ELSEVIER

Journal of Organometallic Chemistry 645 (2002) 146–151

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Palladium(II) induced preferential activation of the σ(C_{sp3}–H) versus the σ($C_{sp^2,\ ferrocene}$–H) bond of (S_C)-[(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH(CO_2Me)CH_2–CH_2–SMe}]

Concepción López [a,*], Amparo Caubet [a], Ramón Bosque [a], Xavier Solans [b], Mercè Font-Bardia [b]

[a] *Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, E-08028 Barcelona, Spain*
[b] *Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, Martí i Franquès s/n, E-08028 Barcelona, Spain*

Received 2 August 2001; received in revised form 9 October 2001

Abstract

The reaction of (S_C)-[(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH(CO_2Me)CH_2–CH_2SMe}] (**1**) with $Na_2[PdCl_4]$ in the presence of NaAcO is studied. This process leads to the formation of the tetrametallic complex: [Pd_2{[C{(CO_2Me)–CH_2–CH_2–SMe}N=CH–(η^5-C_5H_4)]Fe(η^5-C_5H_5)}$_2Cl_2$]·CH_2Cl_2. The X-ray crystal structure of this complex revealed that the ligand exhibits an unusual mode of binding, and that each palladium is bound to a stereogenic $C^*_{sp^3}$ carbon atom. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Iron; C–H activation

---

1. Introduction

Cyclopalladation of N-donor ligands has been widely studied [1] and used [2]. This reaction involves the coordination of the ligand and the subsequent C–H intramolecular activation to form a five- or a six-membered ring with a σ(Pd–C) bond [1]. Among the wide variety of palladacycles described, chiral derivatives [3] have attracted a great interest due to their applications as chiral discriminators or recognitors [4]. Besides, cyclopalladation of N-donor ferrocenyl ligands occurs under mild conditions and has an additional interest since the formation of the σ(Pd–$C_{sp^2,\ ferrocene}$) bond introduces planar chirality [4,5]. As a part of a project directed towards the syntheses of chiral cyclometallated compounds holding ferrocenyl units, we decided to prepare (S_C)-[(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH(CO_2Me)CH_2–CH_2SMe}] (**1**) and to study its reactivity versus palladium(II) salts. Compound **1** has two different σ(C–H) bonds susceptible to activate: a σ($C_{sp^2,}$ ferrocene–H) bond or the σ($C^*_{sp^3}$’H) bond. Besides that ligand **1** has an additional interest due to the prochiral natures of the ferrocenyl unit and the sulfur. This prompted us to study if the presence of the stereogenic center could be important to induce the preferential formation of any of the possible diastereomers of the cyclopalladated complex: [Pd{[(η^5-C_5H_3)–CH=N–CH(CO_2Me)CH_2–CH_2SMe]Fe(η^5-C_5H_5)}Cl] (**2**), which may form through activation of a σ($C_{sp^2,\ ferrocene}$–H) bond. Besides that, the existence of a bulky and electron-withdrawing group in the vicinity of the imine nitrogen could also introduce significant steric effects and electronic effects which may be important in the cyclopalladation process.

2. Results and discussion

The ligand (S_C)-[(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH(CO_2Me)CH_2–CH_2SMe}] (**1**) was prepared by condensation between equimolar amounts of ferrocenecarboxaldehyde and the amine H_2N–CH(CO_2Me)–CH_2–

---

* Corresponding author. Tel.: +34-93-4021274; fax: +34-93-4907725.

E-mail address: conchi.lopez@qi.ub.es (C. López).

PII: S0022-328X(01)01353-5

CH_2–SMe using a Dean–Stark apparatus to remove the benzene–water azeotrope formed during the process. The ligand is a yellow solid and was characterized by elemental analyses, IR and mono- and two-dimensional NMR spectroscopies (see Section 4). The IR spectrum of **1** showed two sharp bands (1728 and 1627 cm^{-1}) due to the $>CO_2$ and >C=N– groups. Furthermore, ^1H- and $^{13}C\{^1H\}$-NMR spectra suggested that only one isomer (*E*-form) was present in solution.

In order to study if palladium(II) salts could induce the activation of the $\sigma(C_{sp^2,\ ferrocene}$–H) bond of **1**, the general procedure described for the cyclopalladation of ferrocenyl Schiff bases was used. This method, which consists of the reaction between equimolar amounts of the ferrocenyl Schiff bases $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}C(R)\text{=}N\text{–}R'\}]$, $Na_2[PdCl_4]$ and NaAcO in methanol, produces cyclopalladated complexes of the general formula: $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}C(R)\text{=}N\text{–}R']Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}Cl)]_2$ [6].

However, when the stoichiometric amounts of **1**, $Na_2[PdCl_4]$ and NaAcO were refluxed for 18 h in methanol, the complex $[Pd_2\{[C\{(CO_2Me)\text{–}CH_2\text{–}CH_2\text{–}SMe\}N\text{=}CH\text{–}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}_2Cl_2]\cdot CH_2Cl_2$ (**3**) was obtained after the work up of an SiO_2-column. (Scheme 1, *step A*).

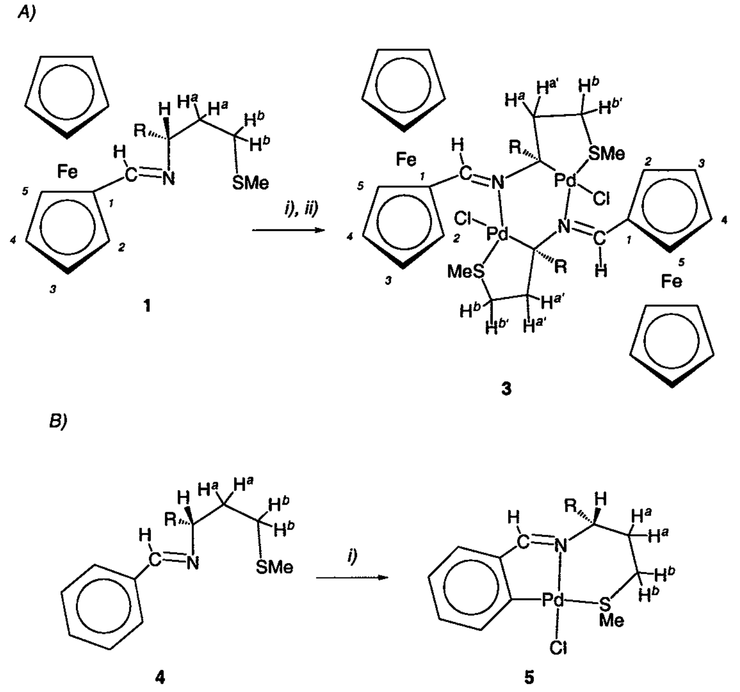
Once the band was collected, the polarity of the eluant was increased progressively, but the release of any other additional band was not observed. In addition, the whitish aspect of the column suggested the absence of any other ferrocene derivative.

Compound **3** was characterized by elemental analyses, IR and NMR spectrocopy and also by X-ray diffraction. The IR spectrum of **3** showed two sharp bands due to the $>CO_2$ and >C=N– groups which appeared at lower frequencies than for **1**. The signal due to the proton of the stereogenic center of **1** (δ = 4.08 ppm) was not observed in the ^1H-NMR spectrum of **3**, thus suggesting that the activation of the $\sigma(C^*_{sp^3}$'H) bond had taken place. This is supported by the results obtained from two-dimensional NMR experiments [NOESY, HMBC and HSQC] and by the low field shift of the resonance due to the stereogenic carbon atom observed in the $^{13}C\{^1H\}$-NMR spectrum.

The crystal structure of **3** (Fig. 1) shows some interesting and uncommon features. The complex contains a central six-membered ring formed by the atoms: Pd(1), Pd(2), N(1), N(2), C(12) and C(29) with a boat conformation, which shares two opposite $\sigma(Pd\text{–}C_{sp^3})$ bonds with two different five-membered palladacycles. The metallacycles have an envelope like-conformation in which the atoms C(30) and C(13) are out of the planes defined by the remaining atoms.

Bond lengths and angles around the palladium atoms (Table 1) are similar to those reported for five-membered cyclopalladated compounds containing Schiff bases, and the Pd–S bond length agrees with those found in palladium(II) thioether compounds [7].

Besides that, the ligand exhibits an unusual mode of coordination since it binds to one of the palladiums through the sulfur and the metallated carbon, while the imine nitrogen is linked to the other palladium. According to the literature [8,9], a similar type of coordination



Scheme 1. R = CO_2Me. (i) $Na_2[PdCl_4]$ and NaAcO in refluxing methanol; (ii) SiO_2 column chromatography using CH_2Cl_2 as eleant.

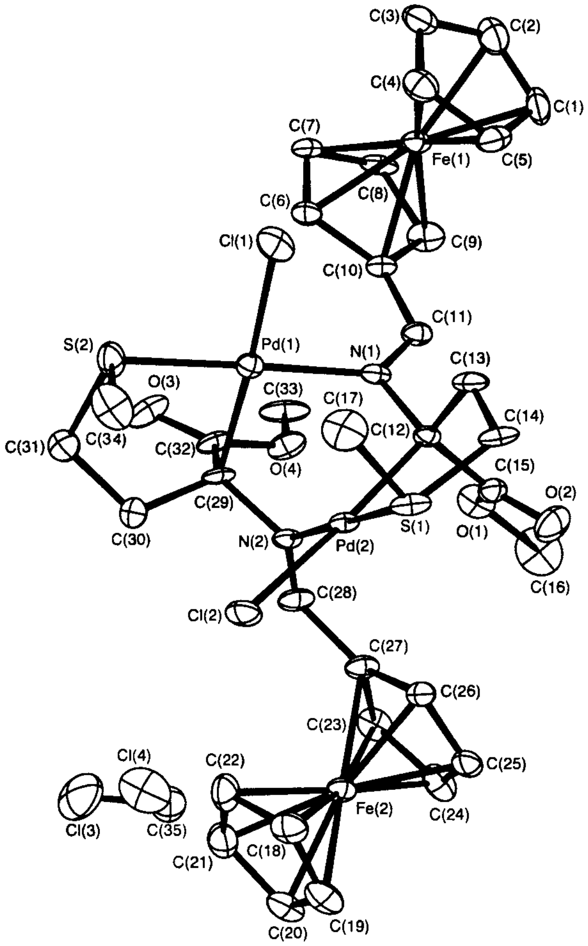


Fig. 1. Molecular structure and atom labelling scheme for **3**.

$(C,N,S)^-$ has only been described in tetrakis[2-*N*-(1-naphthyl)methylidene)benzenethiolato-C,N,S]tetrapalladium(II) which was obtained as a by-product {yield ≈ 1.6%} through the activation of the $\sigma(C_{sp^2},$ aryl–H) bond of the 2-(1-naphthyl)benzothiazolinone [8] or in $[Pd(L)Cl]_2$ where LH represents the imine derived from the condensation of 2-thiophenecarbaldehyde and methionine methyl ester [9]. Thus, **3** is an unusual tetrametallic complex having a rare $(C^*_{sp^3},N,S)^-$ terdentate ligand derived from orthopalladation.

The values of the torsion angles: C(17)–S(1)–C(12)–C(15): 171.5(5)° and C(34)–S(2)–C(29)–C(32): 175.4(5)° indicate that in each one of the two halves of the molecule the $-CO_2Me$ group and the methyl bound to the sulfur are pointing towards opposite sides of the coordination plane of the palladium. If these substituents were on the same side of the plane a strong steric hindrance would arise. So, these results show the importance of the presence of the bulky and electron withdrawing CO_2Me group [10] in the proximity of the donor atoms of **1** upon the diastereoselectivity of the process.

The intradimer Pd···Pd distance {3.0213(15) Å} is shorter than the sum of the van der Waals radii (3.22 Å) [11], which might be indicative of a metal–metal bond. In order to elucidate this, single point molecular orbital calculations at the DFT-B3LYP level [12,14], using the geometry obtained from the X-ray diffraction, followed by a critical point analyses using Bader's Atoms in Molecules methodology were carried out [15,16]. These calculations failed to show any critical point between the palladium atoms or in their vicinity, thus suggesting that for complex **3** the existence of a Pd–Pd bond can be discarded. This fact is in agreement with the relative small tendency of the palladium atom to form metal–metal bonds [17].

Potentially terdentate chelating ligands $[N,C,X]^-$ {where X = N,P,O} and $[C,N,N']^-$ may adopt different bonding modes and hapticities, which is relevant to catalytic processes. On this basis and in order to explore the binding abilities of ligand **1** we proceeded to study the reactivity of complex **3** versus PPh_3. The addition of a stoichiometric amount of PPh_3 to a solution of **3** in $CDCl_3$ at room temperature did not produce significant changes in the ^1H-NMR spectra and only the signal due to the free PPh_3 was observed in the $^{31}P\{^1H\}$-NMR spectrum, and no evidences of the coordination of the PPh_3 was detected by $^{31}P\{^1H\}$-NMR spectroscopy after 7 days of storage. This finding suggests that in complex **3** the Pd–S bond has low lability.

3. Conclusions

The results presented here reveal that despite the great proclivity of ferrocenyl Schiff bases to undergo

Table 1
Selected bond lengths (Å) and bond angles (°) for **3**

Bond lengths			
Pd(1)–S(2)	2.2613(17)	Pd(2)–S(1)	2.2665(16)
Pd(1)–Cl(1)	2.4008(16)	Pd(2)–Cl(2)	2.3996(16)
Pd(1)–N(1)	2.074(5)	Pd(2)–N(2)	2.053(4)
Pd(1)–C(29)	2.073(5)	Pd(2)–C(12)	2.052(5)
N(1)–C(11)	2.073(5)	N(2)–C(28)	1.280(7)
N(12)–C(13)	1.579(8)	C(29)–C(30)	1.511(8)
C(13)–C(14)	1.476(8)	C(30)–C(31)	1.524(8)
C(14)–S(1)	1.807(7)	C(31)–S(2)	1.830(7)
S(1)–C(17)	1.797(7)	S(2)–C(34)	1.796(7)
C(12)–C(15)	1.484(8)	C(29)–C(32)	1.516(7)
Bond angles			
C(29)–Pd(1)–N(1)	91.1(2)	Cl(12)–Pd(2)–N(2)	89.6(2)
C(29)–Pd(1)–S(2)	87.22(17)	C(12)–Pd(2)–S(1)	88.84(16)
S(2)–Pd(1)–Cl(1)	87.51(6)	S(1)–Pd(2)–Cl(2)	87.44(6)
N(1)–Pd(1)–S(2)	178.35(12)	N(2)–Pd(2)–S(1)	177.85(14)
C(11)–N(1)–C(12)	115.3(49)	C(28)–N(2)–C(29)	116.9(5)
Pd(1)–C(29)–N(2)	106.8(3)	Pd(2)–C(12)–N(1)	107.5(3)

Standard deviation parameters are given in parenthesis.

metallation at the substituted pentagonal ring [4–6], for **1**, which contains an electron-withdrawing group in the adjacent position of the coordinative imine nitrogen, the activation of the $\sigma(C^{*}_{sp^3}, \mathrm{H})$ bond takes place giving: $[\mathrm{Pd_2\{[C\{(CO_2Me)-CH_2-CH_2-SMe\}\{N{=}CH-(\eta^5-C_5H_4)]Fe(\eta^5-C_5H_5)\}_2Cl_2]\cdot CH_2Cl_2}$ (**3**) in which the palladium atoms are directly bound to a stereogenic carbon ($\mathrm{C}^{*}_{sp^3}$). Besides, it is well known that: (a) the cyclopalladation of N-donor ligands involves the electrophilic attack of the coordinated palladium(II) to the σ(C–H) bond; (b) the proclivity of the σ(C–H) bond to undergo electrophilic attacks follows the trend: $\sigma(\mathrm{C_{sp^3}{-}H}) < \sigma(\mathrm{C_{sp^2,\ aryl}{-}H}) < \sigma(\mathrm{C_{sp^2,\ ferrocene}{-}H})$. Despite this, for **1** the metallation of the $\mathrm{C}^{*}_{sp^3}$-atom takes place.

These findings are in sharp contrast with those obtained in the cyclopalladation of (S_C)-(+)-$\mathrm{C_6H_5{-}CH{=}N{-}CH(CO_2Me){-}CH_2{-}CH_2{-}SMe}$ (**4**), which can be visualized as derived from **1** by replacement of the ferrocenyl group by a phenyl ring [18]. In this case, the activation of the $\sigma(\mathrm{C_{sp^2,\ phenyl}{-}H})$ bond took place leading to $[\mathrm{Pd\{C_6H_4{-}CH{=}N{-}CH(CO_2Me){-}CH_2{-}CH_2{-}SMe\}Cl}]$ (**5**) (Scheme 1, *step B*) in which the ligand behaves as a $(\mathrm{C_{sp2}},\mathrm{N},\mathrm{S})^-$ terdentate group [18]. The differences observed in the mode of binding of ligands **1** and **4** in the cyclopalladated complexes **3** and **5** suggest that other more subtle factors (i.e. the different strain that may arise from the fusion of the metallacycle and a phenyl or a $\mathrm{C_5H_3}$ ring) may also be important to determine the nature of the final cyclometallated product.

Besides that, since no evidences of the formation of **3** were detected in the reaction of stoichiometric amounts of **1**, $\mathrm{Na_2[PdCl_4]}$ and NaAcO at room temperature using different reaction periods (from 2 to 18 h), we tentatively postulate that compound **3** forms under thermodynamic control.

On the other hand, the Pd–S bond in **3** is less labile than the Pd–S bond in **5**, which reacts with the equimolar amount of $\mathrm{PPh_3}$ to give $[\mathrm{Pd\{C_6H_4{-}CH{=}N{-}CH(CO_2Me){-}CH_2{-}CH_2{-}SMe\}(PPh_3)Cl}]$ (**6**), via the cleavage of the Pd–S bond.

4. Experimental

Elemental analyses (C,H,N and S) were carried out at the (C.S.I.C. Barcelona). Infrared spectra were obtained with a Nicolet Impact 400 instrument using KBr pellets. Proton and the two-dimensional $\{^1\mathrm{H}{-}^1\mathrm{H}\}$-NOESY experiments as well as the heteronuclear $\{^1\mathrm{H}{-}^{13}\mathrm{C}\}$-HMBC and HSQC-NMR experiments were run with a Varian-VXR instrument using $\mathrm{CDCl_3}$ as solvent and $\mathrm{SiMe_4}$ as internal standard. $^{13}\mathrm{C}\{^1\mathrm{H}\}$- and $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectra were recorded with a Bruker-250DXR instrument using $\mathrm{CDCl_3}$ as solvent; $\mathrm{P(OMe)_3}$ was used as internal standard for the $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectroscopy. In all cases the chemical shifts (δ) are given in ppm and the coupling constants (*J*) in Hz. The optical rotation of **1** was determined in $\mathrm{CH_2Cl_2}$ using a VG-Quatro Fissions Instrument and 3-nitrobenzylalcohol as matrix.

4.1. Materials and synthesis

Ferrocenecarboxaldehyde and the hydrochloride of L-methionine methyl ester were obtained from standard sources. The hydrochloride was converted into the corresponding amine before its use in the condensation reaction. Except for benzene, the remaining solvents were dried and distilled before use. The preparation of **1** requires the use of benzene which should be handled with *Caution!*

4.2. (S_C)-(+)-$[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}\{(\eta^5\text{-}\mathrm{C_5H_4}){-}\mathrm{CH{=}N{-}CH(CO_2Me){-}CH_2{-}CH_2{-}SMe}]$ (1)

Ferrocenecarboxaldehyde (500 mg, 2.28 mmol) was dissolved in 25 ml of benzene at 20 °C. Then the stoichiometric amount (372 mg, 2.28 mmol) of the amine: $\mathrm{H_2N{-}CH(CO_2Me){-}CH_2{-}CH_2{-}SMe}$ was added. The reaction flask was connected to a Dean–Stark apparatus (20 ml) and to a condenser. The wine–red reaction mixture was refluxed on an ethyleneglycol bath until ca. 15 ml had condensed on the Dean–Stark apparatus. The hot solution was carefully filtered out and the filtrate was concentrated to dryness on a rotary evaporator giving an oily residue. Addition of *n*-hexane (ca. 20 ml) followed by vigorous stirring at room temperature (r.t.) for 1 h produced a yellow solid, which was collected by filtration and air-dried. Yield: 581 mg (71%). Anal. Calc. for $\mathrm{C_{17}H_{21}FeNO_2S}$: C, 56.82; H, 5.90; N, 3.90; S, 8.92. Found: C, 57.03; H, 5.90; N, 3.95; S, 9.05%. IR: ν(–CO)=1728 and $\nu(>\mathrm{C{=}N}{-}) = 1627\ \mathrm{cm^{-1}}$. ^{1}H-NMR data [19]: 4.78 (s, 1H, $\mathrm{H^2}$), 4.44 (s, 1H, $\mathrm{H^3}$), 4.46 (s, 1H, $\mathrm{H^4}$), 4.71 (s, 1H, $\mathrm{H^5}$), 4.23 (s, 5H, $\mathrm{C_5H_5}$), 8.21 (s, 2H, –CH=N–), 4.08 (t, 1H, =N–CH–), 3.79 (s, 3H, –OMe), 2.10 (s, 3H, –SMe), 2.26 (m, 2H, $-\mathrm{CH^{a,a'}}$) and 2.10 (m, 2H, $>\mathrm{CH^{b,b'}{-}S}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR data [19]: 73.7 ($\mathrm{C^1}$), 71.74 ($\mathrm{C^2}$), 69.3 ($\mathrm{C^3}$), 70.1 ($\mathrm{C^4}$), 71.5 ($\mathrm{C^5}$), 70.0 ($\mathrm{C_5H_5}$), 172.8 ($-\mathrm{CO_2}$), 165.6 ($>\mathrm{C{=}N}-$), 57.8 (OMe), 60.6 ($-\mathrm{N{-}CH}<$) 31.8 ($-\mathrm{CH_2}-$), 30.8 ($-\mathrm{CH_2{-}S}$) and 15.6 (–SMe). $[\alpha]_D(20\ °\mathrm{C}) = +83.2$ ($c = 1.0$ g/100 ml, $\mathrm{CH_2Cl_2}$).

4.3. $[\mathrm{Pd_2\{[C\{(CO_2Me){-}CH_2{-}CH_2{-}SMe\}N{=}CH{-}(\eta^5\text{-}C_5H_4)]Fe(\eta^5\text{-}C_5H_5)\}_2Cl_2]\cdot CH_2Cl_2}$ (3)

Ligand **1** (100 mg, 0.29 mmol), $\mathrm{Na_2[PdCl_4]}$ (85 mg, 0.29 mmol) and NaAcO (24 mg, 0.29 mmol) were suspended in 20 ml of methanol. The resulting mixture was refluxed for 18 h and concentrated to dryness on a rotary evaporator. The residue was treated with $\mathrm{CH_2Cl_2}$

Table 2
Crystal data and details of the refinement of the crystal structure of **3**

	3
Empirical formula	$C_{34}H_{42}Cl_2Fe_2N_2O_4Pd_2S_2 \cdot CH_2Cl_2$
Formula weight	1085.13
Temperature (K)	293(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	11.860(7)
b (Å)	17.5570(17)
c (Å)	19.176(3)
α (°)	90.0
β (°)	90.0
γ (°)	90.0
V (Å^3)	3993(2)
Z	4
D_{calc} (mg × m^3)	1.805
μ (mm^{-1})	2.011
F(000)	2168
Reflections collected	6434
Independent reflections [R(int)]	6389 [$R(\text{int}) = 0.0076$]
Final R indices [$I = 2\sigma(I)$]	$R_1 = 0.0304$, $wR_2 = 0.0609$
R indices (all data)	$R_1 = 0.0749$, $wR_2 = 0.0700$
Absolute structure parameter	0.02(2)

Standard deviation parameters are given in parenthesis.

(15 ml) and passed through an SiO_2 column using CH_2Cl_2 as eluant. The red band released was collected and the slow evaporation of the solution at ca. 20 °C produced deep red crystals of **3**, which were collected and air-dried. Yield: 112 mg (71%). *Characterization data*: Anal. Calc. for $C_{34}H_{42}Cl_2Fe_2N_2O_4Pd_2S_2 \cdot CH_2Cl_2$: C, 38.7; H, 3.9; N, 2.6; S, 5.9. Found: C, 38.5; H, 3.85; N, 2.6; S, 5.85%. IR: $\nu(>C{=}N{-} = 1609\ cm^{-1}$ and $\nu(-CO){=}1683\ cm^{-1}$. ^{1}H-NMR data [19]: 6.63 (s, 2H, H^2), 4.49 (s, 2H, H^3), 4.41 (s, 2H, H^4), 4.65 (s, 2H, H^5), 4.26 (s, 10H, C_5H_5), 7.63 (s, 2H, –CH=N–), 5.28 (s, 2H, CH_2Cl_2), 3.03 (s, 6H, –OMe), 3.02 (s, 6H, –SMe), 3.64 (m, 2H, >CH^a–), 1.66 (m, 2H, >CH$^{a'}$–), 3.39 (m, 2H, >CH^b–S) and 2.62 (2H, >CH$^{b'}$–S). ^{13}C{^{1}H}-NMR data [19]: 81.4 (C^1), 68.2 (C^2), 73.8 (C^3), 71.4 (C^4), 72.2 (C^5), 70.0 (C_5H_5), 173.1 (–CO_2), 167.2 (>C=N–), 51.8 (OMe), 81.4 (C*–Pd), 42.8 (–CH_2–), 37.9 (–CH_2–S) and 22.1 (–SMe).

4.4. Crystal structure determination

A red prismatic crystal of **3** was selected and mounted on a Enraf–Nonius CAD4 four circle diffactometer. Unit cell parameters (Table 2) were calculated from accurate settings of 25 automatically centered reflections in the range $12° < \theta < 21°$ and refined by least-squares method. Intensities were collected with a graphite monochromated Mo–K$_\alpha$ radiation using ω–2θ scan technique. The number of reflections collected (in the range $2.02° = \theta = 29.96°$) was 6434, of which 6398 were non-equivalent by symmetry [R_{int} (on I) = 0.007], and 4609 reflections were assumed as observed. The goodness-of-fit on F^2 was 0.898. The structure was solved by direct methods, using the SHELXS computer program [20] and refined by full-matrix least-squares method with the SHELX-93 computer program [21]. The function minimized was $\Sigma\, w\|F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0289P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were obtained from the literature [22]. The chirality of the structure was defined from the Flack coefficient [23], which is equal to 0.02(2) for the given results. Final R indices and further details concerning the resolution and refinement of the crystal structure of **3** are presented in Table 2.

4.5. Computational details

Calculations were carried out at the B3LYP computational level [13,14] with the GAUSSIAN98 package [12]. The basis set has been chosen as follows: an effective core potential was used to replace the 36 innermost electrons of palladium, 10 innermost electrons of S and Cl; for these atoms the LANDL2DZ basis [24], which is valence doubly-zeta quality, was used; for H, N and O a 6-31G basis was used [25]. Atoms in molecules analyses [15] was preformed with the XAIN program [16].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 135111 for compound **3**. Copies of this information can be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the *Ministerio de Ciencia y Tecnología* and to the *Generalitat de Catalunya* for financial support (projects: BQU2000-0652 and 1997-SGR-0044, respectively).

References

[1] (a) A.D. Ryabov, Chem. Rev. 90 (1990) 403;
(b) G.R. Newkome, W.W. Puckett, V.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451;
(c) I. Omae, Coord. Chem. Rev. 83 (1988) 137.

[2] (a) I. Omae, Applications of Organometallic Compounds, John Wiley, Chichester, UK, 1998, p. 435 Chapter 20;

(b) V.I. Sokolov, Chirality and Optical Activity in Organometallic Compounds, Gordon and Breach, London, UK, 1991;
(c) A.J. Klaus, in: A.E. Peters, H.S. Freeman (Eds.), Modern Colorants: Synthesis and Structure, vol. 3, Blakie Academic Professional, London, UK, 1995, p. 1;
(d) J. Dupont, M. Pfeffer, J. Spencer, Eur. J. Inorg. Chem. (2001) 1917 and references therein;
(e) M. Pfeffer, Recl. Trav. Chim. Pays-Bas. 109 (1990) 567;
(f) M. Ohff, A. Ohff, D. Milstein, Chem. Commun. (1999) 357;
(g) J. Buey, P. Espinet, H.S. Kitzerow, J. Strauss, Chem. Commun. (1999) 441;
(h) M.I. Brice, Angew. Chem. Int. Ed. Engl. 10 (1977) 73.

[3] (a) V.V. Dunina, L.G. Kuz'mina, M.Y. Kazakova, O.N. Gorunova, Y.K. Grishin, E.I. Kazakova, Eur. J. Inorg. Chem. (1999) 1029;
(b) S.B. Wild, Coord. Chem. Rev. 166 (1997) 291 and references therein.

[4] C. López, R. Bosque, D. Sainz, X. Solans, M. Font-Bardía, Organometallics 16 (1997) 3261 and references therein.

[5] For recent studies of cyclopalladation of N-donor ferrocenyl ligands see: (a) G. Zhao, Q.G. Wang, T.C.W. Mak, Organometallics, 17 (1998) 3437;
(b) X.L. Cui, Y.J. Wu, C.X. Du, L.R. Yang, Y. Zhu, Tetrahedron: Asymmetry, 10 (1998) 1255 and references therein.

[6] R. Bosque, C. López, X. Solans, M. Font-Bardía, Organometallics 18 (1999) 1267 and references therein.

[7] F.H. Allen, O. Kennard, R. Taylor, Chem. Design Automation News 8 (1993) 146.

[8] (a) T. Kawamoto, I. Nagasawa, H. Kuna, Y. Kushi, Inorg. Chem. 35 (1996) 2427;
(b) T. Kawamoto, Y. Kushi, Chem. Lett. (1992) 1057.

[9] H.A. Ankersmit, P.T. Witte, H. Kooijman, M.T. Lakin, A.L. Spek, K. Goubitz, K. Vrieze, G. van Koten, Inorg. Chem. 35 (1996) 6053.

[10] C. Hansch, A. Leo, D. Koekman, Exploring QSAR. Hydrophobic, Electronic and Steric Constants, ACS Professor Reference Books, Washington (USA), 1995.

[11] (a) A. Bondi, J. Phys. Chem. 68 (1964) 441;
(b) A.I. Kitaigorodskii, Molecular Crystals and Molecules, Academic press, London, UK, 1973.

[12] GAUSSIAN98 (revision A.6) by M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Peterson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K, Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian Inc. Pittsburg, PA (USA), 1998.

[13] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[14] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[15] R.F.W. Bader, Atoms in Molecules. A Quantum Theory, Clarendon press, Oxford, UK, 1995.

[16] XAIM by J.C. Ortíz, C. Bo, Departament de Química Fisica i Inorgànica, Universitat Rovira i Virgili, Tarragona, Spain, 1998.

[17] G. Aullón, G. Ujarque, A. Lledós, S. Alvarez, P. Alemany, Inorg. Chem. 37 (1998) 804.

[18] X. Riera, C. López, A. Caubet, V. Moreno, X. Solans, M. Font-Bardia, Eur. J. Inorg. Chem. (2001) 2135.

[19] Labelling of the atoms corresponds to that shown in the scheme.

[20] G.M. Sheldrick, Acta Cryst. Sect. A A46 (1990) 467.

[21] G.M. Sheldrick, A computer program for determination of crystal structures, University of Göttingen, Germany, 1994.

[22] Kynoch press, International Tables of X-ray Crystallography, vol. IV, 1974, pp. 99–100 and 149.

[23] H.D. Flack, Acta Crystallogr. A39 (1983) 876.

[24] (a) W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284;
(b) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.

[25] W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 51 (1969) 2657.