(4.41)	6.08(6.46)	1543
Pd_2(fdt)(pdc)$_2$ (r)	82	38.95(39.00)	4.90(5.02)	6.25(6.06)	1535
(m)	69	39.12(39.00)	4.97(5.02)	6.07(6.06)	1533
Pd(fct)(pdc)	67	43.31(43.29)	5.10(5.09)	4.99(5.05)	1535

[a] H_2fdt $\equiv$ N,N,N',N'-tetramethylferrocene-1,1'-dicarbothioamide; Hacac $\equiv$ acetylacetone; Hdpm $\equiv$ dipivaloylmethane; Hedc $\equiv$ N,N-diethyldithiocarbamic acid; Hpdc $\equiv$ N,N-diisopropyldithiocarbamic acid; Hfct $\equiv$ N,N-dimethylferrocenecarbothioamide; (r), racemic; (m) meso.
[b] Measured in Nujol mulls.

TABLE 2. ^{1}H nuclear magnetic resonance spectra of chloroform-d solutions of the ligands and complexes [a]

Compound	δ (ppm with respect to tetramethylsilane) (J(H–H) (Hz))			
	3H	4H	5H	N–CH$_3$
H_2fdt [b]	4.77 t (2.0)	4.43 t (2.0)	4.43 t (2.0)	3.48, 3.34
Pd_2(fdt)Cl_2 [c]	4.90 dd (1.0, 2.8)	4.69 t (2.7)	5.67 br	3.56, 3.53
	5.05 dd (0.9, 3.1)	4.49 t (2.7)	5.28 br	3.83, 3.64
Pd_2(fdt)(acac)$_2$ (r)	4.68 dd (0.9, 2.6)	4.28 t (2.6)	5.03 dd (0.8, 2.3)	3.50,
(m)	4.64 dd (1.0, 2.8)	4.72 t (2.6)	5.14 dd (0.9, 2.4)	3.55, 3.47
Pd_2(fdt)(dpm)$_2$ (r)	4.68 dd (1.0, 2.7)	4.24 t (2.6)	5.07 dd (0.9, 2.4)	3.56, 3.53
(m)	4.49 dd (0.9, 2.9)	4.72 t (2.6)	5.25 dd (0.9, 2.4)	3.55, 3.44
Pd_2(fdt)(edc)$_2$ (r)	4.40 dd (0.9, 2.4)	4.30 t (2.5)	4.95 dd (1.1, 2.6)	3.91, 3.71
(m)	4.56 dd (0.9, 2.2)	4.80 t (2.6)	4.67 dd (1.0, 2.8)	3.64, 3.55
Pd_2(fdt)(pdc)$_2$ (r)	4.38 dd (0.9, 2.2)	4.30 t (2.5)	4.94 dd (0.8, 2.5)	3.91, 3.71
(m)	4.56 dd (0.9, 2.2)	4.80 t (2.6)	4.67 dd (1.0, 2.8)	3.65, 3.55
Pd(fct)(pdc)	(4.54–4.62) [d]			3.55, 3.51
Pd(fct)(acac) [c]	4.53 d (1.5)	4.35 d (1.5)	5.18 t (1.6)	3.50, 3.44

[a] The numbering of atoms is shown in I: d, doublet; t, triplet; br, broad. [b] The signal of 1H: 4.77t(2.0). [c] DMSO-d_6 is used as a solvent. The spectrum was measured for a mixture of isomers. [d] 3H, 4H and 5H signals were overlapped with methine proton signal of dpc and could not be assigned. [c] From ref. 4.

TABLE 3. ^{13}C{^{1}H} nuclear magnetic resonance spectra of the ligands and their complexes [a] in chloroform-d

Compound	δ (ppm with respect to tetramethylsilane)						
	1C	2C	3C	4C	5C	C(=S)	N–CH$_3$
H_2fdt	75.9	88.9	75.9	72.3	72.3	198.3	44.9, 44.5
Pd_2(fdt)(dpm)$_2$ (r)	96.8	90.1	72.2	68.2	75.3	198.4	46.1, 44.8
(m)	95.7	87.7	73.0	71.7	77.5	200.9	45.8, 45.3
Pd_2(fdt)(edc)$_2$ (r)	98.4	90.6	73.8	70.9	[b]	199.6	47.0, 46.0
Pd_2(fdt)(pdc)$_2$ (r)	99.0	90.6	73.6	70.8	78.3	200.7	46.9, 45.9
(m)	98.5	87.6	[b]	73.3	82.3	202.6	46.5, 45.6
Pd(fct)(pdc)	99.3	86.0	72.3	70.0	78.0	204.3	46.3, 44.5
Pd(fct)(acac) [c]	94.7	85.2	70.1	69.6	74.8	202.6	45.6, 44.5

[a] Assignment of 3C and 4C of the complexes may be altered. [b] Obscured by $CDCl_3$ signals; in CD_2Cl_2 5C of r-Pd_2(fdt)(edc)$_2$ is at 78.7 ppm and 3C of m-Pd_2(fdt)(pdc)$_2$ at 77.1 ppm. [c] From ref. 4.

H₂fdt

I

meso

II
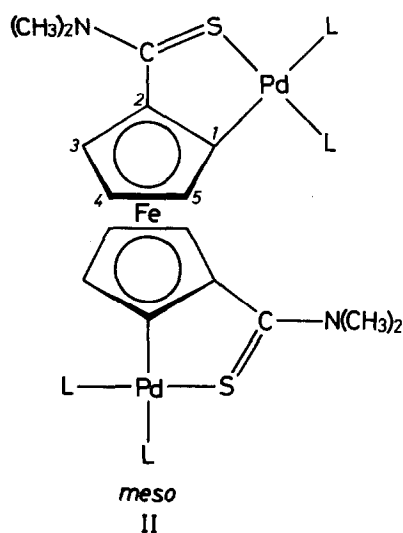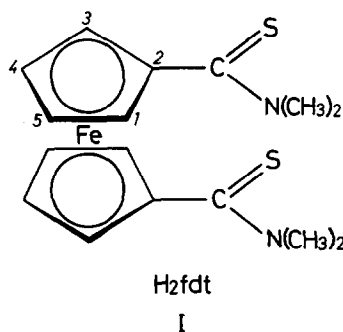
group is attached to an electron-donating moiety; an increase in electron density on the thiocarbamoyl-C atom diminishes conjugation between the C and N atoms (cross-conjugation) to reduce the double-bond

rac

III
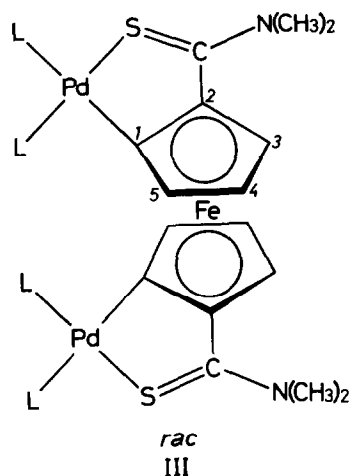
character of the C–N bond relative to a more electron-deficient system [7]. It is thus suggested that the electron density of a ferrocene part is higher for Hfct than for H_2fdt because of the electron-attracting property of the N,N-dimethylthiocarbamoyl group.

In methanol, H_2fdt reacted with lithium tetra-chloropalladate(II) to form a precipitate of the composition $Pd_2(fdt)Cl_2$ (Table 1), the IR spectrum of which showed a higher frequency shift of ν(C–N) compared with that of free H_2fdt, suggesting S coordination of the thioamide groups [8]. $Pd_2(fdt)Cl_2$ was insoluble in most common solvents and only sparingly soluble in dimethylsulphoxide (DMSO) with coordinating ability. The ^1H NMR spectrum of the DMSO-d_6 solution of $Pd_2(fdt)Cl_2$ ($Pd_2(fdt)Cl_2(DMSO-d_6)_2$ may be formed) showed four N–CH₃ peaks and six signals due to cyclopentadienyl (cp) rings (Table 2). The integration of the ^1H signals revealed that two hydrogen atoms were removed from the cp rings and the spectral pattern of free H_2fdt was changed upon complexation; two triplets of free H_2fdt were converted to two triplets, two doublets of doublets, and two broad signals. A ligand exchange (DMSO-d_6 and/or Cl) should occur at the coordination site close to the proton giving the broad signal at a comparable rate with an NMR time scale [9]. After decoupling experiments these signals were assigned on the basis of the presence of two isomers: a $1,1'-R_2-2,2'-Y_2$-substituted ferrocene has *meso* (m) and racemic (r) isomers. The *meso* isomer has a plane of symmetry, and the racemic isomer a twofold axis. In either case the two cp rings are equivalent and the two isomers are not assigned spectroscopically.

To investigate the isomerism, more soluble derivatives were prepared (Table 1). The NMR spectra showed that two isomers existed in the reaction products of $Pd_2(fdt)Cl_2$ with Na(acac), Na(dpm), Na(edc) and Na(pdc) (acac ≡ acetylacetonate ion; dpm ≡ dipivaloylmethanate ion; edc ≡ N,N-diethyldithiocarbamate ion; pdc ≡ N,N-di-iso-propyldithiocarbamate ion). The isomers II and III were separated by chromatography on a silica-gel column with an eluent basified with triethylamine, except for isomers of $Pd_2(fdt)(edc)_2$ which were separated by solubility difference. The rapidly eluted isomer of $Pd_2(fdt)(pdc)_2$ has been characterized by X-ray analysis (see below) to be racemic (hereafter denoted as r-$Pd_2(fdt)(pdc)_2$; L–L ≡ pdc (III)). The rapidly eluted components of $Pd_2(fdt)(acac)_2$ and $Pd_2(fdt)(dpm)_2$ gave r-$Pd_2(fdt)(pdc)_2$ upon reaction with Na(pdc), suggesting that these acac and dpm complexes are racemic isomers. The more soluble isomer of $Pd_2(fdt)(edc)_2$ was identical with the product obtained from the reaction of r-$Pd_2(fdt)(acac)_2$ with Na(edc) and was assigned to the racemic isomer.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of the complexes are given in Tables 2 and 3, where the signals due to β-diketonato and dithiocarbamato ligands are not included because there is nothing unusual in the chemical shifts of the signals. The signals of the cp ring protons consist of two doublets of doublets and one triplet. Their chemical shifts are different between the isomers and also different from the corresponding monopalladated complexes Pd(fct)(L–L) (L–L ≡ acac and pdc). The anisotropic shielding effect of one palladium coordination subunit should mutually affect the ^1H and ^{13}C chemical shifts of the other, but estimation of the effect on each nucleus is difficult because the conformation of the molecule in solution is unknown. The cp ring protons of the two isomers (*meso* and racemic) are in different magnetic environment even if there is free rotation of the two substituted cp rings. The chemical shifts are hence different between the isomers (Tables 2 and 3). Within the same geometrical isomers with a similar type L–L ligand there is a similar trend in the chemical shifts.

It should be noted that the triplet of 4H of the m isomers is significantly deshielded relative to that of the r isomers. The 4H signal of the monopalladated Pd(fct)(L–L) (L–L ≡ pdc and acac) with an unsubstituted counter cp ring is observed at around 4.5 ppm; no anisotropic effect is induced because of the absence of another Pd coordination subunit in the monopalladated complexes. The anisotropic shielding (or deshielding) effect of a Pd coordination subunit should

operate on the chemical shift of 4H of the other subunit and should result in the widespread ^1H chemical shifts of Pd₂(fdt)(L–L)₂ (L–L ≡ edc and pdc) compared with Pd(fct)(pdc). The chemical shift difference in the two N–CH₃ groups of r isomers of dithiocarbamato complexes is larger than that of m isomers and that of the β-diketonato complexes, as well as the monopalladated complexes. The fact may suggest that one N–CH₃ group of the r isomers of the dithiocarbamato complexes is magnetically deshielded by another subunit. In Pd(fct)(pdc), where there is no such effect, the two N–CH₃ signals appear close to each other.

The crystallographic data, the positional parameters and equivalent isotropic temperature factors, the bond distances and the angles of H₂fdt are given in Tables 4, 5, 6 and 7 respectively. A perspective view of H₂fdt is depicted in Fig. 1 together with atomic numbering. The H₂fdt molecule has a twofold axis through the Fe atom and the midpoint between the two S atoms. There are no unusual bond distances and angles. The two planar thiocarbamoyl groups are nearly stacked and make a dihedral angle of 27.8(1)° with respect to the cp rings. The twist angle between the two parallel cp rings is 22.5(2)°. 1,1'-Diacetylferrocene is found to have quite a different conformation; the twist angle is 1.6° and the two acetyl groups are in 1 and 3' positions (the two substituents make a twist angle of 144°) [10]. No reason is clear at the moment for the nearly stacking arrangement of the two more bulky N,N-dimethyl-

TABLE 4. Crystallographic data of H₂fdt and Pd₂(fdt)(pdc)₂·(CH₃)₂CO

Compound	H₂fdt	Pd₂(fdt)(pdc)₂·(CH₃)₂CO
Formula	$C_{16}H_{20}N_2S_2Fe$	$C_{33}H_{52}N_4OS_6Pd_2Fe$
Molecular weight	360.33	981.89
Crystal size (mm × mm × mm)	0.65 × 0.5 × 0.2	0.2 × 0.2 × 0.07
Crystal system	Orthorhombic	Triclinic
Space group	$P2/n2_1/c2_1/a$	$P\bar{1}$
a (Å)	11.752(3)	14.074(3)
b (Å)	14.091(3)	16.152(5)
c (Å)	9.599(3)	9.314(3)
α (°)		93.36(3)
β (°)		101.71(2)
γ (°)		83.00(3)
V (Å³)	1589.7(7)	2056.4(1)
Z	4	2
D (measured) (g cm⁻³)	1.53	1.60
D (calculated) (g cm⁻³)	1.51	1.59
μ (Mo Kα) (cm⁻¹)	11.94	15.26
Scan type	ω–2θ	ω–2θ
2θ	2.0–60	2.0–40
Number of reflections observed ($|F_o| > 3\sigma(|F_o|)$)	1825	1903
R	0.053	0.082
R_w ($w = 1$)	0.057	0.098

TABLE 5. Positional parameters and equivalent temperature factors of H_2fdt

	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	B_{eq} (Å^2)
Fe	2500(0)	5000(0)	10000(0)	2.3
S	1236(1)	6085(1)	6660(1)	3.6
N	3438(2)	6375(2)	6336(3)	3.0
C(1)	2822(2)	6154(2)	8737(3)	2.5
C(2)	3833(3)	5857(3)	9472(4)	2.9
C(3)	3609(3)	5928(3)	10936(4)	3.7
C(4)	2482(4)	6249(3)	11108(4)	3.8
C(5)	1987(3)	6383(2)	9780(4)	3.0
C(6)	2584(3)	6210(2)	7225(3)	2.5
C(7)	4592(3)	6641(4)	6736(5)	4.5
C(8)	3267(4)	6314(3)	4842(4)	4.2
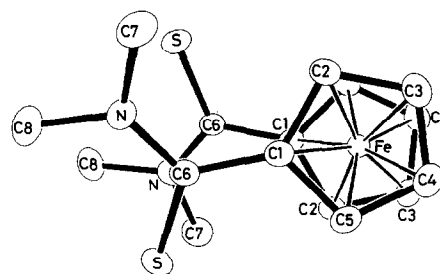
Fig. 1. Perspective view of H_2fdt and the atomic numbering system.

dithiocarbamoyl groups and the sufficiently distant disposition of the two acetyl groups.

The rapidly eluted isomer of $Pd_2(fdt)(pdc)_2$ was crystallographically characterized (Tables 4 and 8–11). A perspective view is shown in Fig. 2 for the isomer. This is racemic and has an idealized twofold axis through the Fe atom. Because of rapid efflorescence of a manicure-coated crystal caused by loss of acetone of crystallization the structural parameters are insufficient (only the thermal parameters of the Pd, Fe and S atoms were refined anisotropically). The bond distances and angles are normal within standard deviations and only a few remarkable features are noted. The *trans* influence is reflected on the Pd–S (pdc) bond distances; Pd–S *trans* to a palladated cyclopentadienyl C atom are 2.39(1) and 2.395(8) Å, while that *trans* to S (thioamide) are 2.334(7) and 2.31(1) Å. The

dihedral angles of 7(1) and 5(1)° between the chelated thioamide group and the cp ring are smaller than that of free H_2fdt (27.8(1)°) and the two cp rings are no larger parallel, the dihedral angle being 6(1)°. Each palladium coordination plane makes a dihedral angle of 3(1) or 9(1)° with respect to the respective cyclopentadienyl ring and the dihedral angle between the two Pd coordination planes is 14.5(2)°. The twist angle between the two cp rings is 19.1(8)° and the two Pd coordination subunits are partially stacked (Fig. 2). The Pd $\cdots$ N (thioamide) separation distances are 3.57(2) and 3.75(2) Å and there is hence no appreciable interaction. Similar structure features have been reported for a double-cycloplatinated ferrocene derivative [11].

The electrochemistry of the ligands and complexes was briefly studied in acetonitrile by hydrodynamic voltammetry (Table 12. Potentials are given against $Ag/0.01$ mol dm^{-3} $AgNO_3$ in acetonitrile). The oxidation potentials $E_{1/2}$ of Hfct and H_2fdt are 0.16 V and 0.24 V respectively ($E_{1/2}$ of ferrocene is 0.08 V),

TABLE 6. Bond distances of H_2fdt

	Bond distance (Å)		Bond distance (Å)		Bond distance (Å)		Bond distance (Å)
S–C(6)	1.684(3)	C(6)–N	1.338(4)	N–C(7)	1.458(6)	N–C(8)	1.450(6)
C(1)–C(6)	1.479(5)	C(1)–C(2)	1.444(5)	C(2)–C(3)	1.434(6)	C(3)–C(4)	1.409(6)
C(4)–C(5)	1.414(6)	C(5)–C(1)	1.440(5)	Fe–C(1)	2.064(3)	Fe–C(2)	2.042(4)
Fe–C(3)	2.053(4)	Fe–C(4)	2.057(5)	Fe–C(5)	2.051(3)		

TABLE 7. Bond angles of H_2fdt

	Bond angle (°)		Bond angle (°)		Bond angle (°)
C(1)–C(6)–S	119.2(2)	C(1)–C(6)–N	119.5(3)	N–C(6)–S	121.2(3)
C(6)–N–C(7)	125.1(3)	C(6)–N–C(8)	121.1(3)	C(7)–N–C(8)	113.8(4)
C(2)–C(1)–C(6)	130.5(3)	C(5)–C(1)–C(6)	122.8(3)	C(1)–C(2)–C(3)	107.9(3)
C(2)–C(3)–C(4)	108.1(4)	C(3)–C(4)–C(5)	108.9(4)	C(4)–C(5)–C(1)	108.5(3)
C(5)–C(1)–C(2)	106.6(3)	C(1)–Fe–C(2)	41.2(1)	C(2)–Fe–C(3)	41.0(2)
C(3)–Fe–C(4)	40.1(2)	C(4)–Fe–C(5)	40.3(2)	C(5)–Fe–C(1)	41.0(1)

TABLE 8. Positional parameters and equivalent temperature factors of $Pd_2(fdt)(pdc)_2 \cdot (CH_3)_2CO$

	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	B_{eq} ($\mathring{A}^2$)
Pd(1)	2763(2)	8595(1)	4083(3)	2.4
Pd(2)	2182(2)	11690(1)	828(3)	2.7
Fe	3210(3)	9480(2)	835(5)	2.3
S(1)	3037(6)	9896(4)	5100(9)	3.1
S(2)	1277(6)	11154(4)	2268(9)	3.5
S(3)	2433(6)	7273(4)	3104(9)	3.2
S(4)	1591(6)	8182(4)	5352(9)	3.1
S(5)	2154(7)	13137(4)	1567(9)	3.7
S(6)	2959(7)	12270(4)	−762(10)	3.8

suggesting that an N,N-dimethylthiocarbamoyl group makes a ferrocene moiety less susceptible to oxidation. The potentials of the palladium complexes are all less positive than those of the ligands, i.e. the cyclopalladated ferrocene group is more easily oxidized than the ferrocene part of the ligands. Dithiocarbamato ligands seem more effective for the reduction of the potentials than β-diketonato ligands, probably because pdc and edc are better electron donors to palladium(II).

3. Experimental details

3.1. Preparation of the ligand H_2fdt

The yields, analytical results and IR spectra are given in Table 1, the ^1H NMR spectra in Table 2 and the $^{13}C\{^1H\}$ NMR spectra are given in Table 3.

A mixture of 98 mmol of butyllithium and 98 mmol of N,N,N',N'-tetramethylethylenediamine in 12 cm^3 of hexane was stirred at room temperature for 10 min under nitrogen [12] and to the mixture was added a hexane solution (300 cm^3) of 40 mmol of ferrocene dropwise under vigorous stirring for 30 min. After stirring for 6 h, the mixture was cooled to $-78°C$ in a dry ice–acetone bath and to this was added a tetrahydrofuran solution (100 cm^3) of 80 mmol of N,N-dimethylthiocarbamoyl chloride dropwise. After stirring at this temperature for a further 1 h, the temperature was allowed to rise slowly to room temperature when the orange-coloured suspension changed to a deep-red solution. The solution was stirred overnight at this temperature and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane, dried (Na$_2$SO$_4$) and subjected to chromatography on an alumina column (activity II–III) with dichloromethane as an eluent. The first yellow band was recovered ferrocene, the second orange band a monosubstituted derivative, and the third red band the desired product, H$_2$fdt. The product was purified by rechromatography and recrystallized from a mixture

of dichloromethane and hexane (melting point, 164–165°C).

3.2. Preparation of the complexes

3.2.1. $Pd_2(fdt)Cl_2$

To a solution of lithium tetrachloropalladate in 20 cm^3 of methanol, prepared in situ from 2 mmol of palladium(II) chloride and 4 mmol of lithium chloride, was added a solution of 1.2 mmol of H$_2$fdt dissolved in a small amount of dichloromethane, and the mixture was stirred at room temperature for 3 h. The brown precipitate was filtered, washed with methanol, dichloromethane and then n-hexane and dried in air.

TABLE 9. Positional parameters and temperature factors of $Pd_2(fdt)(pdc)_2 \cdot (CH_3)_2CO$

	x ($\times 10^3$)	y ($\times 10^3$)	z ($\times 10^3$)	B ($\mathring{A}^2$)
O	623(3)	1438(2)	350(4)	7.9(0.7)
N(1)	396(2)	1100(1)	423(3)	3.4(0.5)
N(2)	60(2)	968(1)	203(3)	3.3(0.5)
N(3)	89(2)	681(2)	405(3)	4.2(0.5)
N(4)	292(2)	1393(1)	−33(3)	3.6(0.5)
C(1)	358(2)	887(1)	273(3)	1.7(0.5)
C(2)	399(2)	967(1)	289(3)	1.4(0.4)
C(3)	457(2)	964(2)	170(4)	3.4(0.6)
C(4)	458(2)	887(2)	103(4)	3.1(0.5)
C(5)	395(2)	843(2)	162(4)	2.8(0.5)
C(6)	374(2)	1024(1)	398(3)	2.1(0.5)
C(7)	448(3)	1139(2)	325(4)	4.4(0.6)
C(8)	363(2)	1158(2)	530(4)	3.3(0.6)
C(9)	231(2)	1054(2)	3(4)	2.8(0.6)
C(10)	175(2)	992(2)	43(3)	3.1(0.5)
C(11)	193(2)	916(2)	−36(4)	2.6(0.5)
C(12)	264(2)	933(2)	−128(4)	3.0(0.5)
C(13)	278(3)	1016(2)	−104(4)	4.1(0.6)
C(14)	117(2)	1020(2)	161(4)	3.2(0.6)
C(15)	42(3)	889(2)	142(4)	4.2(0.6)
C(16)	14(3)	1002(2)	328(4)	4.2(0.6)
C(17)	159(2)	734(2)	422(3)	2.6(0.5)
C(18)	9(3)	687(2)	490(4)	4.4(0.7)
C(19)	−64(2)	764(2)	440(4)	4.0(0.6)
C(20)	45(3)	675(2)	655(4)	5.1(0.7)
C(21)	98(3)	605(2)	294(4)	4.1(0.6)
C(22)	116(3)	526(3)	388(5)	7.5(0.9)
C(23)	20(4)	617(3)	196(6)	8.0(0.9)
C(24)	272(2)	1325(2)	1(4)	3.6(0.6)
C(25)	326(3)	1402(2)	−185(4)	4.8(0.7)
C(26)	441(3)	1354(2)	−141(5)	5.0(0.7)
C(27)	267(3)	1377(2)	−320(4)	4.3(0.6)
C(28)	264(2)	1476(2)	32(4)	4.2(0.6)
C(29)	353(4)	1513(3)	108(6)	8.2(0.9)
C(30)	203(3)	1536(2)	−54(4)	4.3(0.6)
C(31)	600(3)	1307(3)	248(6)	7.5(0.9)
C(32)	583(3)	1370(2)	343(5)	5.8(0.8)
C(33)	518(4)	1364(3)	437(6)	7.6(0.9)

TABLE 10. Bond distances of $Pd_2(fdt)(pdc)_2 \cdot (CH_3)_2CO$

	Bond distance (Å)		Bond distance (Å)		Bond distance (Å)		Bond distance (Å)
Part of Pd(1)							
Pd(1)–S(1)	2.298(7)	Pd(1)–C(1)	1.97(3)	Pd(1)–S(3)	2.334(7)	Pd(1)–S(4)	2.39(1)
C(2)–C(6)	1.40(4)	S(1)–C(6)	1.73(3)	C(6)–N(1)	1.30(3)	C(7)–N(1)	1.50(5)
C(8)–N(1)	1.43(4)	C(17)–S(3)	1.72(4)	C(17)–S(4)	1.67(3)	C(17)–N(3)	1.35(4)
N(3)–C(18)	1.50(5)	N(3)–C(21)	1.58(4)	C(18)–C(19)	1.54(4)	C(18)–C(20)	1.53(5)
C(21)–C(22)	1.55(6)	C(21)–C(23)	1.28(6)	C(1)–C(2)	1.46(3)	C(2)–C(3)	1.50(5)
C(3)–C(4)	1.36(4)	C(4)–C(5)	1.41(5)	C(5)–C(1)	1.37(4)	Fe–C(1)	2.02(3)
Fe–C(2)	2.03(3)	Fe–C(3)	1.96(3)	Fe–C(4)	2.03(3)	Fe–C(5)	1.98(3)
Part of Pd(2)							
Pd(2)–S(2)	2.30(1)	Pd(2)–C(9)	1.96(3)	Pd(2)–S(5)	2.395(8)	Pd(2)–S(6)	2.31(1)
C(10)–C(14)	1.51(5)	S(2)–C(14)	1.73(3)	C(14)–N(2)	1.35(4)	C(15)–N(2)	1.40(4)
C(16)–N(2)	1.50(5)	C(24)–S(5)	1.81(4)	C(24)–S(6)	1.72(3)	C(24)–N(4)	1.25(4)
N(4)–C(25)	1.60(5)	N(4)–C(28)	1.48(4)	C(25)–C(26)	1.69(5)	C(25)–C(27)	1.43(5)
C(28)–C(29)	1.49(6)	C(28)–C(30)	1.39(5)	C(9)–C(10)	1.46(5)	C(10)–C(11)	1.43(4)
C(11)–C(12)	1.50(5)	C(12)–C(13)	1.37(4)	C(13)–C(9)	1.37(4)	Fe–C(9)	2.09(3)
Fe–C(10)	2.06(3)	Fe–C(11)	2.03(3)	Fe–C(12)	1.98(3)	Fe–C(13)	2.06(4)
Part of $(CH_3)_2CO$							
C(31)–C(32)	1.33(6)	C(32)–C(33)	1.40(7)	C(32)–O	1.29(5)		

TABLE 11. Bond angles of $Pd_2(fdt)(pdc)_2 \cdot (CH_3)_2CO$

	Bond angle (°)		Bond angle (°)		Bond angle (°)
Part of Pd(1)					
C(1)–Pd(1)–S(1)	83.5(7)	C(1)–Pd(1)–S(3)	98.8(7)	S(3)–Pd(1)–S(4)	74.4(3)
S(1)–Pd(1)–S(4)	103.2(3)	Pd(1)–C(1)–C(2)	121(2)	C(1)–C(2)–C(6)	118(3)
Pd(1)–S(1)–C(6)	102.0(9)	Pd(1)–C(1)–C(5)	133(2)	C(6)–C(2)–C(3)	138(2)
C(2)–C(6)–S(1)	116(2)	C(2)–C(6)–N(1)	128(3)	S(1)–C(6)–N(1)	117(2)
C(6)–N(1)–C(7)	121(3)	C(6)–N(1)–C(8)	125(3)	C(7)–N(1)–C(8)	113(2)
Pd(1)–S(3)–C(17)	85.6(9)	Pd(1)–S(4)–C(17)	85(1)	S(3)–C(17)–S(4)	115(2)
S(3)–C(17)–N(3)	122(2)	S(4)–C(17)–N(3)	123(3)	C(17)–N(3)–C(18)	125(3)
C(17)–N(3)–C(21)	117(3)	C(18)–N(3)–C(21)	118(3)	N(3)–C(18)–C(19)	109(3)
N(3)–C(18)–C(20)	113(3)	C(19)–C(18)–C(20)	119(3)	N(3)–C(21)–C(22)	105(3)
N(3)–C(21)–C(23)	104(3)	C(22)–C(21)–C(23)	120(4)	C(1)–C(2)–C(3)	105(2)
C(2)–C(3)–C(4)	109(3)	C(3)–C(4)–C(5)	107(3)	C(4)–C(5)–C(1)	113(3)
C(5)–C(1)–C(2)	106(3)				
Part of Pd(2)					
C(9)–Pd(2)–S(2)	84(1)	C(9)–Pd(2)–S(6)	97(1)	S(5)–Pd(2)–S(6)	75.0(3)
S(2)–Pd(2)–S(5)	104.4(3)	Pd(2)–C(9)–C(10)	121(2)	C(9)–C(10)–C(14)	116(2)
Pd(2)–S(2)–C(14)	104(1)	Pd(2)–C(9)–C(13)	134(3)	C(11)–C(10)–C(14)	135(3)
C(10)–C(14)–S(2)	115(2)	C(10)–C(14)–N(2)	121(3)	S(2)–C(14)–N(2)	124(3)
C(14)–N(2)–C(15)	127(3)	C(14)–N(2)–C(16)	114(2)	C(15)–N(2)–C(16)	129(3)
Pd(2)–S(6)–C(24)	91(1)	Pd(2)–S(5)–C(24)	86(1)	S(5)–C(24)–S(6)	108(2)
S(6)–C(24)–N(4)	129(3)	S(5)–C(24)–N(4)	123(3)	C(24)–N(4)–C(25)	121(3)
C(24)–N(4)–C(28)	126(3)	C(25)–N(4)–C(28)	111(3)	N(4)–C(25)–C(26)	99(2)
N(4)–C(25)–C(27)	120(3)	C(26)–C(25)–C(27)	117(3)	N(4)–C(28)–C(29)	109(3)
N(4)–C(28)–C(30)	120(3)	C(29)–C(28)–C(30)	109(3)	C(9)–C(10)–C(11)	110(3)
C(10)–C(11)–C(12)	105(3)	C(11)–C(12)–C(13)	107(3)	C(12)–C(13)–C(9)	113(4)
C(13)–C(9)–C(10)	106(3)				
Part of $(CH_3)_2CO$					
C(31)–C(32)–O	122(5)	C(33)–C(32)–O	117(3)	C(31)–C(32)–C(33)	120(4)
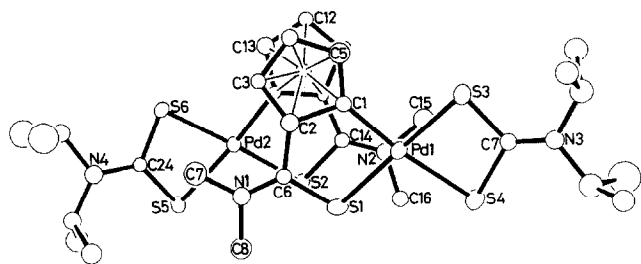
Fig. 2. Perspective view of r-Pd$_2$(fdt)(pdc)$_2$ and the atomic numbering system.

3.2.2. Pd$_2$(fdt)(L–L)$_2$ (L–L ≡ acac, dpm, edc and pdc)

A mixture of 0.3 mmol of Pd$_2$(fdt)Cl$_2$ in 40 cm^3 of dichloromethane and 1.2 mmol of Na(L–L) (Na(acac) and Na(dpm) in 20 cm^3 of methanol or Na(edc) · 3H$_2$O and Na(pdc) in 10 cm^3 of acetone) was stirred until the mixture had become clear. The solution was evaporated to dryness and the residue extracted with dichloromethane. The filtered extract was concentrated to a small volume and mixed with n-hexane to precipitate the product, which was filtered, washed with n-hexane and dried in air.

3.2.3. Pd(fct)(pdc)

The complex was similarly prepared as above from stoichiometric amounts of reactants.

3.3. Separation of isomers

3.3.1. Pd$_2$(fdt)(L–L)$_2$ (L–L ≡ acac and dpm)

The complexes obtained above were chromatographed on a silica-gel column (Merck silica gel

TABLE 12. Oxidation potentials of the ligands and complexes measured by rotating-disk-electrode voltammetry [a]

Compound	$E_{1/2}$ (mV)	$E_{3/4} - E_{1/4}$ (mV)	i_d/c (μA mmol^{-1})
H$_2$fdt	240	70	201
Pd$_2$(fdt)(acac)$_2$ (m)	120	55	74
Pd$_2$(fdt)(dpm)$_2$ (r)	120	50	108
(m)	110	55	89
Pd$_2$(fdt)(edc)$_2$ (r)	50	50	65
Pd$_2$(fdt)(pdc)$_2$ (r)	20	50	62
(m)	30	50	85
Hfct	160	60	131
Pd(fct)(acac)	110	60	110
Pd(fct)(pdc)	30	50	66

[a] Acetonitrile was used as a solvent and the potentials were given against Ag/0.01 mol dm^{-3} AgNO$_3$ in acetonitrile. $E_{1/2}$ is the half-wave potential, i_d the diffusion current, $E_{3/4}$ the potential at $\frac{3}{4}i_d$ and $E_{1/4}$ the potential at $\frac{1}{4}i_d$.

60; 230–400 mesh) with a mixture of ethyl acetate, dichloromethane and triethylamine (15:5:1 (v/v)) as an eluent. Two bands appeared (the first pink and the second dark-red bands for acac, and the first dark-reddish-purple and the second pink bands for dpm) and the effluents were evaporated to dryness. The residue was dissolved in dichloromethane and the filtered solution was concentrated to a small volume. Addition of n-hexane to the solution gave a precipitate, which was collected, washed with n-hexane and dried in air.

A dichloromethane solution of the products from the first band reacted with a stoichiometric amount of Na(pdc) in acetone at room temperature to give racemic Pd$_2$(fdt)(pdc)$_2$, the structure of which was identified by X-ray analysis (see below). The first eluted complexes were therefore racemic and the second complexes meso. No isomerization occurred during the reaction under the experimental conditions.

3.3.2. Pd$_2$(fdt)(pdc)$_2$

The complex was chromatographically separated into two isomers in a similar way to above with a mixture of ethyl acetate and triethylamine (7:3 (v/v)) as an eluent. The isomer obtained from the first dark-brown band was racemic as determined by X-ray analysis and that from the second dark-red band hence meso.

3.3.3. Pd$_2$(fdt)(edc)$_2$

Fractional recrystallization from dichloromethane was effective for the separation of isomers. The more soluble isomer was identical with the product that was obtained from the reaction of racemic Pd$_2$(fdt)(acac)$_2$ with Na(edc) in the above conditions used for the reaction with Na(pdc). The more soluble isomer was hence racemic and the less soluble isomer was meso.

3.4. Measurements

Spectroscopic measurements were carried out by the methods reported previously [4]. Rotating-disk-electrode voltammetry was performed on a Fuso HECS 321B potential sweep unit and a Fuso HECS 317B potentiostat with a GRAPHTEC WX-1000 x–y recorder (200 mV s^{-1}). A glassy-carbon rotating disk (2000 rev min^{-1}) attached to a Yanaco P10-RE Mark II head, a platinum wire and an Ag/Ag$^+$ electrode (Ag/0.01 mol dm^{-3} AgNO$_3$) were used as the working, auxiliary and reference electrodes respectively. The concentration of the sample was 1.0 × 10^{-3} mol dm^{-3} and that of the supporting electrolyte, tetrabutylammonium tetrafluoroborate, 0.1 mol dm^{-3} in acetonitrile. The oxidation wave of ferrocene which was observed at +0.08 V vs. Ag/Ag$^+$ was used as a standard for the electrochemical measurement of each sample.

3.5. X-ray crystal structure determination

3.5.1. H₂fdt

Single crystals grew upon recrystallization from hot acetonitrile. Diffraction data were collected on a Rigaku AFC-5 diffractometer with a graphite monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) at the Institute for Molecular Science (IMS). 2706 reflections were obtained and no sign of decomposition of the crystal was observed during the data collection. The crystallographic data are given in Table 4. All the computations were performed on a HITAC M-680H computer at the Computer Center, IMS, with the program system UNICS III [13]. Absorption corrections were made with the DABEX program of the IMS Computer Center Library. The structure was solved by the usual heavy-atom method and the Fe atom was located at a special position with an occupancy of 0.5.

3.5.2. Pd₂(fdt)(pdc)₂ · (CH₃)₂CO

Recrystallization from acetone gave crystals which effloresced in air. The crystal for data collection was coated with manicure. Diffraction data were collected as above but decomposition of the crystal was observed during the measurements. Independent 1903 reflections with $|F_o| > 3\sigma(|F_o|)$ in the range $2\theta < 40°$ were obtained when the diffraction intensities of three standard reflections fell to 80%. The diffraction intensities were corrected for decay. The crystallographic data are given in Table 4. The calculations were also carried out on a HITAC M-680H computer at the Computer Center, IMS. The positions of an Fe and two Pd atoms were determined by the direct method with SHELX86 [14] and all non-hydrogen atoms were located by the subsequent Fourier synthesis. The structure was refined by block-diagonal least-squares methods but, in order to reduce the number of parameters, only the Pd, Fe and S atoms were refined anisotropically.

4. Supplementary material available

Atomic coordinates for the hydrogen atoms of H₂fdt, anisotropic thermal parameters, and the observed and calculated structure factors of H₂fdt and Pd₂(fdt) (pdc)₂ · (CH₃)₂CO are available from the authors upon request.

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