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Chiral ferrocenylthiazolidines, new ligands for palladium complexes

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Abstract

The reaction of ferrocene with methyl or ethyl esters of L-cysteine in the presence of paraformaldehyde is studied. This process yields the optically pure derivatives: methyl or ethyl (*R*)-3-(ferrocenylmethyl)thiazolidine-4-carboxylates (**1a** or **1b**), together with the corresponding *N*,*N*-bisthiazolidine derivatives (**2a** or **2b**). When the reaction was carried out using the ethyl ester of L-cysteine, small amounts (ca. 9%) of the 1,1'-disubstituted ferrocene derivative (**3b**) were also isolated. The reactivity of compounds **1** versus palladium(II) species is studied, and has allowed us to isolate and characterise: [Pd(η^3-C_3H_5)Br(**1a**)] (**4a**) and [Pd(η^3-C_3H_5)Br(**1b**)] (**4b**), in which the ferrocenyl ligand behaves as a monodentate *S*-donor group. Compounds **4** evolve in the presence of dimethylsulfoxide to produce: [Pd(η^1-C_3H_5)Br(**1**)(dmso)] (**5**) in which the palladium(II) is bound to the terminal carbon of the C_3H_5 group. The reactivity of ligands **1** with $Na_2[PdCl_4]$ is also reported and has allowed us to isolate the dinuclear compounds [Pd_2Cl_4(μ-**1a**)$_2$] (**6a**) and [Pd_2Cl_4(μ-**1b**)$_2$] (**6b**)] in which the thiazolidine behaves as a bridging (N,S) donor group. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thiazolidines; Ferrocene; Palladium; Chiral; S-donor

1. Introduction

The design and development of new metal complexes with application in catalytic asymmetric reactions is a great challenge in organometallic chemistry [1]. C_2-symmetric bis(oxazolines) are among the leading classes of chiral ligands with applications in C–C bond formation reactions [2]. Several bidentate ligands bearing only one oxazoline moiety and another donor group are well documented and in this respect, pyridyloxazolines have found broad applications in this field [3]. The bidentate ligands used usually contain nitrogen, oxygen or phosphine functionalities. Less attention has been paid to sulfur-containing ligands: with certain relevant exceptions [4], there are only a few ligands containing sulfur, such as thiazolidine and thiazoline, derived from L-cysteine, in spite of the relatively easy synthetic access to a wide variety of candidates [5].

Moreover, during the late years, ferrocene derivatives have been used successfully in homogeneous catalysis both in the laboratory and on an industrial scale [6]. The synthesis of most of these ligands starts from easily accessible enantiopure ferrocenyl amines, like (*R*)- or (*S*)-(1-dimethylaminoethyl)ferrocene [7]. Chiral ferrocenyl ligands containing an α-aminoacid derived moiety have been prepared from the appropriate acetoxyalkylferrocene by nucleophilic substitution of the acetoxy group with (*S*)-prolinol [8]. Reactions proceeded with high yields and with retention of configuration on the α-carbon, starting from optically pure (*R*)- or (*S*)-1-acetoxyethylferrocene.

In addition, research has been focused on the study of optically pure palladium(II) compounds, which can be used for the determination of enantiomeric excesses, for the separation of racemic mixtures of Lewis bases (i.e. phosphines) and chiral recognitors [9,10]. The catalytic applications of optically pure palladium(II) bearing both a chiral neutral ligand and a η^3-allyl group in the asymmetric hydrovinylation of olefines have also been reported elsewhere [11]. Furthermore, Pd-cata-

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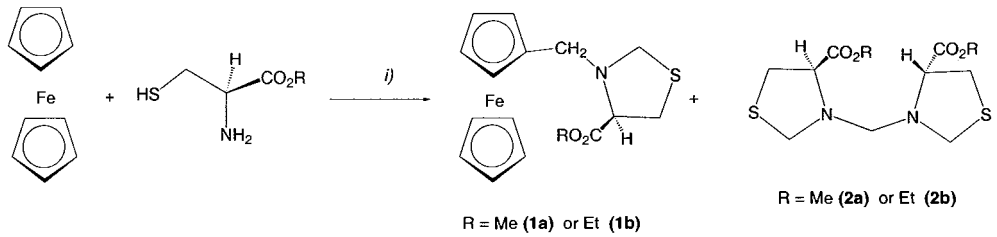


Scheme 1. (i) Solid paraformaldehyde in F_3C–COOH. When L-cysteine ethylester was used as reagent, the 1,1′-disubstituted ferrocene bis(thiazolidine) derivative (**3b**) (depicted in Fig. 1) was also obtained as a by-product (ca. 9%), see text.

lyzed asymmetric allylic substitution reactions offer great potential for the enantioselective formation of new carbon–carbon and carbon–nitrogen bonds [12–14]. The efficiency of ferrocene-based C_2-symmetric oxazoline ligands has been reported [14].

However, none of these cases refers to palladium(II) complexes holding ferrocenylthiazolidine ligands. Therefore on the frame of a project directed towards the design of optically pure palladium(II) compounds holding ferrocenyl units, we were aimed to prepare novel ferrocenylthiazolidines containing a chiral carbon on the thiazolidine ring and an ester functional group (Scheme 1) and to study their reactivity versus palladium(II) species. For the preparation of the ligands, we chose methyl (or ethyl) esters of L-cysteine since they contain both a free amino and a thiol functional group, which are required for the formation of the thiazolidines [15].

2. Results and discussion

2.1. The ligands

Treatment of ferrocene with L-cysteine methyl ester hydrochloride and solid paraformaldehyde (in a 1:5:20 molar ratio) in trifluoroacetic acid as a solvent, gave the monosubstituted compound: methyl (*R*)-3-(ferrocenylmethyl)thiazolidine-4-carboxylate (**1a**) in 40% yield, together with *N*,*N*′-methylenebisthiazolidinedimethyl ester (**2a**) (Scheme 1).

When the reaction was repeated using L-cysteine ethyl ester hydrochloride and solid paraformaldehyde (in the same molar ratio) in trifluoroacetic acid, three compounds were isolated after the work-up of the column: ethyl (*R*)-3-(ferrocenylmethyl)thiazolidine-4-carboxylate (**1b**) (in 33% yield), *N*,*N*′-methylenebisthiazolidinediethyl ester (**2b**) (Scheme 1) and the 1,1′-disubstituted ferrocene derivative (**3b**) (Fig. 1) (in 9% yield). Alternatively, treatment of ferrocene with ethyl (*R*)-thiazolidine-4-carboxylate hydrochloride instead of L-cysteine ethyl ester hydrochloride under these conditions gave similar results. Some features of this transformation deserve comment. First, the yield of the disubstituted compound was much lower than that of the monosubstituted derivative. Second, *N*,*N*′-methylenebisthiazolidine diethyl ester was isolated with high yield (76%) [16]. We suggest that the initial fast formation of the methylenebisthiazolidine in the acidic reaction medium reduces the amount of thiazolidine needed for the electrophilic substitution on the ferrocene. When this substrate was reacted with cysteamine hydrochloride in identical experimental conditions, only *N*,*N*′-methylenebisthiazolidine was isolated and the monosubstituted ferrocene derivative was not detected. Thus the rate of bisthiazolidine formation in this case prevented the electrophilic substitution on the ferrocene.

In conclusion, the reaction of L-cysteine esters (or thiazolidine esters) with ferrocene in the presence of excess of paraformaldehyde is a reliable method to obtain monosubstituted thiazolidines of ferrocene in homochiral form. It may be understood as an initial thiazolidine ring closure, followed by an iminium salt formation with excess of formaldehyde and a final electrophilic substitution reaction on ferrocene. To the best of our knowledge ferrocene derivatives holding thiazolidine rings are not common, and in general their preparation requires a series of consecutive reactions [17], consequently, the most notable feature of the reactions described above is the easy access to these ligands from commercially available compounds in one step.

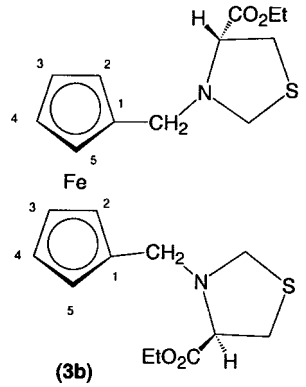
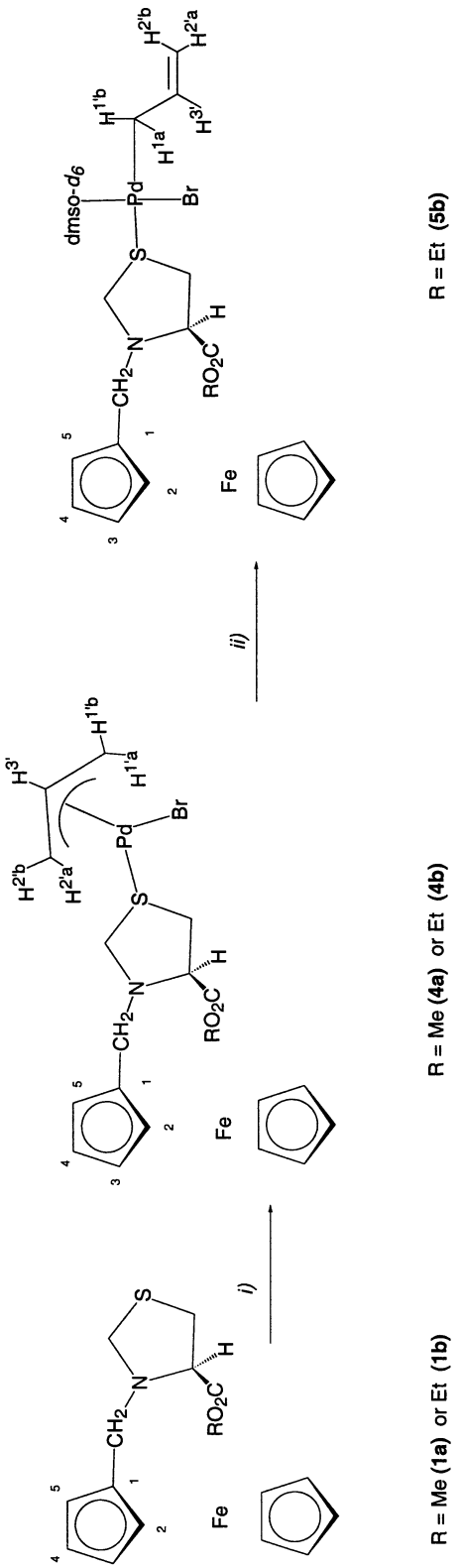


Fig. 1. Schematic view of the 1,1′-disubstituted ferrocenebis(thiazolidine) derivative (**3b**).



Scheme 2. (i) $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$ in CH_2Cl_2 at room temperature. (ii) For R = Et, DMSO-d_6.

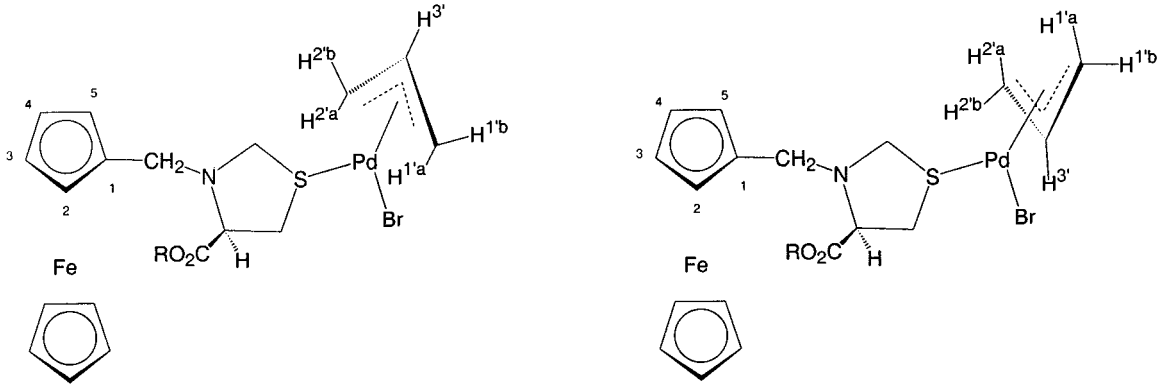


Fig. 2. Schematic view of the two diastereomers of compounds **4**.

Since the new ligands **1a** and **1b** contain heteroatoms with good donor properties we explored their coordination abilities in front of transition metals like palladium(II) species.

2.2. Reaction of ligands *1* with $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$

When ligands **1a** or **1b** were treated separately in CH_2Cl_2 with $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Br)]_2$ [18] (in a **1**:Pd molar ratio equals to 1), a bright yellow solution was obtained at room temperature and the subsequent addition of methanol produced yellow solids (Scheme 2).

Their elemental analyses were consistent with those expected for $[Pd(\eta^3\text{-}C_3H_5)Br(\mathbf{1a})]$ (**4a**) and $[Pd(\eta^3\text{-}C_3H_5)Br(\mathbf{1b})]$ (**4b**) (Scheme 2). These compounds are stable solids at room temperature, poorly soluble in alkanes and methanol, but highly soluble in benzene, CH_2Cl_2 and $CHCl_3$ (free of any traces of acids). The molar conductivity of a 10^{-3}M solution of **4b** in $CHCl_3$ suggested a non-electrolyte nature. The presence of small amounts of acids in the solvents produced a change in the colour of the solution from bright yellow to brownish, and the ^{1}H-NMR spectra of the resulting solutions showed broad signals, suggesting the presence of paramagnetic species. In addition, the conductivity of the initial 10^{-3} M solution of complex **4b** in $CHCl_3$ increased (up to ca. 220–270 $\Omega^{-1}\,cm^2\,mol^{-1}$). These observations suggested that compounds **4** decomposed under these experimental conditions. This may be due to the high proclivity of ferrocene derivatives holding alkyl groups to undergo oxidation [19].

Compounds **4** were characterised by mass spectra (FAB), IR and NMR spectroscopy. A summary of ^{1}H and $^{13}C\{^1H\}$-NMR data is presented in Section 4. The assignments of the signals were carried out with the aid of two-dimensional $^1H\{^{13}C\}$ heteronuclear-NMR experiments. The resonances of the proton and carbon nuclei of the allyl moiety were also assigned by comparison with the data reported for related derivatives [20]. The comparison of the spectroscopic data of compounds **4** and those of the corresponding free ligands **1**, showed that: (a) the coordination of the ligand to the palladium(II) produced a low-field shift of the signal due to the $-CH_2-$ protons of the thiazolidine ring; (b) the signal due to the carbon nucleus of the $S-CH_2-$ fragment in compounds **4** showed lower intensity and appeared at higher fields than in **1**; and (c) the position of the signals due to the proton and carbon nuclei of the –COOR groups did not vary significantly upon coordination. These trends suggest that ligands **1** bind to palladium(II) through the sulphur atom.

It is well known that palladium(II) compounds of general formula $[Pd(\eta^3\text{-}C_3H_5)(X)(L)]$ or $[Pd(\eta^3\text{-}C_3H_5)L_2]X$, where L and L_2 are chiral monodentate and bidentate ligands, respectively, and X = Cl or Br, may be present in two diastereomeric forms in solution (Fig. 2) [21], but only a broad signal for each allyl proton was found even at 200 K. This suggests that a fast interconversion between both diastereomers takes place, even at low temperatures. The phase-sensitive 2D ROESY spectra of compounds **4** (Fig. 3), carried out in

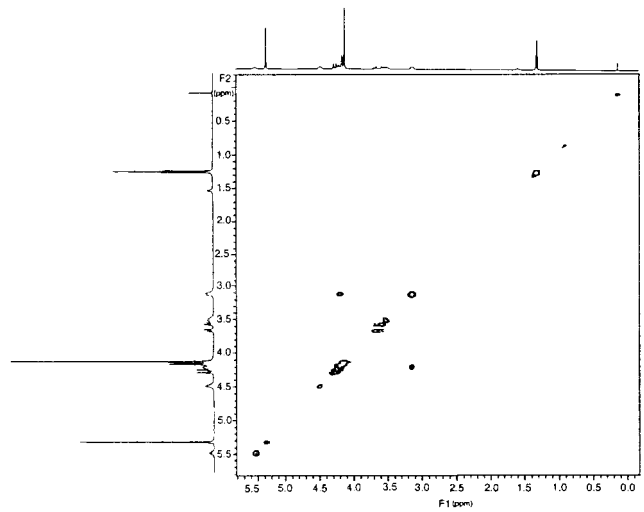


Fig. 3. ROESY $^1H\{^1H\}$-NMR spectrum of compound **4b** in CD_2Cl_2.

$CDCl_3$ solutions, showed a series of positive cross-peaks concerning to the allyl proton $H^{1'}$ and $H^{2'}$ signals, thus confirming the fast interconversion between both diastereomers in solution. Several examples of this kind of interconversion in solution have been described elsewhere, and it is accepted widely that such transformation may occur either by a $\pi \rightarrow \sigma \rightarrow \pi$ interchange or by a pseudorotation process [21].

2.3. Study of the behaviour of compounds **4** in coordinating solvents

One of the main interests of palladium(II) complexes containing π-allylic ligands is their use as catalysts or as precursors for the synthesis of catalytic materials [22], e.g. in hydrovinylation of olefins or in allyl substitution reactions [11–14].

The most common role of these compounds in homogeneous catalysts is associated usually with the changes in the coordination mode of the allylic ligand (from η^3- to η^1-or vice versa). Moreover, for some palladium(II) compounds holding η^3-allylic moieties [including $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}X)]_2$, with X = Cl or Br], the presence of a Lewis base (e.g. a nucleophilic solvent) is sufficient to trigger the dynamic behaviour described in the previous section, due to the formation of new palladium(II) species in which the C_3H_5 ligand binds to the metal through the terminal carbon atom (η^1-mode) [18]. In view of these facts and as a first approach to elucidate whether the presence of the bulky ferrocenyl ligand hinders the change in hapticity of the allyl ligand, we recorded the ^{1}H-NMR spectrum of **4b** in DMSO-d_6 (Scheme 2) at room temperature and compared it with that obtained in non-coordinating solvents, i.e. $CDCl_3$ or CD_2Cl_2. The most relevant changes detected in the spectra were: (a) the signal due to the $H^{3'}$ proton of the allyl group appeared as a quintuplet centred at $\delta = 5.65$ ppm; (b) the signal due to the $H^{1'}$ protons of the allyl group, which appeared at 4.10 ppm in the ^{1}H-NMR spectrum of **4b** in $CDCl_3$, was not observed when the solvent was DMSO-d_6; and a more complex signal appeared at 2.92 ppm. The position and multiplicities of the signals due to the protons of the allyl fragment of **5b** in DMSO-d_6 are consistent with those expected for palladium compounds holding η^1-C_3H_5 ligand [18,20a]. These findings suggest that in the presence of DMSO, complex **4b** evolves to produce: $[Pd(\eta^1\text{-}C_3H_5)Br(\mathbf{1b})(dmso\text{-}d_6)]$ (**5b**) (Scheme 2), in which the C_3H_5 group is σ-bonded to the palladium(II).

2.4. Reactivity of ligands **1** in presence of $Na_2[PdCl_4]$

When ligands **1a** or **1b** were treated separately with equimolar amounts of $Na_2[PdCl_4]$ in methanol at room temperature, an orange solid formed immediately upon mixing (hereinafter referred to as **6a** and **6b**). Their elemental analyses were consistent with the stoichiometry: **1**:Pd:Cl = 1:1:2. When ligand **1b** was used, the microanalyses suggested the occlusion of diethylether in a Pd:Et_2O ratio equal to 4. This was confirmed by the results obtained in the ^{1}H-NMR spectrum (see below). Assuming a four-coordination environment around the palladium(II) in **6b**, its non-electrolyte behaviour in $CHCl_3$ (see below), and the versatility of the coordination modes of ligands **1** [i.e. as a monodentate: S- or N-donor group or as a bidentate (N,S) ligand; as a terminal group or as a bridging ligand], the stoichiometry of compounds **6** could fit a wide variety of complex structures di-, tri-, tetra- or polymeric in general. The FAB(+) spectra of **6** showed peaks at $m/z = 1041$ (for **6a**) and 1036 (for **6b**), which correspond to the fragments expected for a dimeric unit (for **6a**) and to the dimeric unit after the loss of a Cl^- ion (for **6b**), respectively. The molar conductivity of a 10^{-3}M solution of **6b** (assuming a dinuclear structure) in $CHCl_3$ was consistent with that expected for a non-electrolyte material [23].

Compounds **6** were also characterised by IR and NMR spectroscopy. The IR spectra of these derivatives showed an intense band at ca. 1735 cm^{-1}, which is assigned to the stretching of the –COO functional group. The position of this band hardly varied when compared to those of the free ligands. Comparison of ^{1}H- and $^{13}C\{^1H\}$-NMR data of **6** and those of the corresponding parent ligand **1** revealed: (a) a downfield shift of the signals due to the methylene carbon nuclei of the thiazolidine ring upon coordination, which suggests the coordination of the ligand through the sulphur atom; (b) a similar trend was observed for the signals due to the carbon of the $–CH_2–$ fragment which is bound to the ferrocenyl moiety and to the nitrogen. This type of variation was not observed for compounds **4** (described above). The sign and magnitude of this shift could be indicative of the coordination of the ligand through the nitrogen. Furthermore, the resonances due to the ^{1}H and ^{13}C nuclei of the –COOR group (in close vicinity to the nitrogen atom) also varied in comparison with those of the free ligands and compounds **4**. Thus, we suggest a dimeric structure for compounds **6** in which the ferrocenyl ligand behaves as a (N,S) bidentate group. The coordination of the two heteroatoms (N and S) of the ligand to one of the palladium(II) atoms of compounds **6** is unlikely to occur, since this would lead to the formation of a 'PdNCS' four-membered chelate ring that has seldom been reported [24]. In contrast, several polynuclear palladium(II) complexes holding (N,S) donor ligands as bridging groups leading to 'Pd{μ-(–N–C(R_2)–S–)}$_x$Pd' ($x = 1$ or 2) cores have been described elsewhere [25–27]. Those containing dimeric units and central 'Pd{μ-(-N–C(R_2)–S–)}$_2$Pd' rings [25,26] are the most common, whereas trimeric [27], and tetrameric complexes are

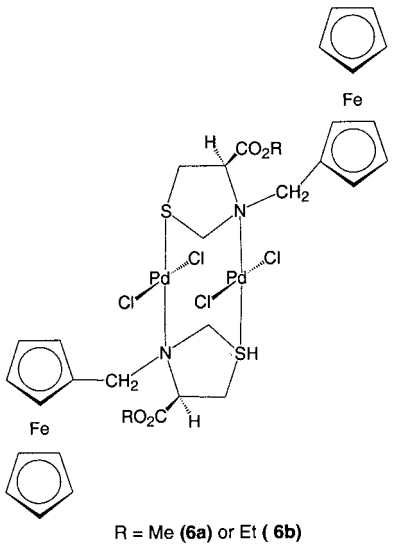


Fig. 4. Schematic view of proposed structure of compounds **6**.

scarce [25]. We thus tentatively propose for compounds **6** a dinuclear structure, containing a 'Pd{μ-ligand}$_2$Pd' central core. In these fragments, two different arrangements of the bridging ligands could be expected in principal (*cis*- or *trans*-). However, the use of molecular models revealed that the arrangement of groups in the *cis*-isomer would introduce strong steric hindrance due to the close vicinity of the ferrocenyl groups and the chlorides. Besides that, previous reports point out that for related compounds the *trans*-isomer is preferred strongly [24,25]. On these bases, we tend to postulate for compounds **6** the arrangement of ligands shown in Fig. 4. Nevertheless, it should be noted that the insolubility of these complexes (especially in the case of **6a**) makes their characterisation difficult and we do not have a conclusive evidence for our proposal.

3. Conclusions

The results presented here provide a useful method for the synthesis of two new optically pure ferrocenyl ligands methyl or ethyl (*R*)-3-(ferrocenylmethyl)thiazolidine-4-carboxylates, holding a cyclic-thioamine group as pendant arm. The study of the reactivity of these substrates in presence of [Pd(η^3-C_3H_5)(μ-Br)]$_2$ has allowed us to prepare and characterise the palladium(II) complexes of general formula [Pd(η^3-C_3H_5)Br(**1a**)] (**4a**) or [Pd(η^3-C_3H_5)Br(**1b**)] (**4b**). The study of the behaviour of compounds **4** in solution reveals that: (a) there is a fast interconversion between the two diastereomers of **4** in non-coordinating solvents; and (b) the use of coordinating solvents such as DMSO-d_6 alters the hapticity of the C_3H_5 fragment yielding [Pd(η^1-C_3H_5)Br(**1b**)(dmso-d_6)] (**5b**), in which the palladium is σ-bonded to the terminal carbon of the allyl group. The reaction of the ligands under study with $Na_2[PdCl_4]$ has allowed us to isolate and characterise the dimeric derivatives in which the ferrocenylthiazolidine ligands behave as a neutral (N,S) bridging group. The comparison of the results obtained in the reactions of ligands **1** with the two palladium(II) compounds provides a fine tuning of not only the mode of coordination of the ligand to the palladium(II) [as an S-donor in **4** and **5** or as a (N,S) donor group in **6**], but also of the nature of the final product (mononuclear in **4** and **5** or dinuclear in **6**).

The ligands and the palladium(II) complexes reported here have an additional interest since the presence of an ester residue, may provide a handle for their subsequent modification. Besides that, since the arrangement of ligands in compounds **4**, is similar to those described for palladium(II) complexes of the type: [Pd(η^3-C_3H_5)(Br)(L)] with catalytic activity, they appear to be good candidates to explore their potential utility in asymmetric catalysis.

4. Experimental

Elemental analyses (C, H and N) were carried out at the Serveis de Microanalisi (C.S.I.C., Barcelona). Infrared spectra were obtained with a Nicolet Impact 400-FTIR instrument using NaCl disks for the ligands **1** and KBr pellets for the palladium(II) complexes. Routine ^{1}H-NMR and ^{13}C{^{1}H}-NMR spectra were recorded at ca. 20 °C on a Gemini 200 MHz or on a Varian 300 MHz instrument. The two-dimensional NMR experiments [ROESY-^{1}H{^{1}H} spectra and the heteronuclear single-quantum coherence (HSQC)] were registered with a Bruker Avance DMX-500 or with a Varian VXR-500 instrument. The solvents and references used in the NMR experiments are specified in the characterisation section of each compound. In all cases the chemical shifts (δ) are given in ppm. The optical rotations were determined with a Perkin–Elmer 241 MC polarimeter [λ(Na) = 589.5 nm and 70 mA] using CH_2Cl_2 as solvent; the concentrations used for these measurements are specified in the characterisation section of each compound. Mass spectra were obtained with a VG-Quatro Fission Instrument using 3-nitrobenzylalcohol (NBA) as matrix. Molar conductivities of 10^{-3} M solutions of compounds **4b** and **6b** were measured in $CHCl_3$ at room temperature (r.t.) (23 °C) using a Crison micro MC2200 conductivitymeter.

4.1. Materials and synthesis

All the reagents used in this study were obtained from commercial sources and used without further modifications, except for compound [Pd(η^3-C_3H_5)(μ-Br)]$_2$ which was prepared as described elsewhere [18].

All the solvents used in this work were dried and distilled before use. TLC plates (Silica Gel 60 F_{254}) were purchased from Merck.

*4.1.1. Preparation of **1a** and **2a***

Ferrocene (0.5 g, 2.69×10^{-3} mol), L-cysteine methyl ester hydrochloride (2.3 g, 13.4×10^{-3} mol) and paraformaldehyde (1.6 g, 53.3×10^{-3} mol) were dissolved in trifluoroacetic acid (25 ml) at 0 °C. The solution was allowed to warm to r.t. and stirred for 6 h. The solvent was evaporated in vacuo under 45 °C, whereupon water (50 ml) was added and brought to neutral pH with $NaHCO_3$. The crude was extracted with Et_2O (3×50 ml) and the organic solvent dried over Na_2SO_4 and evaporated in vacuo to afford a red–brown oil. Purification by SiO_2-column chromatography (hexane–Et_2O, 9:1 v/v) yielded **1a** as a gummy material (0.37 g, 40%, calculated from ferrocene) and *N*,*N*′-methylenebisthiazolidine dimethyl ester (**2a**) as an oil (1.64 g, 40%, calculated from L-cysteine).

*4.1.2. Characterisation data for **1a** and **2a***

For **1a**. FABMS (+): 345 [M^+]. $[\alpha]_D = -109°$ (22 °C, $c = 0.68$g 100 ml^{-1}, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 250 MHz) [28]: $\delta = 3.10$ (dd, $J = 10.8$ and 7.2 Hz, 1H, –CH_2S), 3.25 (dd, $J = 10.8$ and 3.0 Hz, 1H, –CH_2S), 3.43 (d, $J = 12.6$ Hz, 1H, –N–CH_2–S–), 3.60 (d, $J =$ 12.6 Hz, 1H, –N–CH_2–S–), 3.70 (s, 3H, Me), 4.00–4.10 (m, 2H, C_5H_4), 4.14 (s, 5H, C_5H_5), 4.16–4.30 (m, 5H, C_5H_4, >CH–, CH_2N). $R_f = 0.66$ (Et_2O).

For **2a**. Anal. Found: C, 43.40; H, 5.78; N, 9.38. Calc. for $C_{11}H_{18}N_2O_4S_2$: C, 43.12; H, 5.92; N, 9.14%. FABMS (+): 160 [M^+]. $[\alpha]_D = -129°$ (22 °C, $c =$ 0.25g 100 ml^{-1} $CHCl_3$). IR (NaCl, cm^{-1}): ν(COO) 1735. ^{1}H-NMR ($CDCl_3$, 200 MHz) [28]: $\delta = 4.30$ (dd, $J = 7.2$ and 3.2 Hz, 2H, CH_2N), 3.2–3.0 (m, 6H), 3.65 (s, 6H), 4.15 (m, 4H). ^{13}C{^{1}H}-NMR ($CDCl_3$, 50 MHz) [28]: $\delta = 32.6$ (S–CH_2), 52.6 (CH_3), 57.4 (OCH_2), 67.1 (>CH), 73.1 (–N–CH_2–S), 171.4 (COO). $R_f = 0.6$ (Et_2O).

*4.1.3. Preparation of **1b**, **2b** and **3b***

Ferrocene (0.5 g, 2.69×10^{-3} mol), L-cysteine ethyl ester hydrochloride (2.5 g, 13.4×10^{-3} mol) and paraformaldehyde (1.6 g, 53.3×10^{-3} mol) were dissolved in trifluoroacetic acid (25 ml) at 0 °C. The solution was allowed to warm to r.t. and stirred for 6 h. The solvent was evaporated in vacuo under 45 °C, whereupon water (50 ml) was added and brought to neutral pH with $NaHCO_3$. The crude was extracted with Et_2O (3×50 ml), the organic solvent dried over Na_2SO_4 and evaporated in vacuo to afford a red–brown oil. Purification by SiO_2-column chromatography (with hexane–Et_2O, 9:1 v/v) yielded **1b** as a gummy material (0.32 g, 33%), (hexane–Et_2O, 7:3 v/v) **3b** (0.13g, 9%) and *N*,*N*′-methylenebisthiazolidine diethyl ester (**2b**) (1.7 g, 76%, calculated from L-cysteine).

*4.1.4. Characterisation data for **1b**, **2b** and **3b***

For **1b**. FABMS (+): 359 [M]. $[\alpha]_D = -139°$ (22 °C, $c = 1.0$ g 100 ml^{-1}, CH_2Cl_2). IR (NaCl disks, cm^{-1}): ν(COO) 1741. ^{1}H-NMR ($CDCl_3$, 200 Hz) [28]: $\delta = 1.26$ (t, $J = 7.4$, 3H, CH_3), 3.10 (dd, $J = 10.6$ and 7.2 Hz, 1H, –CH_2S), 3.24 (dd, $J = 10.6$ and 3.5 Hz, 2H, –CH_2S), 3.43 (d, $J = 12.4$ Hz, 2H, N–CH_2S), 3.59 (d, $J = 12.4$ Hz, 1H, N–CH_2S), 4.04 (m, 2H, –OCH_2–), 4.11 (s, 5H, C_5H_5), 4.14 (s, 2H, –CH_2–N–), 4.18 (s, 2H, H^3 and H^4), 4.21 (s, 2H, H^2 and H^5), 4.29 (m, 1H, >CH–). ^{13}C{^{1}H}-NMR ($CDCl_3$, 50 MHz) [28]: $\delta =$ 14.17 (–CH_3), 32.42 (–S–CH_2–), 53.03 (–OCH_2–), 58.56 (–CH_2–N), 61.26 (–N–CH_2–S–), 68.25 and 68.42 (C^3 and C^4), 68.60 (C_5H_5), 82.75 (C^1), 69.91 (C^5), 69.95 (C^2), 170.83 (–COO). $R_f = 0.76$ (Et_2O).

For **2b**. Anal. Found: C, 46.89; H, 6.40; N, 8.57. Calc. for $C_{13}H_{22}N_2O_4S_2$: C, 46.69; H, 6.63; N, 8.38%. MS; m/z: (%): 334 (3), 174 (100), 146 (25), 59 (53). $[\alpha]_D = -134°$ (22 °C, $c = 1.0$ g 100 ml^{-1}, $CHCl_3$). IR (NaCl disks, cm^{-1}): 2951, 1739, 1436, 1287, 1221, 1203, 1176, 1079. ^{1}H-NMR ($CDCl_3$, 200 MHz) [28]: $\delta = 1.28$ (t, $J = 7.2$ Hz, 6H, $2CH_3$), 4.36 (dd, $J = 7.8$ and 3.6 Hz, 2H, N–CH_2–N), 3.3–3.1 (m, 6H), 4.23 (m, 8H). ^{13}C{^{1}H}-NMR ($CDCl_3$ 50 MHz) [30]: $\delta = 14.2$ (CH_3), 32.6 (CH_2), 57.4 (CH_2), 61.3 (CH_2), 67.1 (CH), 170.8 (C=O), 73.0 (CH_2). $R_f = 0.65$ (Et_2O).

For **3b**. ^{1}H-NMR ($CDCl_3$, 200 MHz) [29]: $\delta = 1.26$ (t, $J = 7.4$ Hz, 6H, $2CH_3$), 3.23 (dd, $J = 10.8$ and 7.4 Hz, 2H, –CH_2S), 3.10 (dd, $J = 10.8$ and 3.2 Hz, 2H, –CH_2S), 3.40 and 3.55 (d, $J = 12.8$, 2H, –N–CH_2–S) and 3.95–4.15 (m, 18H, 2(H^2, H^3,H^4, H^5, >CH,–CH_2 and OCH_2–)). ^{13}C{^{1}H}-NMR ($CDCl_3$, 50 MHz) [30]: $\delta = 14.2$ (CH_3), 34.2 (–CH_2–S), 58.6 (–OCH_2), 61.2 (–N–CH_2), 52.8 (–N–CH_2–S), 83.2 (C^1), 69.4 (C^2 and C^5), 69.1 (C^3 and C^4), 68.4 (>CH), 170.8 (COO). $R_f = 0.55$ (Et_2O).

*4.1.5. Preparation of [Pd(η^3-C_3H_5)Br(**1a**)] (**4a**)*

A mixture of [Pd(η^3-C_3H_5)(μ-Br)]$_2$ (150 mg, 3.3×10^{-4} mol) and **1a** (228 mg, 6.6×10^{-4} mol) in CH_2Cl_2 (25 ml) was stirred for 30 min at r.t. and the resulting solution was concentrated to dryness in vacuo. The yellow solid obtained was recrystallised from Ac_2O to obtain **4a** in 50% yield (180 mg).

*4.1.6. Characterisation data for **4a***

Anal. Found: C, 39.7; H, 4.2; N, 2.5. Calc. for $C_{19}H_{24}BrFeNO_2PdS$: C, 39.85; H, 4.22; N, 2.45%. FABMS (+): 572 [M^+], 492 [$M - Br$]$^+$. $[\alpha]_D =$ $-53.0°$ (20 °C, $c = 1$ g 100 ml^{-1}, CH_2Cl_2). IR (cm^{-1}): ν(COO) 1745. ^{1}H-NMR ($CDCl_3$, 250 MHz) [28]: ferrocenyl moiety — $\delta = 3.55$–3.68 (m, 4H, –CH_2S, –N–CH_2–S–), 3.71 (s, 3H, Me), 4.11 (s, 5H, C_5H_5),

4.20–4.30 (m, 5H, C_5H_4, >CH–), 4.50 (m, 2H, CH_2N); allylic protons — $\delta = 3.14$ (br s, 1H, $H^{2'}$), 3.09 (br s, 1H, $H^{2''}$), 4.23 (br s, 1H, $H^{1'}$), 4.27 (br s, 1H, $H^{1''}$), 5.5 (m, 1H, $H^{3'}$). $^{13}C\{^1H\}$-NMR (C_6D_6, 75.4 MHz) [28]: ferrocenyl moiety — $\delta = 35.50$ (–CH_2–S), 51.9 (MeO), 68.90 (C^3 and C^4), 69.2 (C_5H_5), 70.40 (C^2 and C^5), 83.50 (C^1), 170.90 (–COO); allylic fragment — $\delta = 65.05$ (–CH_2), 115.10 [>CH–).

4.1.7. Preparation of [Pd(η³-C₃H₅)Br(1b)] (4b)

60 mg (1.3×10^{-4} mol) of [Pd(η³-C_3H_5)(μ-Br)]$_2$ was dissolved in 10 ml of CH_2Cl_2. A solution of ligand **1b** (95 mg, 2.6×10^{-4} mol) in 2 ml of CH_2Cl_2 was then added. The resulting reaction was stirred at r.t. (ca. 20 °C) for 1 h. Then, 10 ml of CH_3OH was added and the mixture was stirred at r.t. for additional 10 min to complete precipitation of the complex. The bright yellow solid formed was collected by filtration and dried under vacuum for 2 days (yield: 109 mg, 81.2%).

4.1.8. Characterisation data for 4b

Anal. Found: C, 41.0; H, 4.55; N, 2.5. Calc. for $C_{20}H_{26}NBrFeO_2SPd$: C, 40.95; H, 4.47; N, 2.39%. FABMS (+): 568.6 [M + 1], 506.1 [M + 1 − Br]. Λ_M = 21 Ω^{-1} cm^2 mol^{-1}. $[\alpha]_D = -49.5°$ (20 °C, $c = 0.1$ g 100 ml^{-1}, CH_2Cl_2). IR (cm^{-1}): ν(–COO) 1734. ^{1}H-NMR ($CDCl_3$, 500 MHz) [28]: ferrocenyl moiety — $\delta = 1.28$ (t, $J = 7.15$ Hz, 3H,–CH_3), 3.57 and 3.59 (m, 2H, –CH_2–), 4.13 (s, 5H, C_5H_5), 4.16 (s, 2H, H^3, H^4), 4.24 (s, 1H, H^2, H^5), 4.28 (s, 2H, –CH_2–N), 4.58 (m, 1H, >CH–); allylic protons — $\delta = 3.09$ (br, 2H, $H^{2'}$), 4.30 (br, 2H, $H^{1'}$), 5.50 (m, 1H, $H^{3'}$). ^{1}H-NMR (CD_2Cl_2, 500 MHz) [28]: ferrocenyl moiety — δ = 1.26 (t, $J = 7.10$ Hz, 3H,–CH_3), 3.64 and 3.58 (dd, $J = 11.14$ and 6.9 Hz, 2H, –N–CH_2–S), 4.13 (s, 5H, C_5H_5), 4.18 (s, 2H, –CH_2–N), 4.21 (s, 2H, H^3 and H^4), 4.25 (s, 2H, H^2 and H^5), 4.50 (m, 1H, >CH–), allylic protons — $\delta = 3.10$ (br, 2H, $H^{2'}$), 4.10 (br, 2H, $H^{1'}$), 5.45 (br m, 1H, $H^{3'}$). ^{1}H-NMR (C_6D_6, 500 MHz) [28]: ferrocenyl moiety — $\delta = 0.89$ (t, $J = 7.$ 0 Hz, 3H, –CH_3), 3.50 (s, 1H, H^3), 3.57 and 3.59 (m, 2H, –CH_2–), 3.59 (s, 1H, H^4), 3.60 (s, 2H, –CH_2–N), 3.86 (s, 1H, H^5), 3.90 (s, 1H, H^2), 3.97 (s, 5H, C_5H_5), 4.22 and 4.60 (dd, $J = 11.0$ and 6.5 Hz, 2H, –N–CH_2–S), 4.58 (m, 1H, >CH–), 3.70–3.90 (m, 2H, OCH_2–), allylic protons — $\delta = 4.65$ (q, $J = 8.2$ Hz, 1H, $H^{3'}$), 3.80 (br, 4H, $H^{1''}$ and $H^{2''}$). $^{13}C\{^1H\}$-NMR (C_6D_6, 125.72 MHz) [28]: ferrocenyl moiety — $\delta = 14.20$ (–CH_3), 35.40 (–CH_2–S), 53.61 (–OCH_2–), 61.01 (–CH_2–N), 64.03 (–N–CH_2–S), 66.23 (>CH–), 67.20 (C^4), 67.60 (C_5H_5), 67.90 (C^3), 68.04 (C^5), 68.70 (C^2), 81.90 (C^1), 168.92 (–COO) allylic fragment: 65.03 (–CH_2) and 102.10 (>CH–).

4.1.9. Preparation [Pd₂(μ-1a)₂Cl₄] (6a)

A mixture of $Na_2[PdCl_4]$ (92 mg, 3.1×10^{-4} mol) and **1a** (108 mg, 3.1×10^{-4} mol) in CH_3OH (25 ml) was stirred for 2 h at r.t. The precipitate formed was filtered and dried to obtain **6a** in 80.6% yield (130 mg).

4.1.10. Characterisation data for 6a

Anal. Found: C, 35.9; H, 3.8; N, 2.8. Calc. for $C_{32}H_{38}Cl_4Fe_2N_2O_4Pd_2S_2$: C, 36.78; H, 3.67; N, 2.68%. FABMS (+): 1041 [M]. IR (cm^{-1}): ν(COO–) 1734.2. ^{1}H-NMR ($CDCl_3$, 250 MHz) [28]: $\delta = 3.20$–3.45 (m, 8H, Me, (*c*-C_3H_5NS)), 3.70–3.80 (m, 12H, *c*-C_3H_5NS, CH_2–N), 4.13–4.25 (m, 18H, 2(C_5H_5), 2(C_5H_4)).

4.1.11. Preparation of (Pd₂(μ-1b)₂Cl₄] (6b)

$Na_2[PdCl_4]$ (80 mg, 2.7×10^{-4} mol) were dissolved in 30 ml of CH_3OH, then a solution containing ligand **1b** (100 mg, 2.7×10^{-4} mol) and 30 ml of CH_3OH was added slowly under continuous stirring at r.t. (20 °C). The reaction mixture was stirred at r.t. for ca. 30 min and the pale orange solid formed was collected by filtration, washed with Et_2O and air-dried (yield: 120 mg, 80.9%).

4.1.12. Characterisation data for 6b

Anal. Found: C, 39.00; H, 4.45; N, 2.73. Calc. for: $C_{34}H_{42}N_2Fe_2S_2O_4Pd_2Cl_4 \cdot \frac{1}{2}(C_4H_{10}O)$: C, 38.95; H, 4.27; N, 2.52%. FABMS (+): 1036 [M − Cl]. $\Lambda_M = 30$ Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(COO–) 1734.7. ^{1}H-NMR ($CDCl_3$, 200 MHz) [28,30]: $\delta = 1.18$ (t, $J = 7.0$ Hz, 3H, Me(Et_2O)), 1.27 (t, $J = 7.1$ Hz, 6H, 2 (CH_3–)), 3.45 (q, $J = 7.0$ Hz, 2H, –OCH_2(Et_2O)), 3.85 (br m, 4H, CH_2N), 4.17 (s, 2H, 2 H^3), 4.20 (s, 12H, 2H^4, 2(C_5H_5)), 4.21 (s, 4H, 2H^2, 2H^5), 4.42–4.50 (m, 4H, 2(–N–CH_2–S–)), 4.61 (m, 2H, >CH–). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 200 MHz) [28]: $\delta = 14.17$ (–CH_3), 35.70 (–S–CH_2–), 51.20 (–OCH_2–), 62.74 (–CH_2–N), 65.45 (–N–CH_2–S–), 68.94 (C_5H_5), 69.13 (C^3, C^4), 70.33 (C^2), 71.03 (C^5), 79.95 (C^1) and 168.90 (–COO).

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[28] Labelling of the atoms correspond to those shown in the schemes.

[29] Labelling of the atoms correspond to those shown in Fig. 1.

[30] In this case, the signal due to the protons of the –OCH_2– moiety is masked partially by the groups of signals observed in the range 3.80–4.10 ppm.