

# Study on the Lability of the $\sigma(\text{Pd-S})$ Bond of Novel Palladacycles with $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}(\text{thienyl})]^-$ Pincer Ligands

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The reaction of  $[(\text{Cp})\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(CH}_2)_n\text{-(C}_4\text{H}_3\text{S)}\}]$  ( $\text{Cp} = (\eta^5\text{-C}_5\text{H}_5)$  and  $n = 1$  (**1b**) or 2 (**1c**)) with  $\text{Na}_2[\text{PdCl}_4]$  and  $\text{NaAcO}\cdot 3\text{H}_2\text{O}$  gave  $[(\text{Cp})\text{Fe}\{(\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(CH}_2)_n\text{-(C}_4\text{H}_3\text{S)}\}\text{Cl}]$  ( $n = 1$  (**2b**) or 2 (**2c**)) with a  $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}(\text{thienyl})]^-$  ligand. The study of the reactivity of **2b** or **2c** with  $\text{PPh}_3$  under different experimental conditions has afforded the isolation of  $[(\text{Cp})\text{Fe}\{(\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(CH}_2)_n\text{-(C}_4\text{H}_3\text{S)}\}\text{Cl}(\text{PPh}_3)]$  ( $n = 1$  (**3b**) or 2 (**3c**)) and  $[(\text{Cp})\text{Fe}\{(\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(CH}_2)_n\text{-(C}_4\text{H}_3\text{S)}\}\text{-(PPh}_3)_2][\text{BF}_4]$  ( $n = 1$  (**4b**) or 2 (**4c**)) where **1b** or **1c** behave as a

bidentate  $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}]^-$  (in **3b** and **3c**) or as a terdentate  $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}(\text{thienyl})]^-$  (in **4b** and **4c**) ligand. The crystal structures of **3b** $\cdot 1/2\text{CH}_2\text{Cl}_2$ , **3c** $\cdot 2\text{H}_2\text{O}$  and **4c** $\cdot \text{CH}_2\text{Cl}_2$  confirm the mode of binding of the ligands. The results obtained from these studies and the solution behaviour of **4b** and **4c** reveal that the  $\sigma(\text{Pd-S})$  bond of **2b**, **2c**, **4b** and **4c** is more labile than in  $[(\text{Cp})\text{Fe}\{(\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2SMe)}\}\text{Cl}]$  or  $[(\text{Cp})\text{Fe}\{(\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2SMe)}\}\text{(PPh}_3)_2][\text{BF}_4]$  with a  $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}(\text{thioether})]^-$  ligand.

## Introduction

Palladium(II) complexes derived from polydentate ligands containing two or more donor atoms with different hardness have attracted great interest due to their potential hemilability,<sup>[1]</sup> which may be important in the view of their applications in different areas, including homogeneous catalysis.<sup>[2]</sup> Besides that, during the last decade the relevance of palladacycles with  $(\text{C}, \text{E})^-$  ( $\text{E} = \text{N}$  or  $\text{S}$ ),  $(\text{E}, \text{C}, \text{E})^-$  or  $(\text{C}, \text{N}, \text{E})^-$  ligands and a  $\sigma[\text{Pd-C}(\text{sp}^2, \text{aryl})]$ , or to a lesser extent a  $\sigma[\text{Pd-C}(\text{sp}^3)]$ , bond has increased considerably,<sup>[3–10]</sup> mainly due to their utility as building blocks in Macromolecular Chemistry,<sup>[3,8]</sup> or as precursors in synthesis<sup>[3,4b,5a,9]</sup> and homogeneous catalysis.<sup>[3,4h,5d,9]</sup> In addition, pallada-

cycles with antitumoral activity have also been published.<sup>[3,4f,6e]</sup>

However, despite the potential interest of the presence of three atoms of different hardness<sup>[11]</sup> bound to the metal and the prochiral nature of the ferrocenyl moiety in the cyclo-metallation process,<sup>[12]</sup> only two different types of mononuclear complexes with “ $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}]^-$ ” ligands have been reported.<sup>[13,14a]</sup> One of them,  $[(\text{Cp})\text{Fe}\{(\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(C}_6\text{H}_4\text{-2SMe)}\}\text{Cl}]$  (**2a**), is the first example of a palladacycle with a  $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}]^-$  pincer ligand that catalyzes the allylic alkylation of (*E*)-3-phenyl-2-propenyl (cinnamyl) acetate with the sodium salt of diethyl 2-methylmalonate under mild experimental conditions.<sup>[14b]</sup>

In view of this and a) the increasing interest of ferrocene derivatives containing heterocyclic systems,<sup>[15]</sup> b) the relevance of palladium(II) in the chemistry of thiophene derivatives,<sup>[16]</sup> c) the attractiveness of palladacycles with  $[\text{C}, \text{N}, \text{S}]^-$  ligands,<sup>[13,14]</sup> and d) the potential utility of palladium(II) compounds with labile Pd-S bonds in catalysis or in synthesis, we decided to study the cyclopalladation of the ferrocenyl Schiff bases  $[(\text{Cp})\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(CH}_2)_n\text{-(C}_4\text{H}_3\text{S)}\}]$  ( $n = 1$  (**1b**) or 2 (**1c**))<sup>[17]</sup> (Scheme 1), that contain a thienyl unit. Ligands **1b** and **1c** have an additional interest since they could produce different types of metallacycles. These may differ in: a) the nature of the metallated carbon  $\text{C}(\text{sp}^2, \text{ferrocene})$  or  $\text{C}(\text{sp}^2, \text{thienyl})$  (if the *anti*-(*E*)  $\rightarrow$  *syn*-(*Z*) isomerization of the ligand takes place) or b) the denticity of the ligands in the palladacycles (bi- or terdentate).

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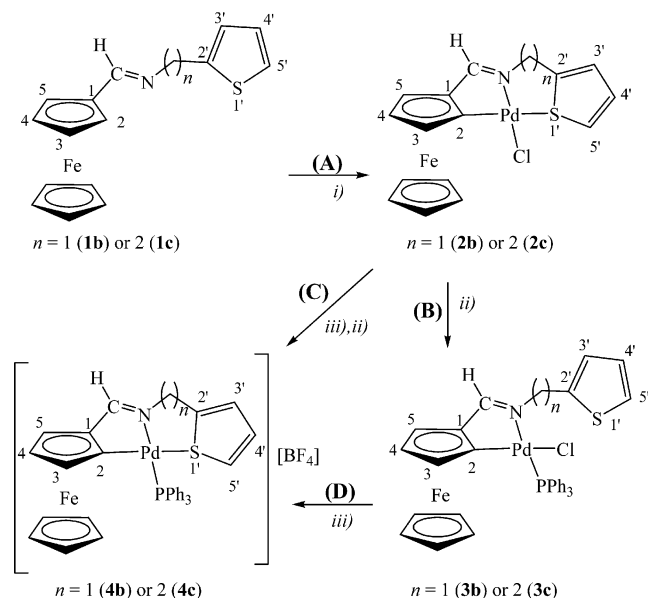
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Scheme 1. i) Equimolar amount of  $\text{Na}_2[\text{PdCl}_4]$  and  $\text{NaAcO} \cdot 3\text{H}_2\text{O}$  in methanol at 298 K for 24 h, followed by the work up of a  $\text{SiO}_2$  column using  $\text{CH}_2\text{Cl}_2$  as eluant. ii)  $\text{PPh}_3$  in a molar ratio (**2b** or **2c**): phosphane = 1 in  $\text{CH}_2\text{Cl}_2$  at 298 K. iii) Addition of a slight excess (10%) of  $\text{Tl}[\text{BF}_4]$  in acetone at 298 K, followed by the removal of the  $\text{TlCl}$  and the unreacted thallium(I) salt.

## Results and Discussion

Treatment of the corresponding ligand  $[(\text{Cp})\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-CH=N-(CH}_2)_n\text{-(C}_4\text{H}_3\text{S)}\}]$  ( $n = 1$  (**1b**) or  $2$  (**1c**))<sup>[17]</sup> with an equimolar amount of  $\text{Na}_2[\text{PdCl}_4]$  and  $\text{NaAcO} \cdot 3\text{H}_2\text{O}$  in methanol at 298 K for 24 h, followed by the work up of a  $\text{SiO}_2$  column gave small amounts of ferrocenecarbaldehyde and deep red solids (**2b** and **2c** for  $n = 1$  and  $2$ , respectively) (Scheme 1, step A). Compounds **2b** and **2c** were identified as  $[(\text{Cp})\text{Fe}\{(\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(CH}_2)_n\text{-(C}_4\text{H}_3\text{S)}\}\text{Cl}]$  ( $n = 1$  (**2b**) or  $2$  (**2c**)). In their IR spectra the band due to the stretching of the  $>\text{C=N}$ -group appeared at lower energies than for the free ligands,<sup>[17]</sup> thus suggesting the coordination of the nitrogen.

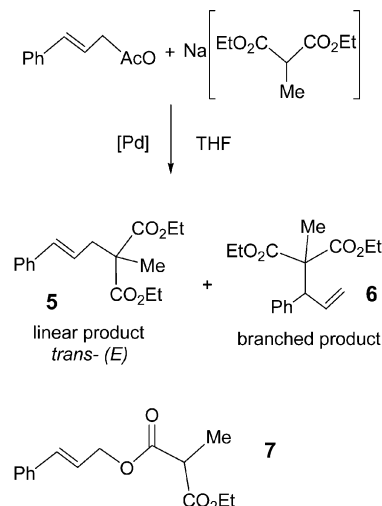
$^1\text{H}$  NMR spectra of **2b** and **2c** showed: a) a singlet in the range 7.70–7.90 ppm due to the imine proton, b) two (for **2b**) or four (for **2c**) multiplets assigned to the protons of the  $\text{-(CH}_2)_n\text{-}$  chain, and c) a group of four signals of relative intensities 5:1:1:1 due to the protons of the ferrocenyl unit. This is the typical pattern observed for palladacycles with  $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}]^-$  or  $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}]^-$  ligands.<sup>[13,14]</sup>

In the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra the resonance of the  $\text{C}^2$  nuclei exhibited low intensity and appeared at lower fields than for **1b** or **1c**.<sup>[17]</sup> Besides,  $\{^1\text{H}-^{13}\text{C}\}$ -HSQC spectra suggested the existence of a  $\sigma(\text{Pd-C}^2)$  bond in **2b** and **2c**. Furthermore, the resonances of the  $\text{C}^{2'}$  and  $\text{C}^{5'}$  atoms of the thienyl ring were high- and low-field shifted respectively compared with the free ligands.<sup>[17]</sup> All these findings indicated that in **2b** and **2c**, the Schiff bases (**1b** or **1c**) behaved

as a  $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}(\text{thienyl})]^-$  ligand. Palladium(II) complexes with this type of pincer ligands have not been reported before.

Since in **2b** and **2c** the environment of the palladium(II) is similar to that of **2a** that catalyzes the allylic alkylation of (*E*)-3-phenyl-2-propenyl (cinnamyl) acetate with the sodium salt of diethyl 2-methylmalonate,<sup>[14b]</sup> we also explored the effect produced by the presence of catalytic amounts of **2b** or **2c** in the same catalytic process. As shown in Table 1 (entries I–II), **2b** and **2c** are active in this process giving the linear *trans*-(*E*) compound (**5**), the branched derivative (**6**) and 1-cinnamyl-3-ethyl-2-methylmalonate (**7**). For **2b** and **2c** the regioselectivity of the process towards the linear product was smaller than that reported for **2a** (Table 1, entry III), but greater than those obtained when the catalytic precursors were formed in situ by treatment of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})]_2$  with **1b** or **1c**.<sup>[17]</sup>

Table 1. Results of the catalytic allylic alkylation of cinnamyl acetate with the sodium compound of diethyl 2-methylmalonate.<sup>[a,b]</sup>



Entry	[Pd]	<i>t</i> [h]	% Conv.	Molar ratio <b>5</b> : <b>6</b> : <b>7</b>	Ref.
I	<b>2b</b>	138	97.0	84:5:11 <sup>[c]</sup>	this work
II	<b>2c</b>	138	97.0	78:7:15 <sup>[c]</sup>	this work
III	<b>2a</b>	44	90.5	98.6:1.4	<sup>[14b]</sup>

[a] Experimental conditions: mixtures containing  $5.0 \times 10^{-3}$  mmol of **2b**, **2c** or **2a**, 0.5 mmol of the allylic substrate, 1 mmol of the sodium diethyl 2-methylmalonate, THF (5 mL) and decane (0.258 mmol) at 293 K. [b] Compound **7** is also formed when cinnamyl acetate is treated with the nucleophile in THF at room temperature in the absence of any catalyst. Thus, the formation of **7** reduces the interest of **2b** and **2c** in this process. [c] Determined by GC.

Since it is well known that changes in the hapticities or binding modes of pincer ligands in the complexes are relevant in view of their applications,<sup>[3,4,6,7]</sup> we also studied the reactions of **2b** (or **2c**) with  $\text{PPh}_3$ . Addition of  $\text{PPh}_3$  to **2b** or **2c** (in a 1:1 molar ratio) in  $\text{CH}_2\text{Cl}_2$  at 298 K gave  $[(\text{Cp})\text{Fe}\{(\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(CH}_2)_n\text{-(C}_4\text{H}_3\text{S)}\}\text{Cl-(PPh}_3)]$  (**3b**)·1/2 $\text{CH}_2\text{Cl}_2$  and  $[(\text{Cp})\text{Fe}\{(\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(CH}_2)_2\text{-(C}_4\text{H}_3\text{S)}\}\text{Cl-(PPh}_3)]$  (**3c**)·2 $\text{H}_2\text{O}$ , respectively (Scheme 1, step B). X-ray diffraction studies revealed that

crystals of **3b**·1/2CH<sub>2</sub>Cl<sub>2</sub> contain [(Cp)Fe{(μ-η<sup>5</sup>-Fe-η<sup>1</sup>-Pd-C<sub>5</sub>H<sub>3</sub>)-CH=N-(CH<sub>2</sub>)<sub>2</sub>-(C<sub>4</sub>H<sub>3</sub>S)}Cl(PPh<sub>3</sub>)](**3b**) (Figure 1) and CH<sub>2</sub>Cl<sub>2</sub> molecules (in a 2 to 1 ratio); while in **3c**·2H<sub>2</sub>O there is a 2:1 molar ratio of H<sub>2</sub>O and [(Cp)Fe{(μ-η<sup>5</sup>-Fe-η<sup>1</sup>-Pd-C<sub>5</sub>H<sub>3</sub>)-CH=N-(CH<sub>2</sub>)<sub>2</sub>-(C<sub>4</sub>H<sub>3</sub>S)}Cl(PPh<sub>3</sub>)] (Figure 2).

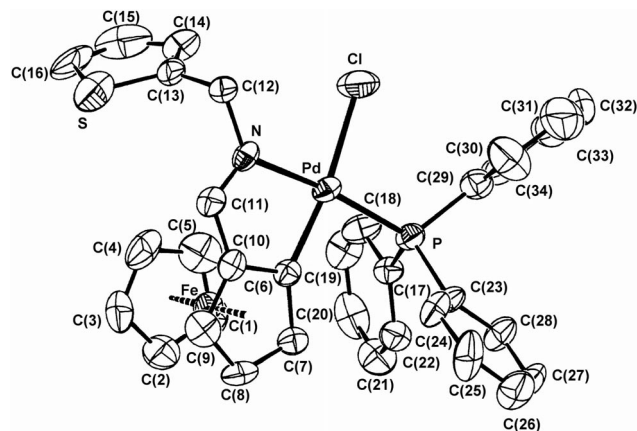


Figure 1. ORTEP plot of molecules of [(Cp)Fe{(μ-η<sup>5</sup>-Fe-η<sup>1</sup>-Pd-C<sub>5</sub>H<sub>3</sub>)-CH=N-(CH<sub>2</sub>)<sub>2</sub>-(C<sub>4</sub>H<sub>3</sub>S)}Cl(PPh<sub>3</sub>)] found in the crystal structure of **3b**·1/2CH<sub>2</sub>Cl<sub>2</sub>. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–C(6) 1.976(5), Pd–N 2.134(4), Pd–P 2.236(2), Pd–Cl 2.359(2), C(10)–C(11) 1.410(6), N–C(11) 1.270(5), N–C(12) 1.484(5), C(12)–C(13) 1.499(6), C(13)–C(14) 1.428(7), C(14)–C(15) 1.339(7), C(15)–C(16) 1.342(8), S–C(13) 1.695(6), S–C(16) 1.713(6), C(6)–Pd–N 80.3(2), C(6)–Pd–P 92.5(1), N–Pd–Cl 93.1(1), P–Pd–Cl 94.33(7), C(10)–C(11)–N 116.2(5), C(11)–N–C(12) 118.3(4), N–C(12)–C(13) 111.8(4), C(12)–C(13)–C(14) 126.3(5), C(13)–C(14)–C(15) 107.4(6), C(14)–C(15)–C(16) 121.4(7), C(15)–C(16)–S 106.8(6), C(16)–S–C(13) 93.1(3), S–C(13)–C(12) 122.0(4) and S–C(13)–C(14) 111.3(4).

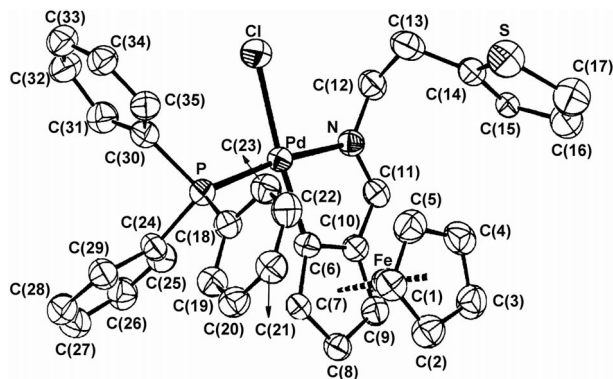


Figure 2. ORTEP plot of molecules of [(Cp)Fe{(μ-η<sup>5</sup>-Fe-η<sup>1</sup>-Pd-C<sub>5</sub>H<sub>3</sub>)-CH=N-(CH<sub>2</sub>)<sub>2</sub>-(C<sub>4</sub>H<sub>3</sub>S)}Cl(PPh<sub>3</sub>)] found in the crystal structure of **3c**·2H<sub>2</sub>O. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd–C(6) 1.993(7), Pd–N 2.111(5), Pd–P 2.235(2), Pd–Cl 2.391(3), C(10)–C(11) 1.423(9), C(11)–N 1.315(9), N–C(12) 1.469(9), C(12)–C(13) 1.527(2), C(13)–C(14) 1.565(1), C(14)–C(15) 1.375(9), C(15)–C(16) 1.527(1), C(16)–C(17) 1.286(2), S–C(14) 1.728(8), S–C(17) 1.765(1), C(6)–Pd–N 81.0(2), C(6)–Pd–P 90.3(2), N–Pd–Cl 92.9(2), P–Pd–Cl 95.65(8), C(10)–C(11)–N 115.4(6), C(11)–N–C(12) 116.5(2), N–C(12)–C(13) 113.2(6), C(12)–C(13)–C(14) 109.7(7), C(13)–C(14)–C(15) 131.0(7), S–C(14)–C(15) 112.1(6), S–C(14)–C(13) 117.0(6) and S–C(17)–C(16) 112.1(10).

In **3b** and **3c**, the palladium(II) is bound to the N and C(6) atoms of the ferrocenyl unit. A chloride and the PPh<sub>3</sub> ligand occupy the remaining two coordination sites. Bond lengths around the Pd<sup>II</sup> atom fall in the ranges reported for related palladacycles.<sup>[5b,7,18]</sup> The metallated carbon, C(6), and the P atom are in a *cis*-arrangement in good agreement with the so-called *transphobia effect*.<sup>[19]</sup>

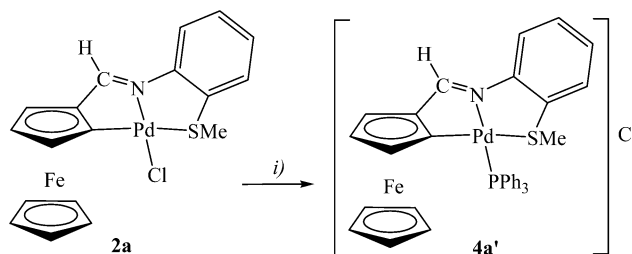
The molecules of **3b** and **3c** contain a practically planar metallacycle that forms an angle of 5.9° (in **3b**) or of 2.8° (in **3c**) with the C<sub>5</sub>H<sub>3</sub> ring of the ferrocenyl moiety.

The thienyl unit is planar and its bond lengths and angles are consistent with those reported for monosubstituted thiophene derivatives<sup>[18]</sup> and the S atom and the Cp ring are on the same side of the coordination plane of palladium(II).

Bond lengths and angles of the ferrocenyl moieties agree with the values reported for most ferrocene derivatives.<sup>[5b,7,13,14,18]</sup> The two rings are practically parallel {*tilt angles* = 2.7° (for **3b**) and 4.2° (for **3c**)} and they deviate by ca. 4.7° (in **3b**) or 7.2° (in **3c**) from the ideal eclipsed conformation. The distance Cl(1)···C(12) [3.405 (in **3b**) and 3.399 (in **3c**) Å] suggests a weak C–H···Cl interaction. The separation Fe<sup>II</sup>···Pd<sup>II</sup> {3.521 Å (for **3b**) and 3.614 Å for (**3c**)} exceeds the sum of their van der Waals radii.<sup>[20]</sup>

The position of the singlet detected in the <sup>31</sup>P{<sup>1</sup>H}-NMR spectra of **3b**·1/2CH<sub>2</sub>Cl<sub>2</sub> (δ = 37.5 ppm) and **3c**·2H<sub>2</sub>O (δ = 37.8 ppm) is similar to those of [(Cp)Fe{(μ-η<sup>5</sup>-Fe-η<sup>1</sup>-Pd-C<sub>5</sub>H<sub>3</sub>)-C(R<sup>1</sup>)=N-R<sup>2</sup>}Cl(PPh<sub>3</sub>)] (R<sup>1</sup> = H or Me and R<sup>2</sup> = phenyl or benzyl groups).<sup>[21]</sup>

The results obtained in the reactions of **2b** and **2c** with PPh<sub>3</sub> reveal that the σ[Pd–S(thienyl)] bond of **2b** and **2c** is more labile than the σ[Pd–S(thioether)] bond of **2a**, which (under identical experimental conditions) gave [(Cp)Fe{(μ-η<sup>5</sup>-Fe-η<sup>1</sup>-Pd-C<sub>5</sub>H<sub>3</sub>)-CH=N-(C<sub>6</sub>H<sub>4</sub>-2SMe)}(PPh<sub>3</sub>)]Cl (**4a'**)<sup>[7b]</sup> (Scheme 2).



Scheme 2. *i*) Addition of the equimolar amount of PPh<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.<sup>[7b]</sup>

No evidence of the cleavage of the σ(Pd–N) bond of **2b** (or **2c**) was detected by NMR when larger excesses of the entering ligand (PPh<sub>3</sub>) were used. Thus, indicating that the σ(Pd–N) bond exhibits low lability under the conditions applied. In order to force a tridentate coordination we tried to abstract the Cl<sup>–</sup> ligand by the use of Ti<sup>I</sup> salts.

Treatment of acetone solutions of **2b** or **2c** with TIBF<sub>4</sub> (10% excess) produced thallium(I) chloride. After removal of TiCl and unreacted Ti[BF<sub>4</sub>], the addition of PPh<sub>3</sub> at 298 K gave [(Cp)Fe{(μ-η<sup>5</sup>-Fe-η<sup>1</sup>-Pd-C<sub>5</sub>H<sub>3</sub>)-CH=N-(CH<sub>2</sub>)<sub>n</sub>-(C<sub>4</sub>H<sub>3</sub>S)}(PPh<sub>3</sub>)] [BF<sub>4</sub>] [*n* = 1 (**4b**) or 2 (**4c**)] (Scheme 1, step C). These compounds were also obtained when the corre-



sponding complex **3** (in acetone) was treated with a 10% excess of  $\text{Ti}[\text{BF}_4]$  (Scheme 1, step **D**). Elemental analyses and mass spectra were consistent with the proposed formulae and their IR spectra showed typical absorptions of the  $[\text{BF}_4]^-$  anion.<sup>[22]</sup>

The crystal of  $4\text{c} \cdot \text{CH}_2\text{Cl}_2$  contains a 1:1:1 array of  $[(\text{Cp})\text{Fe}\{\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3\}\text{-CH=N-(CH}_2)_2\text{-C}_4\text{H}_3\text{S}\}\text{(PPh}_3\text{)}]^+ [\text{BF}_4]^-$  and molecules of  $\text{CH}_2\text{Cl}_2$ . In the cations (Figure 3), the  $\text{Pd}^{\text{II}}$  atom is bound to the N, S and C(6) atoms of the ferrocenyl unit and the  $\text{PPh}_3$  occupies the fourth coordination site. The  $\text{Pd-C(6)}$  and  $\text{Pd-N}$  bond lengths and the bond angle  $\text{C(6)-Pd-N}$  is similar to that of  $3\text{c} \cdot 2\text{H}_2\text{O}$ . However, in  $4\text{c} \cdot \text{CH}_2\text{Cl}_2$  the  $\text{Pd-P}$  bond is longer [2.264(1) Å] than in  $3\text{c} \cdot 2\text{H}_2\text{O}$  [2.235(2) Å].

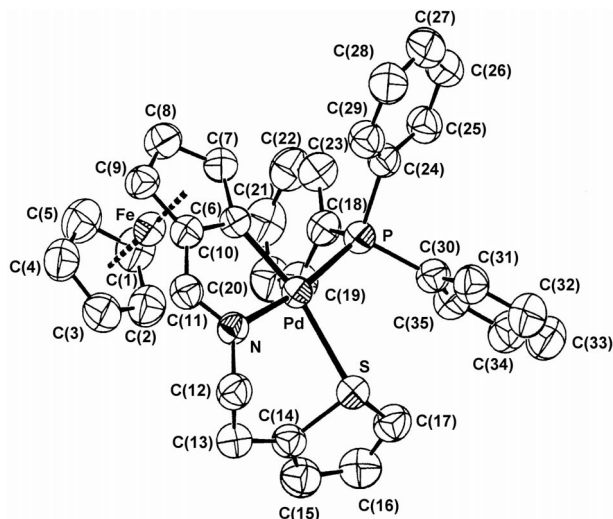


Figure 3. ORTEP plot of the heterodimetallic cations found in the crystal structure of  $[(\text{Cp})\text{Fe}\{\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3\}\text{-CH=N-(CH}_2)_2\text{-C}_4\text{H}_3\text{S}\}\text{(PPh}_3\text{)}]^+ (4\text{c}) \cdot \text{CH}_2\text{Cl}_2$ . The  $\text{CH}_2\text{Cl}_2$  molecule and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg):  $\text{Pd-C(6)}$  1.995(4),  $\text{Pd-N}$  2.123(3),  $\text{Pd-P}$  2.264(1),  $\text{Pd-S}$  2.458(1),  $\text{C(10)-C(11)}$  1.434(6),  $\text{C(11)-N}$  1.276(5),  $\text{N-C(12)}$  1.476(5),  $\text{C(12)-C(13)}$  1.504(6),  $\text{C(13)-C(14)}$  1.493(6),  $\text{C(14)-C(15)}$  1.329(7),  $\text{C(15)-C(16)}$  1.426(8),  $\text{C(16)-C(17)}$  1.328(7),  $\text{C(17)-S}$  1.719(5),  $\text{C(6)-Pd-N}$  80.8(1),  $\text{N-Pd-S}$  85.76(9),  $\text{S-Pd-P}$  103.9(4),  $\text{P-Pd-C(6)}$  90.6(1),  $\text{Pd-C(6)-C(10)}$  111.3(3),  $\text{C(6)-C(10)-C(11)}$  117.1(3),  $\text{C(10)-C(11)-N}$  116.7(4) and  $\text{C(11)-N-C(12)}$  120.0(3).

The cationic arrays of  $4\text{c} \cdot \text{CH}_2\text{Cl}_2$  contain a [5.6.5.5] tetracyclic system which is formed by the thienyl unit, a six-membered chelate ring, a five-membered palladacycle and the 1,2-disubstituted ring of the ferrocenyl unit. The six-membered ring has a boat conformation in which the S and the C(12) atoms are out of the plane defined by the remaining atoms of this cycle in the same direction as the iron(II).

The two pentagonal rings of the “ $(\text{Cp})\text{Fe}(\eta^5\text{-C}_5\text{H}_3)$ ” moiety are practically parallel (tilt angle =  $5.0^\circ$ ) and they deviate  $1.4^\circ$  from the ideal eclipsed conformation. The separation  $\text{Fe}^{\text{II}} \cdots \text{Pd}^{\text{II}}$  atoms (3.564 Å), exceeds the sum of their van der Waals radii.<sup>[20]</sup>

The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **4b** and  $4\text{c} \cdot \text{CH}_2\text{Cl}_2$  in  $\text{CDCl}_3$  at 298 K showed a singlet at higher fields [ $\delta$  = 35.8 ppm (for **4b**) and 35.4 ppm (for  $4\text{c} \cdot \text{CH}_2\text{Cl}_2$ )] than for

**3b** ( $\delta$  = 37.5 ppm) and **3c** ( $\delta$  = 37.8 ppm). This trend is similar to those reported for:  $[(\text{Cp})\text{Fe}\{\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3\}\text{-CH=N-(CH}_2)_n\text{-NMe}_2\}\text{(PPh}_3\text{)}][\text{BF}_4]$  and  $[(\text{Cp})\text{Fe}\{\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3\}\text{-CH=N-(CH}_2)_n\text{-NMe}_2\}\text{Cl(PPh}_3\text{)}]$  that contain a  $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{N}']^-$  and a  $\sigma[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}]^-$  ligand, respectively.<sup>[23]</sup>

Proton-NMR spectra (500 MHz) of **4b** and  $4\text{c} \cdot \text{CH}_2\text{Cl}_2$  in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  at 298 K were more complex than expected and exhibited broad signals. This finding is in sharp contrast with that observed for  $[(\text{Cp})\text{Fe}\{\mu\text{-}\eta^5\text{-Fe-}\eta^1\text{-Pd-C}_5\text{H}_3\}\text{-CH=N-(C}_6\text{H}_4\text{-2SMe)}\}\text{(PPh}_3\text{)}][\text{BF}_4]$  (**4a**) whose  $^1\text{H}$ -NMR spectra showed sharp and well-defined signals under identical conditions.<sup>[7b]</sup> At 183 K the resolution of the spectra improved and for **4b** at least two sets of superimposed signals were detected. It is interesting to note that when  $\text{CD}_2\text{Cl}_2$  solutions of **3b** (or **3c**) were treated with the equimolar amount of NaOD (in  $[\text{D}_4]$ methanol), their  $^1\text{H}$  NMR spectra at 298 K were identical to those of **4b** (or **4c**). This indicates that the solution behaviour of **3b** and **3c** in the presence of NaOD is similar to those of **4b** and **4c**, respectively. Unfortunately, experimental data available at present does not allow us to clarify the origin of the solution behaviour of **4b** and **4c**.

## Conclusions

A new type of palladacycles with  $[\text{C}(\text{sp}^2, \text{ferrocene}), \text{N}, \text{S}(\text{thienyl})]^-$  ligands have been prepared and characterized. The study of the alkylation of (*E*)-3-phenyl-2-propenyl acetate with sodium diethyl 2-methylmalonate in the presence of catalytic amounts of **2b** or **2c** produced linear *trans*-(*E*) compound **5** and the branched derivative **6** as the major products. The regioselectivity of these reactions were smaller than that reported for **2a**<sup>[14b]</sup> and the amount of the side-product **7** increased.

On the other hand, the study of: i. the reactivity of **2b** and **2c** with  $\text{PPh}_3$  and ii. the solution behaviour of **4b** and  $4\text{c} \cdot \text{CH}_2\text{Cl}_2$  have shown that  $\sigma[\text{Pd-S}(\text{thienyl})]$  bond of **2b** and **2c**, **4b** and  $4\text{c} \cdot \text{CH}_2\text{Cl}_2$  is more labile than the  $\sigma[\text{Pd-S}(\text{thioether})]$  bond of **2a** and **4a**.<sup>[7b]</sup> The lability of the  $\sigma(\text{Pd-S})$  bond of **2b** and **2c** is interesting in view of their potential utility as precursors in organometallic synthesis, since it may ease the coordination of an entering ligand such as CO, alkynes, alkenes or isonitriles. In fact, preliminary studies on the reactivity of **2b** and **2c** with symmetric alkynes reveal that for **2b** and **2c** the insertion of hex-3-yne takes place under milder experimental conditions than for **2a**, and it does not require the presence of the highly toxic  $\text{Ti}^{\text{I}}$  salts. This increases the relevancy of the palladacycles presented here. Further work in this field is currently under way.

## Experimental Section

**Materials and Methods:** Ligands **1b** and **1c** were synthesized as reported before.<sup>[17]</sup> The sodium salt of diethyl 2-methylmalonate (0.5 M in THF) was prepared from diethyl 2-methylmalonate and

NaH in THF at 273 K. The remaining reagents used in this work were obtained from commercial sources and used as received. The solvents were dried and distilled before use.<sup>[24]</sup>

**Caution:** The preparation of **4b** and **4c** require the use of the *highly hazardous* salt,  $\text{Ti}[\text{BF}_4]$ , which should be handled with great care!

Elemental analyses (C, H, N, S) were carried out at the *Serveis de Recursos Científics i Tècnics* (Univ. Rovira i Virgili, Tarragona). Mass spectra ( $\text{ESI}^+$ ) were performed at the *Servei d'Espectrometria de Masses* (Univ. Barcelona) with a Waters Micromass instruments. IR spectra were recorded with a Nicolet 400FTIR instrument using KBr pellets. Routine  $^1\text{H}$ - and  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were obtained with a Gemini 200 MHz, a Bruker 250-DXR or a Mercury 400 MHz instrument. High resolution mono- and two-dimensional [ $^1\text{H}$ - $^1\text{H}$ ]-NOESY and COSY and [ $^1\text{H}$ - $^{13}\text{C}$ ]-HSQC and HMBG NMR experiments were recorded with either a Varian VRX-500 or with a Bruker Avance DMX 500 instruments at 298 K. Except where quoted: *a*) the solvent used for the NMR studies was  $\text{CDCl}_3$  (99.8%) and  $\text{SiMe}_4$  was used as internal reference and *b*)  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopic data presented for each compound was obtained at 298 K with a Varian VRX-500 or with a Bruker Avance DMX 500 instruments. NMR studies at 183 K were carried out with a Bruker Avance DMX 500 instrument using  $\text{CD}_2\text{Cl}_2$  (99.8%) as solvent.  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **3b**· $1/2\text{CH}_2\text{Cl}_2$ , **3c**· $2\text{H}_2\text{O}$ , **4b**, and **4c**· $\text{CH}_2\text{Cl}_2$  [solutions in  $\text{CDCl}_3$  (99.9%),  $\text{P}(\text{OMe})_3$  as reference,  $\delta^{31}\text{P}\{\text{P}(\text{OMe})_3\} = 140.17$  ppm] were obtained with a Bruker 250-DXR instrument. The product distribution of the alkylation experiments was measured on a Trace-DQS apparatus equipped with a HP-5 column (25 m of length, 0.5  $\mu\text{m}$  of film thickness and 0.2 mm of inner diameter) and an electron-impact mass detector.

#### Preparation of the Compounds

**[(Cp)Fe{( $\mu$ - $\eta^5$ -Fe- $\eta^1$ -Pd-C $_5$ H $_3$ )-CH=N-(CH $_2$ ) $_n$ -(C $_4$ H $_9$ S)}]Cl] (**1**) (**2b**) or **2** (**2c**):** A  $1.3 \times 10^{-3}$  mol amount of the corresponding ligand (402 mg of **1b** or 420 mg of **1c**),<sup>[17]</sup>  $\text{Na}_2[\text{PdCl}_4]$  (383 mg,  $1.3 \times 10^{-3}$  mol) and  $\text{NaAcO} \cdot 3\text{H}_2\text{O}$  (177 mg,  $1.3 \times 10^{-3}$  mol) were dissolved in 40 mL of methanol. The reaction mixture was protected from the light with aluminium foil and stirred at 298 K for 24 h. The red solid formed was collected by filtration and air-dried overnight. This material was then dissolved in  $\text{CH}_2\text{Cl}_2$  ( $\approx 20$  mL) and passed through a  $\text{SiO}_2$  column (2.0 cm  $\times$  3.0 cm). Elution with  $\text{CH}_2\text{Cl}_2$  produced the release of a red band that was collected and concentrated to dryness on a rotary evaporator. The solid formed was collected and dried; yields: 363 mg (62%) for **2b** and 356 mg (59%) for **2c**. Characterization data for **2b**:  $\text{C}_{16}\text{H}_{14}\text{ClFeNPdS}$  (450.1) calcd. for  $\text{C}_{16}\text{H}_{14}\text{ClFeNPdS}$ : C 42.70, H 3.14, N 3.11, S 7.12%; found C 42.6, H 3.2, N 3.05, S 6.9%. MS ( $\text{ESI}^+$ ):  $m/z = 413.9\{[\text{M}] - \text{Cl}\}^+$  and  $454.9\{[\text{M}] - \text{Cl} + (\text{CH}_3\text{CN})\}^+$ . For **2c**:  $\text{C}_{17}\text{H}_{16}\text{ClFeNPdS}$  (464.1): calcd. for  $\text{C}_{17}\text{H}_{16}\text{ClFeNPdS}$ : C 44.00, H 3.47, N 3.02, S 6.91%; found C 43.9, H 3.5, N 3.0, S 6.85%. MS ( $\text{ESI}^+$ ):  $m/z = 427.9\{[\text{M}] - \text{Cl}\}^+$  and  $468.9\{[\text{M}] - \text{Cl} + \text{CH}_3\text{CN}\}^+$ .

**[(Cp)Fe{( $\mu$ - $\eta^5$ -Fe- $\eta^1$ -Pd-C $_5$ H $_3$ )-CH=N-(CH $_2$ ) $_n$ -(C $_4$ H $_9$ S)}]Cl(PPh $_3$ )] (**3b**)· $1/2\text{CH}_2\text{Cl}_2$ :** To a solution formed by **2b** (81 mg,  $1.8 \times 10^{-4}$  mol) and 15 mL of  $\text{CH}_2\text{Cl}_2$ , the equimolar amount of  $\text{PPh}_3$  was added. The reaction mixture was stirred at 298 K for 30 min. The undissolved material were removed by filtration and the filtrate was concentrated to dryness on a rotary evaporator giving an orange solid that was collected and dried in vacuo for 2 d; yield 120 mg (88%). Crystals suitable for X-ray analyses were obtained by evaporation of a  $\text{CH}_2\text{Cl}_2$  solution of the solid. Characterization data:  $\text{C}_{34}\text{H}_{29}\text{ClFeNPdS} \cdot 1/2\text{CH}_2\text{Cl}_2$  (754.8) calcd. for: C 54.9, H 4.01, N 1.86, S 4.25%; found C 55.0, H 4.1, N 1.8, S 4.15%. MS ( $\text{ESI}^+$ ):  $m/z = 675.9\{[\text{M}] - (1/2\text{CH}_2\text{Cl}_2) - \text{Cl}\}^+$ .

**[(Cp)Fe{( $\mu$ - $\eta^5$ -Fe- $\eta^1$ -Pd-C $_5$ H $_3$ )-CH=N-(CH $_2$ ) $_2$ -(C $_4$ H $_9$ S)}]Cl(PPh $_3$ )] (**3c**)· $2\text{H}_2\text{O}$ :** This product was obtained as described for **3b**· $1/2\text{CH}_2\text{Cl}_2$  but using **2c** (97 mg,  $2.1 \times 10^{-4}$  mol) as starting material and the equimolar amount of  $\text{PPh}_3$ ; yield 148 mg, (92%) for **3c**· $2\text{H}_2\text{O}$ . This solid was dissolved in ethanol and evaporation of the solvent at 298 K produced crystals of **3c**· $2\text{H}_2\text{O}$ . Characterization data:  $\text{C}_{35}\text{H}_{35}\text{ClFeNO}_2\text{PPdS}$  (762.4): calcd. for C 55.14, H 4.63, N 1.84, S 4.21%; found C 55.2, H 4.75, N 1.8, S 4.15%. MS ( $\text{ESI}^+$ ):  $m/z = 690.0\{[\text{M}] - (2\text{H}_2\text{O}) - \text{Cl}\}^+$ .

**[(Cp)Fe{( $\mu$ - $\eta^5$ -Fe- $\eta^1$ -Pd-C $_5$ H $_3$ )-CH=N-(CH $_2$ ) $_n$ -(C $_4$ H $_9$ S)}](PPh $_3$ )]-[BF $_4$ ] (**4n**) (**4b**) or **2** (**4c**):** These products can be obtained using two alternative procedures that differ in the nature of the starting material: **2b** or **2c**: Method A; **3b**· $1/2\text{CH}_2\text{Cl}_2$  or **3c**· $2\text{H}_2\text{O}$ : Method B.

**Method A:** **2b** (91 mg,  $2.0 \times 10^{-4}$  mol) or **2c** (93 mg,  $2.0 \times 10^{-4}$  mol) was dissolved in 25 mL of acetone, then 64 mg ( $2.2 \times 10^{-4}$  mol) of  $\text{TiBF}_4$  were added (*caution!*). The mixture was protected from the light with aluminium foil and stirred at 298 K for 1 h. Afterwards, it was filtered with Whatman paper and the filtrate was concentrated to dryness on a rotary evaporator. The residue was treated with 15 mL of  $\text{CH}_2\text{Cl}_2$  and stirred for 10 min. The undissolved materials were filtered out and discarded. Afterwards, 53 mg ( $2.0 \times 10^{-4}$  mol) of  $\text{PPh}_3$  were added to the filtrate and the mixture was stirred at 298 K for 20 min. Concentration of the solution to dryness on a rotary evaporator gave **4b** or **4c** as crystalline materials that were collected and dried in vacuo for 2 d; yields: 128 mg (84%) for **4b** and 150 mg (79%) for **4c**· $\text{CH}_2\text{Cl}_2$ .

**Method B:** To a solution containing 76 mg of **3b**· $1/2\text{CH}_2\text{Cl}_2$  ( $1.0 \times 10^{-4}$  mol) or 91 mg of **3c**· $2\text{H}_2\text{O}$  ( $1.2 \times 10^{-4}$  mol) and 15 mL of acetone,  $\text{Ti}[\text{BF}_4]$  [32 mg ( $1.1 \times 10^{-4}$  mol) for **4b** or 38 mg ( $1.3 \times 10^{-4}$  mol) for **4c**] was *carefully* added. The mixture was protected from the light with aluminium foil and stirred for 1 h at 298 K. After this period, the  $\text{TiCl}$  formed was removed by filtration with Whatman paper and the filtrate was concentrated to dryness on a rotary evaporator. The deep orange for **3b** (or red for **3c**) solids obtained were then treated with 15 mL of  $\text{CH}_2\text{Cl}_2$ . The undissolved materials were removed by filtration and slow evaporation of the filtrate gave **4b** and **4c**. These products were collected and dried in vacuo for 2 d; yields: 61 mg (80%) for **4b** and 79 mg (76%) for **4c**· $\text{CH}_2\text{Cl}_2$ .

**4b:**  $\text{C}_{34}\text{H}_{29}\text{BF}_4\text{FeNPdS}$  (763.9): calcd. C 53.47, H 3.83, N 1.83, S 4.20%; found C 53.6, H 3.9, N 1.8, S 4.15%. MS ( $\text{ESI}^+$ ):  $m/z = 676.1\{[\text{M}] - [\text{BF}_4] - \text{Cl}\}^+$ . For **4c**· $\text{CH}_2\text{Cl}_2$ :  $\text{C}_{36}\text{H}_{33}\text{BCl}_2\text{F}_4\text{FeNPdS}$  (862.7): calcd. C 50.13, H 3.86, N 1.62, S 3.72%; found C 49.9, H 3.8, N 1.6, S 3.65%. MS ( $\text{ESI}^+$ ):  $m/z = 690.1\{[\text{M}] - (\text{CH}_2\text{Cl}_2) - [\text{BF}_4] - \text{Cl}\}^+$ .

**Catalytic Studies:** The catalytic reactions were performed under nitrogen at 298 K in THF (5 mL) using  $5.0 \times 10^{-3}$  mmol of **2b** or **2b**, cinnamyl acetate (0.5 mmol) and sodium salt of diethyl 2-methylmalonate (1.0 mmol). The reaction was monitored by taking samples from the reaction mixture. Each aliquot was diluted with  $\text{Et}_2\text{O}$ , washed with  $\text{H}_2\text{O}$  and dried with  $\text{MgSO}_4$ . Aliquots then were analysed by GC using decane (0.258 mmol) as the internal standard.

**Crystallography:** A prismatic crystal (sizes in Table 2) of **3b**· $1/2\text{CH}_2\text{Cl}_2$ , **3c**· $2\text{H}_2\text{O}$  or **4c**· $\text{CH}_2\text{Cl}_2$  was selected and mounted on a Enraf-Nonius CAD-4 (for **3b**· $1/2\text{CH}_2\text{Cl}_2$ ) or on a MAR345 diffractometer (for **3c**· $2\text{H}_2\text{O}$  or **4c**· $\text{CH}_2\text{Cl}_2$ ) with a image plate detector. For **3b**· $1/2\text{CH}_2\text{Cl}_2$ , unit cell parameters were determined from automatic centring of 25 reflections in the range  $12^\circ < \theta < 21^\circ$ ; while for **3c**· $2\text{H}_2\text{O}$  and **4c**· $\text{CH}_2\text{Cl}_2$  these parameters were obtained from 210 (for **3c**· $2\text{H}_2\text{O}$ ) and 4427 (for **4c**· $\text{CH}_2\text{Cl}_2$ ) reflections in the

Table 2. Crystal data and details of the refinement of the crystal structures of compounds  $[(\text{Cp})\text{Fe}\{(\mu-\eta^5\text{-Fe}-\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(CH}_2\text{)}_2\text{-(C}_4\text{H}_3\text{S)}\}\text{Cl(PPh}_3\text{)}](\mathbf{3b})\cdot 1/2\text{CH}_2\text{Cl}_2$ ,  $[(\text{Cp})\text{Fe}\{(\mu-\eta^5\text{-Fe}-\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(CH}_2\text{)}_2\text{-(C}_4\text{H}_3\text{S)}\}\text{Cl(PPh}_3\text{)}](\mathbf{3c})\cdot 2\text{H}_2\text{O}$  and  $[(\text{Cp})\text{Fe}\{(\mu-\eta^5\text{-Fe}-\eta^1\text{-Pd-C}_5\text{H}_3)\text{-CH=N-(CH}_2\text{)}_2\text{-(C}_4\text{H}_3\text{S)}\}\text{Cl(PPh}_3\text{)}](\mathbf{4c})\cdot \text{CH}_2\text{Cl}_2$ .

	<b>3b</b> ·1/2CH <sub>2</sub> Cl <sub>2</sub>	<b>3c</b> ·2H <sub>2</sub> O	<b>4c</b> ·CH <sub>2</sub> Cl <sub>2</sub>
Crystal sizes /mm × mm × mm	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1
Empirical formula	C <sub>69</sub> H <sub>60</sub> Cl <sub>4</sub> Fe <sub>2</sub> N <sub>2</sub> P <sub>2</sub> D <sub>2</sub> S <sub>2</sub>	C <sub>35</sub> H <sub>35</sub> ClFeNO <sub>2</sub> PPdS	C <sub>36</sub> H <sub>33</sub> BCl <sub>2</sub> F <sub>4</sub> FeNPPdS
Formula weight	1509.55	762.37	862.62
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1̄	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	13.066(5)	10.296(7)	18.829(8)
<i>b</i> /Å	25.341(3)	13.599(8)	11.249(3)
<i>c</i> /Å	10.311(3)	13.979(8)	18.829(5)
<i>a</i> /deg	90	106.35(3)	90
<i>β</i> /deg	102.29(4)	106.70(3)	116.12(2)
<i>γ</i> /deg	90	101.30(4)	90
<i>T</i> /K	293(2)	293(2)	293(2)
<i>λ</i> /Å	0.71073	0.71073	0.71073
<i>V</i> /Å <sup>3</sup>	3336(3)	1715(2)	3581(2)
<i>D</i> <sub>calcd.</sub> /Mg × m <sup>-3</sup>	1.503	1.474	1.600
<i>μ</i> /mm <sup>-1</sup>	1.269	1.163	1.208
<i>F</i> (000)	1524	776	1736
<i>θ</i> range for data collection/deg	2.18 to 29.97	2.69 to 29.00	2.55 to 29.99
Number of collected reflections	9698	10851	24627
Number of unique reflections { <i>R</i> <sub>int</sub> (on <i>I</i> )}	9698 {0.0563}	7370 {0.0647}	8729 {0.0661}
Number of parameters	388	388	433
Goodness of fit on <i>F</i> <sup>2</sup>	0.768	1.143	1.245
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0394, <i>wR</i> <sub>2</sub> = 0.0523	<i>R</i> <sub>1</sub> = 0.0695, <i>wR</i> <sub>2</sub> = 0.1946	<i>R</i> <sub>1</sub> = 0.0536, <i>wR</i> <sub>2</sub> = 0.1281
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.2752, <i>wR</i> <sub>2</sub> = 0.0840	<i>R</i> <sub>1</sub> = 0.0695, <i>wR</i> <sub>2</sub> = 0.1992	<i>R</i> <sub>1</sub> = 0.0538, <i>wR</i> <sub>2</sub> = 0.1281

range 3° < *θ* < 31°). In the three cases the unit cell parameters were refined by least-squares method. Intensities were collected with graphite-monochromatized Mo-*K*<sub>α</sub> radiation.

The number of reflections measured was 9698 for **3b**·1/2CH<sub>2</sub>Cl<sub>2</sub>, 10851 for **3c**·2H<sub>2</sub>O and 24627 for **4c**·CH<sub>2</sub>Cl<sub>2</sub> (in the ranges 2.18° ≤ *θ* ≤ 29.97°, 2.69° ≤ *θ* ≤ 29.00° and 2.55° ≤ *θ* ≤ 29.99°, respectively). The number of non-equivalent reflections by symmetry was 7370 for **3c**·2H<sub>2</sub>O {*R*<sub>int</sub>(on *I*) = 0.064} and 8729 for **4c**·CH<sub>2</sub>Cl<sub>2</sub> {*R*<sub>int</sub>(on *I*) = 0.066}, and the number of reflections assumed as observed applying the condition *I* > 2σ(*I*) was 9698, 6592 and 8685 for **3b**·1/2CH<sub>2</sub>Cl<sub>2</sub>, **3c**·2H<sub>2</sub>O and **4c**·CH<sub>2</sub>Cl<sub>2</sub>, respectively. Lorentz-polarization corrections were made and for **3b**·1/2CH<sub>2</sub>Cl<sub>2</sub> and **4c**·CH<sub>2</sub>Cl<sub>2</sub> absorption corrections were also carried out.

The structures were solved by Direct Methods, using SHELXS computer program<sup>[25]</sup> and refined by full-matrix least-squares method with the SHELX97 computer program<sup>[26]</sup> using 9698 (**3b**·1/2CH<sub>2</sub>Cl<sub>2</sub>), 10851 (for **3c**·2H<sub>2</sub>O) and 24627 (for **4c**·CH<sub>2</sub>Cl<sub>2</sub>) reflections (very negative intensities were not assumed). The function minimized was Σ $w||F_o|^2 - |F_c|^2||^2$ , where  $w = [\sigma^2(I) + (0.0033P)^2]^{-1}$  (for **3b**·1/2CH<sub>2</sub>Cl<sub>2</sub>),  $[\sigma^2(I) + (0.0587P)^2 + 8.5293P]^{-1}$  (for **3c**·2H<sub>2</sub>O) and  $[\sigma^2(I) + (0.0369P)^2 + 5.8424P]^{-1}$  (for **4c**·CH<sub>2</sub>Cl<sub>2</sub>, respectively) and  $P = (|F_o|^2 + 2|F_c|^2)/3$ ; were taken from the literature.<sup>[27]</sup>

In the three cases all the hydrogen atoms were computed and refined using a riding model with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atoms to which is linked. Further details concerning the resolution and refinement of these crystal structures are presented in Table 2.

CCDC-740457 (for **3b**·1/2CH<sub>2</sub>Cl<sub>2</sub>) and -740459 (for **3c**·2H<sub>2</sub>O and **4c**·CH<sub>2</sub>Cl<sub>2</sub>) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supporting Information** (see also the footnote on the first page of this article): <sup>1</sup>H NMR spectra (500 MHz) of a CD<sub>2</sub>Cl<sub>2</sub> solution of

**4b**. CH<sub>2</sub>Cl<sub>2</sub> at 298 K and at 183 K (Figure S1) and IR and NMR spectroscopic data for the new compounds.

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