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Heterodimetallic palladium(II) compounds containing terdentate $[Csp^2(ferrocene),N,N']^-$ ferrocenyl ligands

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Abstract

The reaction of the novel ferrocenyl Schiff base containing an amino group as pendant arm: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4){-}CH{=}N{-}CH_2{-}CH_2{-}CH_2{-}NMe_2\}]$ (**1**) with palladium(II) salts is reported. Treatment of **1** with the stoichiometric amount of $Na_2[PdCl_4]$ produced: *cis*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4){-}CH{=}N{-}CH_2{-}CH_2{-}CH_2{-}NMe_2\}Cl_2]$ (**2**). However, when the reaction is performed in the presence of sodium acetate it leads to mixtures of **2** and $[Pd\{[(\eta^5\text{-}C_5H_3){-}CH{=}N{-}CH_2{-}CH_2{-}CH_2{-}NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (**3**). Compound **3** arises from the activation of the $\sigma[Csp^2$ (ferrocene)–H] bond. Further treatment of **3** with deuteriated pyridine (py-d_5) or triphenylphosphine (PPh_3) produced the cleavage of the Pd–N(amine) bond and the formation of the neutral compounds: $[Pd\{[(\eta^5\text{-}C_5H_3){-}CH{=}N{-}CH_2{-}CH_2{-}CH_2{-}NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$, with L = py-$d_5$ (**4**) or PPh_3 (**5**). The reaction of **3** with $Tl[BF_4]$ in acetone followed by the addition of PPh_3 yielded $[Pd\{[(\eta^5\text{-}C_5H_3){-}CH{=}N{-}CH_2{-}CH_2{-}CH_2{-}NMe_2]Fe(\eta^5\text{-}C_5H_5)\}(PPh_3)][BF_4]$ (**6**). NMR-studies reveal that the ligand acts as a neutral bidentate (N,N′) group, in **2**, as a monoanionic bidentate $[Csp^2$ (ferrocene), N$]^-$, in **4** and **5** or terdentate $[Csp^2$ (ferrocene),N,N′$]^-$ ligand, in **3** and **6**. The X-ray crystal structures of **2** and **3** are also reported and confirm the mode of binding of the ligand to the palladium. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: N,N′Ferrocenyl ligands; Cyclometallation; Ferrocenylimines; C–H activation

1. Introduction

Cyclopalladated compounds [1] containing (C, N)$^-$ bidentate groups and a $\sigma[Pd{-}Csp^2$ (aryl)] bond, or to a lesser extent a $\sigma[Pd{-}Csp^3]$ bond or a $\sigma[Pd{-}Csp^2$ (ferrocene)] bond, have generated considerable interest in recent decades mainly due to their applications in several fields [2–8], including organic or organometallic synthesis [3], and homogeneous catalysis [4]. Furthermore, recent reports have shown the utility of this sort of compounds as auxiliary reagents for chiral recognition or discrimination [5], as well as building blocks for the syntheses of polynuclear organometallic complexes [6].

During the last 5 years a great effort has been made in order to achieve the synthesis of palladacycles having [C, N, X]$^-$ (X = N, O, P, S) terdentate groups [9–12], mainly due to the potential hemilability of the σ(Pd–X) bond in these systems [13], which may play an important role in homogeneous catalysis. Among all the examples reported so far those containing terdentate $[Csp^2$(ferrocene), N,N′$]^-$ ligands are scarce [14].

In the view of these facts and as a part of a project directed towards the synthesis of cyclometallated compounds containing $[Csp^2$ (ferrocene), N, X$]^-$ (X = N, O, S, P) ligands, we have now centred our attention on ferrocenyl substrates derived from $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4){-}CH{=}N{-}R'\}]$ by the incorporation of a heteroatom (X) in the dangling R′ group.

On this basis, we decided to prepare the novel ferrocenyl Schiff base: $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4){-}CH{=}N{-}CH_2{-}CH_2{-}CH_2{-}NMe_2\}]$ (**1**) (Scheme 1) and to

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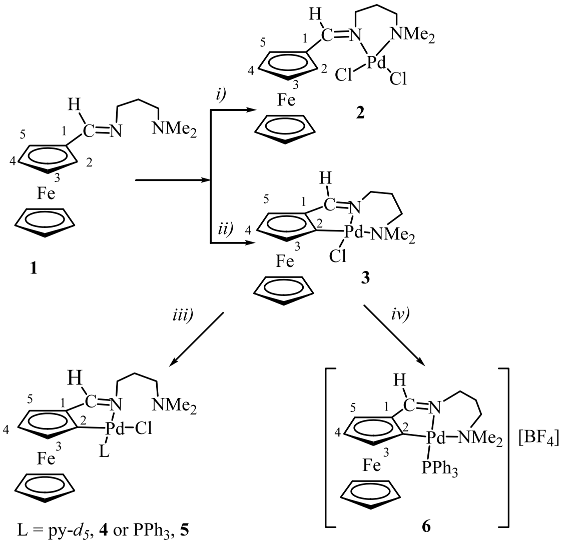

Scheme 1. (i) $Na_2[PdCl_4]$ in methanol. (ii) $Na_2[PdCl_4]$ and $Na(CH_3COO)$ in methanol (see text). (iii) py-d_5 or PPh_3 at room temperature. (iv) $Tl[BF_4]$ in acetone, followed by the addition of PPh_3.

study its reactivity versus palladium(II) salts. Ligand **1** contains two nitrogen atoms [N(imine) and N(amine)] with different donor properties and the formation of cyclopalladated complexes may have an additional interest due to the potential hemilability of the NMe_2 group. In this paper, we report several examples of palladium(II) compounds, in which **1** acts as a neutral (N,N′) ligand, as a monoanionic [Csp^2 (ferrocene), N]$^-$ or [Csp^2 (ferrocene), N,N′]$^-$ ligand.

2. Results and discussion

2.1. Synthesis

Compound $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-CH_2-CH_2-CH_2-NMe_2\}]$ **(1)** was prepared according to the general procedure described before for the syntheses of ferrocenyl Schiff bases of general formula $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-R'\}]$ where R′ represents a phenyl, benzyl or naphthyl group [15]. This procedure consists of the reaction of stoichiometric amounts of ferrocenecarbaldehyde and the corresponding amine in refluxing benzene. The synthesis requires the use of a Dean–Stark apparatus to remove the benzene–water azeotrope formed in the course of the reaction. For the preparation of **1**, *N*,*N*-dimethyl-1,3-propanediamine was used and the reaction yielded, after work up, a deep red gummy material (Scheme 1).

The reaction of **1** with the stoichiometric amount of $Na_2[PdCl_4]$ in methanol at room temperature for 2 h produced an orange solid. Its characterisation data (see below) were consistent with those expected for *cis*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)-CH=N-CH_2-CH_2-CH_2-NMe_2\}Cl_2]$ (**2**) in Scheme 1.

More interesting are the results obtained when the reaction of **1** and $Na_2[PdCl_4]$ was carried out in the presence of stoichiometric amounts of sodium acetate in methanol at room temperature, using reaction periods varying from 8 to 48 h (Scheme 1) since two different palladium(II) compounds could be isolated. One of them precipitated in the reaction medium and its characterisation data agreed with those obtained for **2**. The slow evaporation of the filtrate, obtained after the removal of **2**, yielded a deep-red microcrystalline material, which was identified (see below) as: $[Pd\{[(\eta^5\text{-}C_5H_3)-CH=N-CH_2-CH_2-CH_2-NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (**3**). This compound, in which the ligand acts as a [Csp^2 (ferrocene), N,N′]$^-$ ligand, arises from the activation of the σ[Csp^2 (ferrocene)–H] bond.

It should be noted that the **2**:**3** molar ratio decreases with time [16], which suggests that **2** is an intermediate in the transformation of **1** to **3**. This finding is similar to those obtained for the cycloplatination and cyclopalladation of the thioimines: $C_6H_5-CH=N-CH_2-CH_2-SEt$ [17] or $C_6H_5-CH=N-CH(CO_2Me)-CH_2-CH_2-SMe$ [12a].

In a first attempt to explore the lability of the Pd–N(amine) bond in **3**, we decided to study its reactivity toward deuteriated pyridine (py-d_5) and triphenylphosphine (PPh_3). When a $CDCl_3$ solution of **3** was treated with the stoichiometric amount of py-d_5 at room temperature, the ^{1}H- and $^{13}C\{^1H\}$-NMR spectra showed two superimposed sets of signals. One of them was coincident with that of the starting material, while the other was consistent with that expected for: $[Pd\{[(\eta^5\text{-}C_5H_3)-CH=N-CH_2-CH_2-CH_2-NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl(\text{py-}d_5)]$ (**4**), (Scheme 1) which arises from the cleavage of the Pd–N(amine) bond and the incorporation of a pyridine-d_5 ligand in the coordination sphere of the palladium. The complete conversion of **3** to **4** was easily achieved using a large excess of the entering ligand.

Similar results were obtained when **3** was treated with PPh_3 and in this case the formation of $[Pd\{[(\eta^5\text{-}C_5H_3)-CH=N-CH_2-CH_2-CH_2-NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ (**5**), required a PPh_3:**3** molar ratio equal to 1.30. In compounds **4** and **5**, the ferrocenyl Schiff base acts as a (C,N)$^-$ group.

Despite the use of excess of the entering ligands (py-d_5 or PPh_3) in these reactions, no evidence of the cleavage of the Pd–N(imine) bond was detected by NMR.

The results obtained from these experiments suggest that in **3**, the Pd–N(amine) bond is less prone to cleave than in $[Pd\{[(\eta^5\text{-}C_5H_3)-CH=N-CH_2-CH_2-NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl]$, which reacted with the stoichiometric amount of py-d_5 or PPh_3 to give $[Pd\{[(\eta^5\text{-}C_5H_3)-CH=N-CH_2-CH_2-NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl(L)]$ (with L = py-d_5, PPh_3) [14c]. Since compound **3** and

[Pd{[(η^5-C_5H_3)–CH=N–CH_2–CH_2–NMe_2]Fe(η^5-C_5H_5)}Cl], differ exclusively in the size of the chelate ring formed by the binding of the two nitrogen atoms to the palladium, the differences observed in their proclivity to undergo the cleavage of the Pd–N(amine) bond may be related to the greater strain arising from the presence of a [5,5,5] tricyclic system in [Pd{[(η^5-C_5H_3)–CH=N–CH_2–CH_2–NMe_2]Fe(η^5-C_5H_5)}Cl] when compared with that of the [5,5,6] tricyclic system in **3**.

In the view of the results obtained in the reaction of **3** with PPh_3, we decided to explore whether it could be possible to achieve the synthesis of cationic complexes with 'Pd(C,N,N′)(PPh_3)' cores using a different strategy based on the addition of thallium(I) salts, such as Tl[BF_4], followed by the addition of the phosphine. This lead to a red solid which was identified as [Pd{[(η^5-C_5H_3)–CH=N–CH_2–CH_2–NMe_2]Fe(η^5-C_5H_5)}(PPh_3)][BF_4] (**6**). In this compound the ligands behave as a $[C,N,N']^-$ terdentate group.

2.2. Characterisation

The ligand was characterised by infrared, mono- [^1H and $^{13}C\{^1H\}$] and two-dimensional NMR spectroscopy. The infrared spectrum showed a sharp and intense band at 1640 cm^{-1} due to the stretching of the >C=N– group. NMR-data for **1** is presented in the Section 3 and the assignments of the signals has been performed with the aid of HSQC and HMBC-NMR experiments. The proton and $^{13}C\{^1H\}$-NMR spectra of **1**, showed the typical pattern of monosubstituted ferrocene derivatives and suggested that only one isomer (*anti*-form) of **1** was present in solution. In the ^1H-NMR spectrum of **1**, the signals due to the protons of the –CH=N– and –NMe_2 fragments appeared as singlets of relative intensities 1:6 at $\delta = 8.11$ and 2.23 ppm, respectively. Besides that only one signal due to ^{13}C nuclei of the two methyl groups was observed in the $^{13}C\{^1H\}$-NMR spectrum of **1**. Thus, suggesting that these two methyl groups were equivalent.

The palladium(II) compounds, (except for **4**, which was prepared in solution) were also characterised by elemental analyses (see Section 3), infrared, mono- [^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ (for **5** and **6**)] and two-dimensional NMR spectroscopy. Compounds **2** and **3** were also characterised by X-ray diffraction (see below).

The most outstanding feature observed in the infrared spectra is the presence of a intense band (in the range 1550–1650 cm^{-1}), which is assigned, according to the literature [18], to the stretching of the >C=N– group. For the palladium(II) compounds, this absorption shifts to lower energies as compared with **1**. This finding suggests the co-ordination of the imine nitrogen [18]. The infrared spectra of **6** also exhibited the typical bands of the $[BF_4]^-$ anion [19].

In all cases, the assignment of the signals detected in the ^1H- and $^{13}C\{^1H\}$-NMR spectra was carried out with the aid of two-dimensional NMR experiments [HSQC and HMBC]. For the free ligand, all these experiments suggested that only one isomer (*anti*-form) of **1** was present in solution. The proton NMR spectrum of **2** showed the typical patterns of monosubstituted ferrocenyl derivatives [20]. The signal due to the imine proton in **2** ($\delta = 7.80$ ppm) is upfield shifted compared with the free ligand ($\delta = 8.11$ ppm). The sign and magnitude of this shift suggested that in **2** the Schiff base adopted the *E*- (*anti*-) conformation [21,22]. The X-ray crystal structure of **2** (see below) confirmed this finding.

As mentioned above, NMR spectroscopic data of the free ligand also agreed with a *trans*-arrangement of the ferrocenyl group and the substituent on the imine nitrogen (*E*-form). Thus, the results obtained from the NMR spectra suggest that for **1** the co-ordination of the '$PdCl_2$' fragment does not modify the conformation of the ligand. This finding is in sharp contrast with the results obtained for the closely related Schiff base: [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH_2–CH_2–NMe_2}] and its palladium(II) complex, *cis*-[Pd{[(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH_2–CH_2–NMe_2}]}Cl_2], [14c] which showed that the co-ordination of the '$PdCl_2$' unit to the two nitrogen atoms of the ligand involved the *E* (*anti*-)→*Z* (*syn*-) isomerisation of the ligand.

The resonances due to the protons of the methyl groups appeared as a singlet for **1** and compounds **4** and **5**. Besides that the position and multiplicities of the signal due to the carbon nuclei of the 'NMe_2' moiety in **4** and **5** were very similar to those observed for the free ligand. These findings suggests that in **4** and **5** the amine nitrogen was not bound to the palladium(II). In contrast, for **2** and **3**, the signal due to the protons of the NMe_2 unit appeared as two singlets in the ^1H-NMR spectra, and two signals due to the methyl carbon atoms were detected in the $^{13}C\{^1H\}$-NMR spectra. This indicates the existence of a Pd–N(amine) bond. The HSQC-NMR spectra of **3**–**6** showed only three cross-peaks due to the substituted pentagonal ring of the ferrocenyl group, thus suggesting that ortho-metallation had taken place. It is worth to mention that the resonances of the protons of the –$(CH_2)_3$– fragment of the chelate ring in **6** appeared as broad and poorly resolved signals when the spectrum was recorded at room temperature (20 °C) with a 500 MHz instrument, but their resolution improved considerably when the ^1H-NMR spectrum was registered at −50 °C. This finding can be attributed to conformational changes of the six-membered chelate ring.

All these observations allowed us to elucidate the mode of binding of the ligand in the palladium(II) compounds: as a neutral bidentate (N,N′) group in **2**, as a monoanionic bidentate [Csp^2 (ferrocene), N]$^-$ ligand in **4** and **5** or as a terdentate [Csp^2 (ferrocene), N,N′]$^-$ group in **3** and **6**.

The differences observed in the position of the signal due to the H^3 proton in the ^{1}H-NMR spectra of compounds **4**, **5** and **6** when compared with **3**, can be explained, according to the literature [15a,15b] in terms of the ring currents of the phenyl or pyridine rings of the neutral ligands bound to the palladium.

Compounds **5** and **6** were also characterised by ^{31}P{^{1}H}-NMR spectroscopy. The spectrum of **5** showed a singlet at $\delta = 37.2$ ppm. The position of this signal is similar to those obtained for palladacycles of general formula: $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}R']\}Fe\{[(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$ [15,23] in which the phosphine and the imine nitrogen are in a *trans*-arrangement. This is the usual result of the reaction between (C,N)$^-$ cyclometallated compounds and phosphines [24] due to the *transphobia* effect [25].

For **6**, the singlet due to the phosphorous nucleus appeared at higher fields ($\delta = 33.07$ ppm) than for **5**. The magnitude of the shift is similar to that reported for the cyclopalladated complexes of general formula: $[Pd\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{–}CH{=}N\text{–}CH_2\text{–}CH_2OH\}Cl(PPh_3)]$ and $[Pd\{C_6H_2\text{-}4,5\text{-}(OMe)_2\text{-}2\text{–}CH{=}N\text{–}CH_2\text{–}CH_2OH\}(PPh_3)]Cl$ {containing a σ[Csp^2 (phenyl), N]$^-$ or a σ[Csp^2 (phenyl), N,O]$^-$ ligand, respectively}, [10a] in which the phosphine is *trans*- to the imine nitrogen.

Compounds **2** and **3** were also characterised by X-ray diffraction. A perspective drawing of their molecular structures together with their atom labelling schemes are depicted in Figs. 1 and 2, respectively, and a selection of bond lengths and angles are presented in Tables 1 and 2.

The structure of **2** consists of discrete molecules of *cis*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}NMe_2\}Cl_2]$ and water molecules in a 1:1 molar ratio. The palladium atom is tetracoordinate, bound to two chlorine {Cl(1) and Cl(2), respectively} and the two nitrogen atoms {N(1) and N(2)} of the ferrocenyl ligand in a slightly distorted square-planar environment [26].

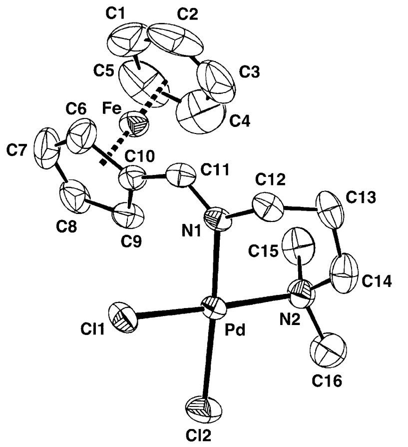

Fig. 1. Molecular structure and atom numbering scheme for **2**.

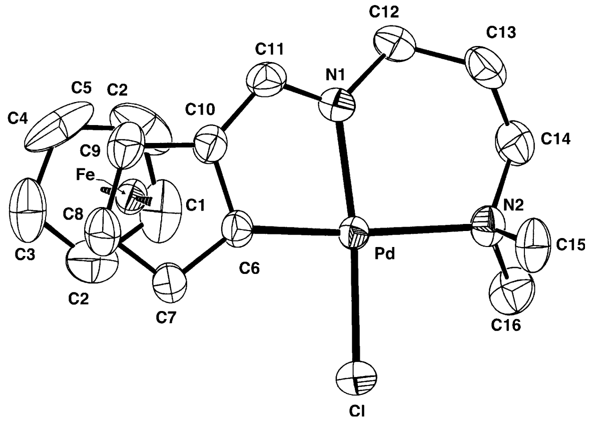

Fig. 2. Molecular structure and atom labelling scheme for **3**.

Table 1
Selected bond lengths (Å) and angles (°) for *cis*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}NMe_2\}Cl_2]\cdot H_2O$ (**2**)

Bond lengths			
Pd–N(1)	1.9938(15)	Pd–N(2)	2.1020(17)
Pd.–Cl(1)	2.2990(5)	Pd–Cl(2)	2.3102(6)
N(1)–C(11)	1.287(3)	N(1)–C(12)	1.466(3)
N(2)–C(14)	1.498(3)	N(2)–C(15)	1.504(3)
N(2)–C(16)	1.470(3)	C(10)–C(11)	1.437(3)
C(12)–C(13)	1.540(3)	C(13)–C(14)	1.531(4)
Fe–C [a]	2.029(12)	C–C [a]	1.40(7)
Bond angles			
N(1)–Pd–N(2)	87.52(7)	N(1)–Pd–Cl(1)	87.90(4)
N(2)–Pd–Cl(2)	95.46(5)	Cl(1)–Pd–Cl(2)	89.17(2)
C(10)–C(11)–N(1)	125.53(17)	C(11)–N(1)–C(12)	118.03(16)
N(1)–C(12)–C(13)	109.43(17)	C(14)–C(13)–C(12)	113.77(19)
C(14)–N(2)–C(15)	105.9(2)	C(16)–N(2)–C(14)	107.2(2)

Standard deviation parameters are given in parenthesis.
[a] Average value for the ferrocenyl moiety.

Table 2
Selected bond lengths (Å) and angles (°) for $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (**3**)

Bond lengths			
Pd–C(6)	1.964(3)	Pd–N(1)	2.052(3)
Pd–N(2)	2.205(3)	Pd–Cl	2.3143(9)
N(1)–C(11)	1.287(5)	N(1)–C(12)	1.485(5)
N(2)–C(14)	1.491(5)	N(2)–C(15)	1.475(5)
N(2)–C(16)	1.476(5)	C(11)–C(10)	1.440(5)
C(12)–C(13)	1.515(6)	C(13)–C(14)	1.494(7)
Fe–C [a]	2.041(16)	C–C [a]	1.407(24)
Bond angles			
C(6)–Pd–N(1)	81.02(12)	N(1)–Pd–N(2)	94.56(11)
C(6)–Pd–Cl	91.27(10)	N(2)–Pd–Cl	92.86(8)
C(11)–N(1)–C(12)	119.3(3)	C(15)–N(2)–C(16)	107.1(4)
C(15)–N(2)–C(16)	111.1(3)	C(16)–N(2)–C(14)	106.6(3)
N(1)–C(12)–C(13)	112.0(3)	C(14)–C(13)–C(12)	115.3(4)
N(2)–C(14)–C(13)	115.5(3)	N(1)–C(11)–C(10)	115.7(3)
C(9)–C(10)–C(11)	134.9(3)	C(6)–C(10)–C(11)	114.9(3)

Standard deviation parameters are given in parenthesis.
[a] Average value for the ferrocenyl moiety.

The variations observed in the two Pd–Cl bond lengths [2.2990(5) and 2.3102(6) Å] can be related to the different influence of the donor atoms in a *trans*-arrangement [N(amine) and N(imine), respectively].

The six-membered chelate ring has a chair-conformation [27], in which the Pd and C(13) atoms are 1.1978 and −0.6869 Å, respectively, out of the plane defined by the set of atoms: N(1), N(2), C(12) and C(14).

The functional >C=N– group, which is not included in the six-membered chelate ring (*exocyclic*) forms an angle of ca. 111.7° with the co-ordination plane of the metal and the value of the torsion angle: C(10)–C(11)–N(1)–C(12) is 174.08(4)°, indicating that the ligand adopts the *anti*- (*E*) form.

An interesting feature of the crystal structure of **2** is that the short distance between the chloro, Cl(2) and the H(16A) atom of the methyl group [2.861 Å] is smaller than the sum of the van der Waals radii of these two atoms [Cl, 1.75 and H, 1.20 Å] [28]. This suggests a weak Cl(2)···H(16A)···C(16) interaction. Similar type of intramolecular interactions have also been described for related palladium(II) compounds of general formula [Pd(ligand)Cl_2] [29].

The molecular structure of **3** (Fig. 2) consists of discrete molecules of [Pd{[(η^5-C_5H_3)–CH=N–CH_2–CH_2–CH_2–NMe_2]Fe(η^5-C_5H_5)}Cl] separated by van der Waals contacts. In each molecule the palladium is bound in a slightly distorted square-planar geometry [30] to the C(6) atom, the imine and the amine nitrogen atoms [N(1) and N(2), respectively] of the ferrocenyl ligand and to a chlorine.

In **3**, the two Pd–N bond lengths are significantly greater than in **2**. This finding can be ascribed to the different influence of the ligand in the *trans* position: a metallated carbon, C(6) in **3** or a chlorine, Cl(1) in **2**. The Pd–Cl bond length [2.3143(9) Å] is larger, if significant, than the distance between the palladium and the chlorine in a *trans*-arrangement to the imine nitrogen {Cl(2)} found in **2**.

Each molecule contains a [5,5,6] tricyclic system derived from the fusion of the six-membered chelate ring formed by the co-ordination of the two nitrogen atoms of the ligand to the palladium, a five-membered metallacycle and the metallated C_5H_3 ring of the ferrocenyl fragment.

The six-membered chelate ring which is defined by the atoms: Pd, N(1), N(2), C(12), C(13) and C(14) has a chair-conformation [31], in which the Pd and the C(13) atoms deviate by ca. −0.3420 and 0.7180 Å, respectively, from the main plane defined by the remaining atoms.

The five-membered metallacycle, which contains the >C=N– functional group (*endocyclic*) is practically planar [32] and forms an angle of ca. 5.30° with the C_5H_3 ring of the ferrocenyl fragment. Similarly to what happened in **2**, for complex **3**, the short distance between the Cl and H(16B) atoms suggests a weak Cl···H(16)···C(16) interaction.

In the two structures, the >C=N bond length is similar to those reported for related palladium(II) compounds containing ferrocenyl Schiff bases, which fall in the range [1.25–1.31 Å] [22]. In compounds **2** and **3**, the ferrocenyl fragment and the '–$(CH_2)_3NMe_2$' moiety are in a *trans*-arrangement, thus confirming that the ligand also adopts the *anti*-conformation. The imine forms an angle of 22.5° (in **2**) and 7.2° (in **3**) with the C_5H_3 ring of the ferrocenyl fragment.

Bond lengths and angles of the ferrocenyl moiety in **2** and **3** are similar to those reported for most ferrocene derivatives [33]. The two pentagonal rings are planar, nearly parallel (*tilt angles*: 3.46° and 2.43° for **2** and **3**) and they deviate by ca. 10.6° in **2** or 13.7° in **3** from the ideal eclipsed conformation. The distance between the two metals [4.90 Å for **2** and 3.60 Å for **3**] exceed the sum of the van der Waals radii of these atoms [28], thus suggesting that there is no direct interaction between the two metals.

To sum up, the results summarised in this work have allowed the isolation and characterisation of hetero-bimetallic palladium(II) compounds in which the ferrocenyl Schiff base **1**, acts as a bidentate [N,N′] (in **2**) or [Csp^2(ferrocene),N]$^-$ ligand (in **4** and **5**), or as a terdentate [Csp^2(ferrocene),N,N′]$^-$ group (in **3** and **6**) as well as the performance of a comparative study of the reactivity of the Pd–NMe_2 and Pd–N(imine) bonds in compounds of general formula [Pd{[(η^5-C_5H_3)–CH=N–$(CH_2)_n$–NMe_2]Fe(η^5-C_5H_5)}Cl] (with $n = 2$ or 3). Despite the tiny differences between the two compounds, in **3**, the Pd–NMe_2 bond is more reluctant to cleave than in: [Pd{[(η^5-C_5H_3)–CH=N–CH_2–CH_2–NMe_2]Fe(η^5-C_5H_5)}Cl], which contains three fused five-membered rings. These findings have been attributed to the different strain of the tricyclic systems. However, in the two compounds the Pd–N(imine) bond exhibits poor lability, since it does not cleave in the presence of large excesses of PPh_3. Besides the cyclopalladated compounds presented in this work, specially complex **3**, have an additional interest since they may be potentially useful in a wide variety of processes, i.e. as precursors for the synthesis of other organometallic derivatives through the insertion of small molecules (i.e. alkynes, alkenes, CO, etc...) into the σ(Pd–Csp^2, ferrocene) bond. Further work on this field is currently on the way.

3. Experimental

3.1. Materials and synthesis

All the reagents used for the preparations described in this work were obtained from Aldrich. The solvents except C_6H_6 were dried and distilled before use. Some of the preparations described below require the use of HIGHLY HAZARDOUS MATERIALS, such as C_6H_6 or thallium(I) salts, which should be handled with *CAUTION!*

Elemental analyses (C, H and N) were carried out at the Serveis Cientifico-Tècnics (Universitat de Barcelona) and at the Instituto de Química Bio-Orgánica, C.S.I.C. (Barcelona). Mass spectra were obtained with a VG-Quatro Fission Instrument using 3-nitrobenzylalcohol (NBA) as matrix. Infrared spectra were obtained with a Nicolet Impact-400-FTIR instrument using NaCl discs for the free ligand and KBr pellets for the palladium(II) compounds. Routine ^{1}H-NMR spectra and $^{13}C\{^{1}H\}$-NMR spectra were obtained with a Gemini-200 MHz and with a Bruker 250-DXR instruments, respectively. $^{31}P\{^{1}H\}$-NMR spectra of compounds **5** and **6** were registered with a Bruker 250DXR instrument and in these cases trimethylphosphite was used as internal reference [$\delta\,^{31}P$ for $P(OMe)_3 = 140.17$ ppm]. High resolution ^{1}H-NMR spectra and the two-dimensional NMR experiments [heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond coherence (HMBC)] were recorded with either a Varian VRX-500 or with a Bruker Advance-DMX 500 instrument. In all cases the solvents used for the NMR experiments are specified in the characterisation section of the corresponding compound. The chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz.

3.2. Preparation of the compounds

3.2.1. Preparation of $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}NMe_2\}]$ (*1*)

Commercial ferrocenecarboxaldehyde (1.00 g, 4.67×10^{-3} mol) was dissolved in 20 ml of benzene. The resulting solution was stirred at room temperature (r.t.) for 20 min and filtered out. The undissolved materials were discarded, and the filtrate was transferred to a flask. Then, 588 µl (4.67×10^{-3} mol) of *N*,*N*-dimethyl-1,3-propanediamine was added. The flask was connected to a Dean–Stark apparatus and the reaction mixture was refluxed until ca. 10 ml had condensed on the Dean–Stark apparatus. The hot solution was filtered out and the filtrate was concentrated to dryness on a rotary evaporator, giving a deep orange gummy residue. Yield: 0.970 g, 69.2%. IR: $\nu(>C{=}N\text{–}) = 1640$ cm^{-1}. ^{1}H-NMR data (in $CDCl_3$): $\delta = 4.17$ (s, 5H, C_5H_5), 4.63 (t, 2H, H^2 and H^5), 4.35 (t, 2H, H^3 and H^4), 8.11 (s, 1H, –CH=N–), 3.47 (t, 2H, $\text{–N–}CH_2\text{–}$, $J = 7$), 1.82 (m, 2H, $\text{–}CH_2\text{–}$, $J = 7$), 2.29 (t, 2H, $\text{–}CH_2\text{–}N$, $J = 7$) and 2.23 (s, 6H, 2Me). $^{13}C\{^{1}H\}$-NMR data (in $CDCl_3$): $\delta = 68.5$ (C_5H_5), 79.6 (C^1), 69.3 (C^2 and C^5), 66.9 (C^3 and C^4), 160.3 (–CH=N–), 58.8 ($=N\text{–}CH_2\text{–}$), 28.0 ($\text{–}CH_2\text{–}$), 56.6 ($\text{–}CH_2N\text{–}$) and 44.5 (Me).

3.2.2. Preparation of *cis*-$[Pd\{(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}NMe_2\}Cl_2]$ (*2*)

Ligand **1** (0.356 g, 1.19×10^{-3} mol) was dissolved in 20 ml of MeOH, then 0.351 g (1.19×10^{-3} mol) of $Na_2[PdCl_4]$ was added. The reaction mixture was protected from the light with aluminium foil and stirred at r.t. (ca. 20 °C) for 30 min. The orange solid formed was collected by filtration, washed with three (5 ml) portions of MeOH and air-dried. Yield: 0.461 g, 81.2%. Anal. (%) Calc. for $C_{16}H_{22}Cl_2N_2FePd\cdot H_2O$: C, 38.94; H, 4.90 and N, 5.68. Found: C, 39.0; H, 4.9 and N, 5.7. Mass spectra, FAB^{+}: 439 (M–Cl). IR: $\nu(>C{=}N\text{–}) = 1629$ cm^{-1}. ^{1}H-NMR data (in $CDCl_3$): $\delta = 4.33$ (s, 5H, C_5H_5), 5.55 (m, 1H, H^2), 4.74 (m, 1H, H^3), 4.80 (m, 1H, H^4), 6.14 (m, 1H, H^5), 7.80 (s, 1H, –CH=N–), 3.80 (br. m, 2H, $=NCH_2\text{–}$), 1.90 (br. m, 2H, $\text{–}CH_2\text{–}$), 2.32 (br. m, 2H, $CH_2\text{–}N$), 2.76 (s, 3H, Me) and 2.57 (s, 3H, Me).

3.2.3. Preparation of $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl]$ (*3*)

Compound **1** (0.356 g, 1.19×10^{-3} mol), $Na_2[PdCl_4]$ (0.351 g, 1.19×10^{-3} mol) and $NaAcO\cdot 3H_2O$ (0.162 g, 1.19×10^{-3} mol) were dissolved in 20 ml of MeOH. The reaction mixture was protected from the light with aluminium foil and stirred at r.t. (ca. 20 °C) for 48 h. After this period the solid formed, **2**, was collected and the red filtrate concentrated to dryness on a rotary evaporator. The residue was then dissolved in the minimum amount of CH_2Cl_2. The undissolved materials were removed by filtration and the filtrate was passed through an SiO_2-column chromatography. Elution with a CH_2Cl_2–MeOH (100:0.1) mixture produced the release of a red band, which was collected and concentrated to ca. 5 ml on a rotary evaporator. Addition of *n*-hexane produced deep-red crystals of **3**, which were collected by filtration and air-dried. Yield: 0.369 g, 73.95%. A second band was released using a CH_2Cl_2–MeOH (100:0.5) mixture, which led to after work up small amounts (20 mg) of unreacted **2**. Anal. (%) Calc. for $C_{16}H_{21}ClN_2FePd$ (Found): C, 43.77 (43.85); H, 4.82 (4.89) and N, 6.39 (6.31). Mass spectra, FAB^{+}: 440.0 [M^{+}], 404.5 [M–Cl]$^{+}$. IR: $\nu(>C{=}N\text{–}) = 1578$ cm^{-1}. ^{1}H-NMR data (in $CDCl_3$): $\delta = 4.32$ (s, 5H, C_5H_5), 4.40 (s, 1H, H^3), 4.39 (s, 1H, H^4), 5.07 (s, 1H, H^5), 8.03 (s, 1H, –CH=N–), 3.42 (br. m, 2H, $N\text{–}CH_2\text{–}$), 1.86 (m, 2H, $\text{–}CH_2\text{–}$), 2.57 (m, 2H, $\text{–}CH_2\text{–}N$), 2.68 (s, 3H, Me) and 2.65 (s, 3H, Me). $^{13}C\{^{1}H\}$-NMR data (in $CDCl_3$): $\delta = 69.2$ (C_5H_5), 84.8 (C^1), 95.9 (C^2), 68.6 (C^3), 65.1 (C^4), 75.9 (C^5), 172.7 (–CH=N–), 56.6 ($=N\text{–}CH_2\text{–}$), 25.8 ($\text{–}CH_2\text{–}$), 62.5 ($\text{–}CH_2N\text{–}$), 48.3 (Me) and 47.0 (Me).

3.2.4. Preparation of $[Pd\{[(\eta^5\text{-}C_5H_3)\text{–}CH{=}N\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}NMe_2]Fe(\eta^5\text{-}C_5H_5)\}Cl(py\text{-}d_5)]$ (*4*)

This compound was prepared in situ in an NMR tube and characterised by ^{1}H and $^{13}C\{^{1}H\}$-NMR spectroscopy. For the synthesis of **4** the following procedure was used. A 30 mg (6.8×10^{-5} mol) amount of **3** was dissolved in deuteriated pyridine, py-d_5, (0.7 ml). The reaction mixture was shaken vigorously for 5 min. During this time the colour of the initial mixture changes from red-wine to deep orange. ^{1}H-NMR data (in $CDCl_3$): $\delta = 4.15$ (s, 5H, C_5H_5), 3.90 (s, 1H, H^3), 4.22 (s, 1H, H^4), 4.46 (s, 1H, H^5), 8.02 (s, 1H, –CH=N–), 3.46 and 3.82 (br. m, 2H, N–CH_2–), 1.70–2.01 (br. m, 2H, –CH_2–), 2.49–2.53 (m, 2H, –CH_2–N) and 2.28 (s, 6H, Me). $^{13}C\{^1H\}$-NMR data (in $CDCl_3$): $\delta = 69.21$ (C_5H_5), 84.8 (C^1), 95.9 (C^2), 66.1 (C^3), 62.0 (C^4), 72.0 (C^5), 173.1(–CH=N–), 56.4 (=N–CH_2–), 28.2 (–CH_2–), 58.1 (–CH_2N–), 44.1 (Me) and 48.0 (Me).

*3.2.5. Preparation of [Pd{[(η^5-C$_5$H$_3$)–CH=N–CH$_2$–CH$_2$–CH$_2$–NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl(PPh$_3$)] (**5**)*

Compound **3** (0.200 g, 4.70×10^{-4} mol) was dissolved in the minimum amount of CH_2Cl_2. Then a solution formed by PPh_3 (0.160 g, 6.10×10^{-4} mol) and 5 ml of CH_2Cl_2 was added. The reaction mixture was stirred at r.t. (ca. 20 °C) for 1 h. The resulting solution was then concentrated on a rotary evaporator to ca. 4 ml and passed through an SiO_2-column chromatography. The elution with a CH_2Cl_2–MeOH (100:0.1) mixture produced the release of an orange–red band which was collected and concentrated to dryness on a rotary evaporator. The solid formed was collected and dried in vacuum for 2 days. Yield: 0.260 g, 72%. Anal. (%) Calc. for: $C_{34}H_{36}ClN_2FePPd\cdot CH_2Cl_2$ (Found): C, 54.47(54.1); H, 4.90 (4.1) and N, 3.65 (3.7). IR: $\nu(>C{=}N–) = 1595$ cm^{-1}. ^{1}H-NMR data (in $CDCl_3$): $\delta = 3.86$ (s, 5H, C_5H_5), 3.31 (d, 1H, H^3, $J = 5$), 4.05 (t, 1H, H^4, $J = 5$), 4.38 (d, 1H, H^5, $J = 5$), 8.10 (d, 1H, –CH=N–, $^3J_{P-H} = 8.4$), 3.58 and 3.70 (br. m, 2H, =NCH_2–), 1.85 and 2.20 (br. m, 2H, –CH_2–), 2.30 and 2.45 (m, 2H, –CH_2N), 2.26 (s, 6H, Me), 5.12 (s, 2H, CH_2Cl_2) and 7.40–7.82 (br. m, 15H, aromatic). $^{13}C\{^1H\}$-NMR data: $\delta = 70.0$ (C_5H_5), 97.1 (C^1), 106.2 (d, C^2), 70.4 (C^3), 68.4 (C^4), 72.8 (C^5), 170.5 (–CH=N–), 57.0 (=NCH_2–), 29.2 (–CH_2–), 56.2 (–CH_2N–), 45.5 (Me) and four additional doublets centred at ca. 134.6, 131.0, 130.3 and 128.0 due to the carbon nuclei of the phenyl rings of PPh_3. $^{31}P\{^1H\}$-NMR data (in $CDCl_3$): $\delta = 37.22$.

*3.2.6. Preparation of [Pd{[(η^5-C$_5$H$_3$)–CH=N–CH$_2$–CH$_2$–CH$_2$–NMe$_2$]Fe(η^5-C$_5$H$_5$)}(PPh$_3$)][BF$_4$] (**6**)*

A 0.100 g (2.35×10^{-4} mol) amount of **3** was dissolved in 20 ml of acetone. Then, 0.072 g (2.50×10^{-4} mol) of Tl[BF_4] was carefully added. The reaction mixture was stirred at r.t. for 1 h and filtered through *Celite* to remove the TlCl formed. Triphenylphosphine (0.065 g, 2.48×10^{-4} mol) was added to the filtrate, and the resulting solution was stirred for 10 additional min. The resulting red solution was filtered out and the filtrate was concentrated to dryness on a rotary evaporator. The deep-red residue was then treated with 3 (10 ml) portions of $CHCl_3$. The organic solution was extracted and dried over Na_2SO_4. Finally, the filtrate was concentrated on a rotary evaporator to ca. 10 ml and slow evaporation of the solvent lead to a polycrystalline material which was collected, air-dried and then dried in vacuum for 2 days. Anal. (%) Calc. for: $C_{34}H_{36}BFeF_4N_2PPd$ (Found): C, 54.25 (53.9); H, 4.82 (4.7) and N, 3.72 (3.4). IR: $\nu(CN) = 1578$ cm^{-1}. ^{1}H-NMR data (in $CDCl_3$ at 223 K): $\delta = 3.89$ (s, 5H, C_5H_5), 3.32 (s, 1H, H^3), 4.50 (s, 1H, H^4), 3.99 (s, 1H, H^5), 8.37 (d, 1H, –CH=N–, $^3J_{P-H} = 7.8$), 3.72 and 3.57 (br. m, 2H, =NCH_2–), 2.20 and 1.90 (br. m, 2H, –CH_2–), 3.00 (m, 2H, –CH_2N), 2.02 (s, 3H, Me) and 2.60 (s, 3H, Me) and 7.30–7.90 (br. m, 15H, aromatic). $^{13}C\{^1H\}$-NMR data: $\delta = 71.2$ (C_5H_5), 85.8 (C^1), 102.8 (d, C^2), 70.0 (C^3), 67.9 (C^4), 65.03 (C^5), 174.6 (–CH=N–), 58.4 (=NCH_2–), 25.7 (–CH_2–), 56.4 (–CH_2N–), 48.0 (br, Me), and four additional doublets centred at ca. 135.7, 131.0, 130.2 and 129.16 ($C_{aromatic}$). $^{31}P\{^1H\}$-NMR data (in $CDCl_3$): $\delta = 33.07$.

3.3. Crystallography

A prismatic crystal of **2** or **3** ($0.1\times0.1\times0.2$ mm) was selected and mounted on a MAR345 diffractometer with image plate detector. Unit cell parameters were determined from automatic centring of 9309 (for **2**) or 11 270 reflections (for **3**) in the ranges: $3<\Theta<31°$ for **2** and $3<\Theta<21°$ for **3** and refined by least-squares method. Intensities were collected with graphite monochromatized Mo–K_α radiation. For **2**, the number of reflections measured in the range $3.97\le\Theta\le31.61°$ was 11 963 of which 5137 were non-equivalent by symmetry $\{R_{int}$ (on $I) = 0.037\}$ and 4243 reflections were assumed as observed applying the condition $I>2\sigma(I)$. For **3**, the number of reflections measured in the range $3.24\le\Theta\le31.54°$ was 15 220 of which 5390 were non-equivalent by symmetry $\{R_{int}$ (on $I) = 0.041\}$ and 4243 reflections were assumed as observed applying the condition $I>2\sigma(I)$. Lp and absorption corrections were made in the two cases.

The structures were solved by Direct methods, using SHELXS computer program [34] and refined by full-matrix least-squares method with the SHELX97 computer program [35] using 5137 (for **2**) and 5390 (for **3**) reflections (very negative intensities were not assumed). The function minimised was $\Sigma w||F_o|^2-|F_c|^2|^2$, where $w=[\sigma^2(I)+(0.0494P)^2+0.0722P]^{-1}$ for **2**, $w=[\sigma^2(I)+(0.0394P)^2+3.4824P]^{-1}$ for **3** and $P=(|F_o|+2|F_c|^2)/3$. f, f' and f'' were taken from *International Tables of X-Ray Crystallography* [36]. For **2**, 22 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 atom attached. For **3**, all hydrogen atoms were located from a difference

Table 3
Crystal data and details of refinement of the crystal structures of *cis*-[Pd{(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–CH_2–CH_2–CH_2–NMe_2}Cl_2]·H_2O (**2**) and [Pd{[(η^5-C_5H_3)–CH=N–CH_2–CH_2–CH_2–NMe_2]Fe(η^5-C_5H_5)}Cl] (**3**)

	2	**3**
Empirical formula	$C_{16}H_{24}Cl_2FeN_2POPd$	$C_{16}H_{21}ClFeN_2Pd$
Formula weight	493.52	439.05
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	10.1950(10)	11.09030(10),
b (Å)	12.2890	12.5630(10)
c (Å)	14.7610	12.5060(10)
$\alpha = \gamma$ (°)	90.0	90.0
β (°)	96.5500(10)	111.037(10)
V (Å^3)	1837.3(3)	1626.7(2)
Z	4	4
D_{calc} (mg m^{-3})	1.784	1.793
Absorption coefficient (mm^{-1})	2.063	2.155
F(000)	992	880
Theta range for data collection (°)	From 3.97 to 31.61	From 3.24 to 31.54
Number of collected reflections	11 963	15 220
Number of unique reflections (R_{int})	5137 {$R_{int} = 0.0378$}	5390 {$R_{int} = 0.0419$}
Number of data	5137	5390
Number of parameters	203	274
Goodness of fit on F^2	1.076	1.098
Final *R* indices {$I > 2\sigma(I)$}	$R_1 = 0.0265$, $wR_2 = 0.0731$	$R_1 = 0.0390$, $wR_2 = 0.0944$
R indices (all data)	$R_1 = 0.0376$, $wR_2 = 0.0764$	$R_1 = 0.0549$, $wR_2 = 0.1013$
Largest difference peak and hole (e Å^{-3})	0.523 and −0.548	0.865 and −0.835

synthesis and refined with an overall isotropic temperature factor. The final R(on F) factors were 0.026 (for **2**) and 0.039 (for **3**), wR(on $|F|^2$) = 0.073 and 0.094 (for **2** and **3**, respectively). Further details concerning the resolution and refinement of the crystal structure of **3** are presented in Table 3.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 167881 and 167882. Copies of data can be obtained free of charge on applications to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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