Synthesis, characterisation and study of the reactivity of the first platinum(II) complex having a [C(sp^2, ferrocene),N,N′]$^-$ terdentate ligand

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Received (in Montpellier, France) 15th November 2002, Accepted 5th February 2003
First published as an Advance Article on the web 15th May 2003

The study of the reactivity of [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–$(CH_2)_3$–NMe_2}] (**1**) with *cis*-[$PtCl_2(dmso)_2$] is reported. These studies have allowed the isolation and characterisation of two isomeric forms of *cis*-[Pt{(η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–$(CH_2)_3$–NMe_2]}Cl_2] (**2a** and **2b**), which differ in the conformation of the ligand [*syn*-(*Z*) in **2a** and *anti*-(*E*) in **2b**], and the first platinacycle containing a terdentate [C(sp^2, ferrocene),N,N′]$^-$ ligand: [Pt{[(η^5-C_5H_3)–CH=N–$(CH_2)_3$–NMe_2]Fe(η^5-C_5H_5)}Cl] (**3**). The relative importance of the factors governing the formation of **3** is discussed. The X-ray crystal structures of **2a** and **3** are described and confirm the mode of binding of the ligand to the platinum(II). The study of the reactivity of **3** with PPh_3 or CH_3I is also reported.

Introduction

The study of cyclometallated complexes[1] containing platinum or palladium has attracted much interest in the past decade, mainly due to their applications in different areas.[2–6] A wide variety of cycloplatinated complexes containing (C,N)$^-$ bidentate and [N,C(sp^2, aryl),N′]$^-$ or [C(sp^2, aryl),N,X]$^-$ (X = N, O, S or P) terdentate ligands have been described in recent years.[7–10] Among them, square-planar platinacycles with *mer*-tridentate [N,C(sp^2, aryl),N′]$^-$ or [C(sp^2, aryl),N,N′]$^-$ coordinating ligands present an additional interest due to their spectroscopic and photochemical properties.[11,12] On the other hand, during the last decade, a few cycloplatinated compounds containing a [C(sp^2, ferrocene),N]$^-$ bidentate group, such as [Pt{[(η^5-C_5H_3)–C(R)=N–R′]Fe(η^5-C_5H_5)}Cl(dmso)], [Pt{[(η^5-C_5H_3)–CH_2–NMe_2]Fe(η^5-C_5H_5)}Cl(dmso)] or the 1,1′-bis(cycloplatinated) derivative [Pt_2{Fe[(η^5-C_5H_3)–CH_2–N-Me_2]$_2$}$Cl_2(dmso)_2$] (**A**, **B** and **C** in Fig. 1) have also been described;[13–15] among these, complex **C** is particularly relevant due to its antitumoural activity.[15] However, to the best of our knowledge, platinacycles with [C(sp^2, ferrocene),N,N′]$^-$ groups have not been described so far.

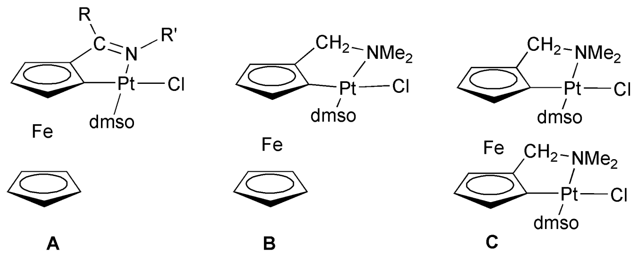


Fig. 1 Schematic view of some platinacycles containing [C(sp^2, ferrocene),N]$^-$ bidentate ligands described so far.

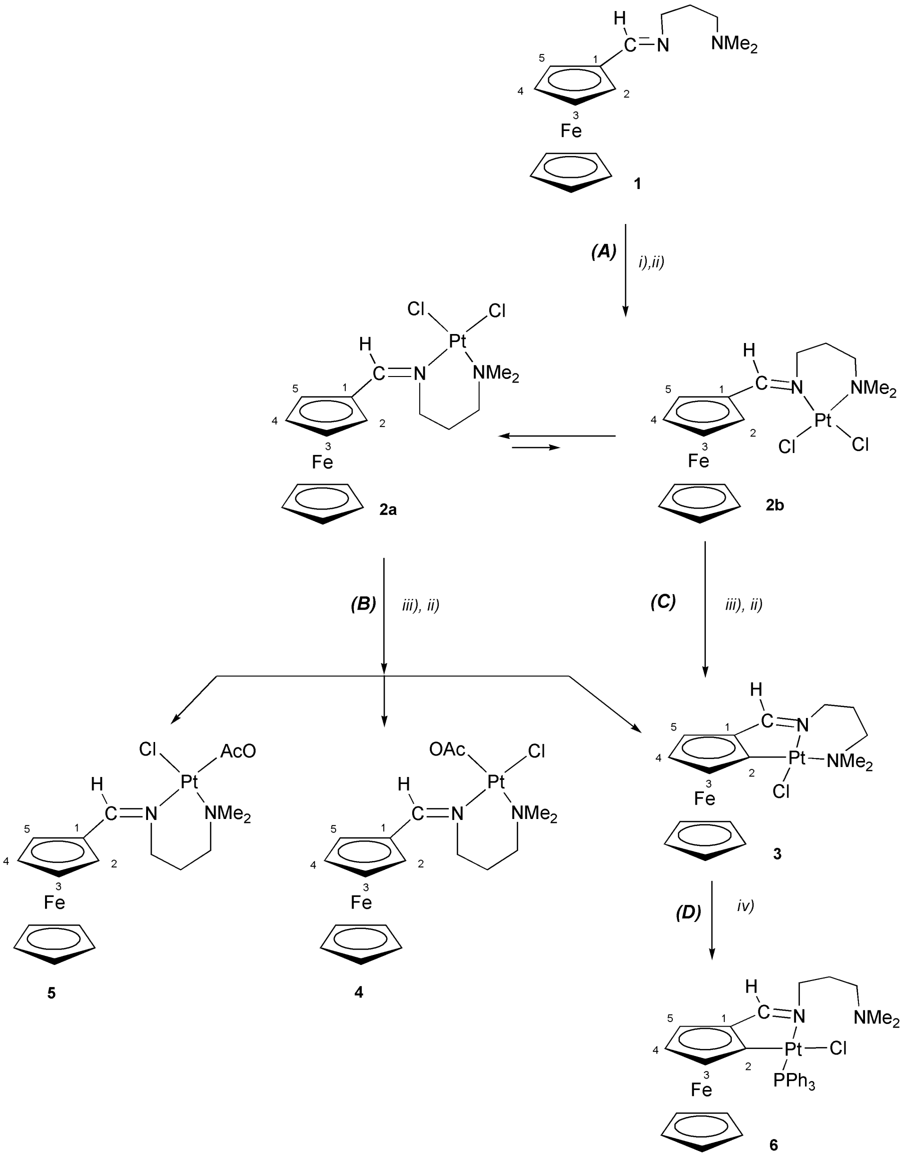
As part of a project focused on the synthesis of palladium(II) and platinum(II) complexes containing [C(sp^2, ferrocene),N,N′]$^-$ terdentate ligands, we have recently reported the synthesis of [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–$(CH_2)_3$–NMe_2}][16] (**1**) (Scheme 1). In principal, and depending on the mode of coordination of **1**, different sorts of metal compounds could be formed. For instance, in addition to complexes where **1** behaves as a neutral (N), (N′) or (N,N′) group, if the activation of the σ[C(sp^2, ferrocene)–H)] bond occurs, the ligand may also act as a monoanionic (C)$^-$, (C,N)$^-$ or (C,N,N′)$^-$ group. Recent studies based on the reactivity of **1** with palladium(II) salts have allowed us to isolate the cyclopalladated complexes with a [C(sp^2, ferrocene),N]$^-$ or a [C(sp^2, ferrocene),N,N′]$^-$ ligand, showing the high versatility in the coordination modes of **1** with palladium.[16] In view of these results we were prompted to elucidate whether the activation of the ortho σ[C(sp^2, ferrocene)–H] bond of **1** could also be promoted by platinum(II) salts. In this paper we report the results obtained in the reaction of **1** with *cis*-[$PtCl_2(dmso)_2$][17] under different experimental conditions. Since it has been reported that the reaction of C_6H_5–C(Et)=N–OH with *cis*-[$PtCl_2(dmso)_2$] produced [$PtCl_3$(SMe){C_6H_4–C(Et)=N–OH}],[13c] in principle the formation of platinum(IV) species in the reaction under study cannot be discarded. The results presented in this work have allowed us to prepare the first cycloplatinated complex with a terdentate [C(sp^2, ferrocene),N,N′]$^-$ ligand, to elucidate the factors that control its formation and to study its spectroscopic properties as well as its reactivity with PPh_3 or MeI.

Results and discussion

Synthesis

When ligand **1** (100 mg) was treated with a stoichiometric amount of *cis*-[$PtCl_2(dmso)_2$][17] in refluxing methanol for 1 h

DOI: 10.1039/b211346e



Scheme 1 *Reagents and conditions*: *i)* *cis*-[$PtCl_2(dmso)_2$] in refluxing methanol (HPLC grade), see text. *ii)* SiO_2 column chromatography, see text. *iii)* Na(CH_3COO) in refluxing methanol. *iv)* PPh_3 in $CDCl_3$.

[Scheme 1, step A], three different compounds were isolated. The major component (≈45 mg) was identified (*vide infra*) as *cis*-[Pt{(η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–$(CH_2)_3$–NMe_2]}Cl_2] (**2a**). NMR spectroscopic data as well as the X-ray crystal structure of **2a** (see below) indicated that in this compound the ligand behaves as a neutral (N,N′) group and adopt the *Z* (*syn*) conformation. Since the free ligand, **1**, has the *E* (*anti*) conformation,[16] the formation of **2a** requires the *E* (*anti*) → *Z* (*syn*) isomerisation of the ligand in the course of the process. Characterisation data of the second component were coincident with those reported for ferrocenecarboxaldehyde,[18] which may form through hydrolysis of the Schiff base. This finding is similar to those reported for the cycloplatination of the diimine derived from the condensation of benzaldehyde and (1*R*,2*R*)-diaminocyclohexane[9a] or for the cyclopalladation of: C_6H_5–CH=N–$(CH_2)_2$–SEt,[19] which also lead to small amounts of benzaldehyde.[9a,19]

Characterisation data of the minor component (≈10 mg, **2b**, *vide infra*) suggest that it is an isomeric form of **2**, in which the ligand has the *E* (*anti*) conformation. It is worth pointing out that when **1** was treated with a stoichiometric amount of *cis*-[$PtCl_2(PhCN)_2$], the solid formed consisted also in a mixture of **2a** and **2b** (in a **2a**/**2b** molar ratio of 1.2).

Several authors have reported that in the reaction of N-donor ligands with platinum(II) salts the activation of the σ(C–H) bond is usually promoted by the presence of a base.[20] Despite the basic nature of **1** and the presence of ferrocenecarboxaldehyde as a side product (which suggests a partial hydrolysis of the ligand), no evidence of the formation of any platinacycle was detected by NMR, even after 48 h under reflux.

In view of this, we decided to elucidate whether the activation of the σ[C(sp^2, ferrocene)–H] bond could be achieved in the presence of a stoichiometric amount of a base such as sodium acetate. With this aim, equimolar amounts of **1**, *cis*-[$PtCl_2(dmso)_2$] and Na(CH_3COO) were refluxed in methanol for different reaction periods (*t*) ranging from 15 h to 12 days. For $t = 15$ h, the work-up of the column allowed is to collect three orange bands (which lead to ferrocencarboxaldehyde, **2a** and traces of **2b**) and a purple band that yielded a small amount (< 10 mg) of a violet solid (**3**). An increase of the reaction period (*t*) from 15 h to 6 days improved the yield of **3** and produced a decrease of the **2a**/**3** molar ratio [from 1.47 ($t = 15$ h) to 0.40 ($t = 6$ days)]. However, the yield of **3** did not improve significantly when the mixture was refluxed for 12 days when compared with that obtained after 6 days. The crystal structure of **3** (described below) indicates that it is [Pt{[(η^5-C_5H_3)–CH=N–$(CH_2)_3$–NMe_2]Fe(η^5-C_5H_5)}Cl] (Scheme 1) in which the ligand acts as a [C(sp^2, ferrocene),N,N′]$^-$ terdentate group and the imine has the *E* (*anti*-) conformation.

These findings suggested that **2a** might be an intermediate in the transformation of **1** to **3**. In order to confirm this hypothesis, **2a** was treated with a stoichiometric amount of Na(CH_3COO) in refluxing methanol for 6 days [Scheme 1, step B]. During this period, the reaction mixture became deep-red and the formation of platinum(0) was observed. The ^{1}H-NMR spectrum of the crude material revealed the presence of the aldehyde, **2a**, **3**, and small amounts of two by-products [**4** (10 mg) and **5** (4 mg), *vide infra*].

Although these results confirm that **2a** is an intermediate complex in the transformation of **1** to **3**, the molar ratio **3**/**2a** was not very high (*ca.* 0.34). This finding is in sharp contrast with the results obtained for the palladium(II) analogue *cis*-[Pd{(η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–$(CH_2)_3$–NMe_2]}Cl_2], which reacted with a stoichiometric amount of Na(CH_3COO) in refluxing methanol ($t = 2$ h) to give the cyclopalladated complex.[16]

Characterisation data available for **4** and **5** agree with those expected for *cis*-[Pt{(η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–$(CH_2)_3$–NMe_2]}(AcO)Cl]. In both cases the ^{1}H spectra show the signals due to the methyl protons of a coordinated acetate ligand and the resonances due to the carbon nuclei of the acetato group are also observed in their ^{13}C{^{1}H}-NMR spectra, thus indicating the presence of this ligand in the coordination sphere of the platinum(II). These findings suggest that **4** and **5** may be the two isomers of *cis*-[Pt{(η^5-C_5H_5)Fe[(η^5-C_5H_4)–CH=N–$(CH_2)_3$–NMe_2]}(AcO)Cl]. Their {^{1}H–^{1}H}-NOESY spectra suggest that in both cases the ligand adopts the *Z* (*syn*) conformation. Besides this, the spectrum of **4** shows a cross-peak between the methyl protons of the acetato ligand and the H^5 proton of the C_5H_4 ring of the ferrocenyl unit, which is not observed in the {^{1}H–^{1}H}-NOESY spectrum of **5**. On this basis, we postulate that in **4** the acetato ligand is in a cis arrangement to the imine nitrogen, while in **5**, it is trans. It should be noted that when **1** was refluxed with *cis*-[$PtCl_2$(dmso)$_2$] in the presence of Na(CH_3COO) for 6 days no evidence of the formation of **4** and **5** was detected by NMR spectroscopy.

The results obtained from the reaction of **2a** with Na(CH_3COO) in refluxing methanol revealed that although this procedure allows the partial conversion of **2a** to **3**, the process involves the formation of other non-desired by-products (**4** and **5**).

More interesting are the results obtained when the reaction was repeated using **2b** as the starting material. In this case and due to the small amounts of **2b** available, the progress of the reaction was monitored by ^{1}H-NMR spectroscopy. When **2b** was treated with a stoichiometric amount of Na(CH_3COO) in refluxing methanol, the colour of the mixture changed gradually and after 22 h it was nearly violet [Scheme 1, step C]. The ^{1}H-NMR spectrum of the solution revealed the coexistence of **2b** and **3** (in a **3**/**2b** molar ratio of 3.5). The relative proportions of **3** and **2b** were time-dependent (**3**/**2b** molar ratio = 9.0 after 56 h). These findings suggest that the conversion of **2b** into **3** is faster than that of **2a** under identical experimental conditions. This observation is not surprisingly since the transformation **2a** → **3** requires the isomerisation of the coordinated ligand and subsequent cycloplatination, while for **2b** only the activation of the σ(C–H) bond is required. In view of this we assume that in the cycloplatination of **1**, the rate-determining step may be the isomerisation of the coordinated ligand in **2b**, which appears to the key factor in this process.

The sequence of reactions A–C presented in Scheme 1, as well as the nature of some of the products formed there, are markedly different from that reported by Wu *et al.*[13a] for the reaction of stoichiometric amounts of *cis*-[$PtCl_2$(dmso)$_2$], Na(CH_3COO) and the ferrocenylimines [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–C(R) = N–R′}] (with R = H or Me and R′ phenyl groups) in refluxing methanol, and reveal the importance of the incorporation of an additional nitrogen donor atom in the dangling R′ group. The comparison of all the results presented here allow us to conclude that the direct reaction between stoichiometric amounts of **1**, *cis*-[$PtCl_2$(dmso)$_2$] and sodium acetate in refluxing methanol for 6 days appears to be the most convenient procedure to achieve the preparation of **3**, since it can be obtained in a higher yield and the number of undesirable by-products formed in the process is smaller.

Reactivity of compound 3

It is well-known that changes in the hapticities or the binding modes of potentially terdentate chelating ligands $[C,N,X]^-$ (X = N, P, O, S), such as the lability of the σ(M–X) bond, are relevant to their applications. As a first approach to determine if the mode of binding or the hapticity of **1** could be modified under mild experimental conditions, the reaction of **3** with PPh_3 was studied in solution. When PPh_3 was added to a $CDCl_3$ solution of **3** (in a PPh_3/**3** molar ratio = 1) at room temperature (20 °C), a red solid was isolated [Scheme 1, step D]. Its elemental analyses as well as the spectroscopic data (*vide infra*) agree with those expected for [Pt{[(η^5-C_5H_3)–CH=N–$(CH_2)_3$–NMe_2]Fe(η^5-C_5H_5)}Cl(PPh_3)] (**6**). This suggests that the formation of **6** involves the cleavage of the Pt–N(amine) bond and the incorporation of a PPh_3 group in the coordination sphere of the metal. The ^{31}P{^{1}H}-NMR spectrum of **6** suggests a cis arrangement between the metallated carbon and the PPh_3 group. This is the usual result of the reaction between $(C,N)^-$ cyclometallated compounds and phosphines[21] due to the so-called *transphobia* effect.[22] The results obtained in the reaction of **3** with PPh_3 are similar to those reported for the cycloplatinated derivatives containing a [C(sp^2, phenyl),N,N′]$^-$ ligand.[7d]

One of the most interesting reactions of square-planar cycloplatinated complexes is based on the oxidative addition of alkyl halides to platinacycles containing a *mer*-[C(sp^2, phenyl),N,N′]$^-$ ligand.[7d,10a,23] However, the addition of a large excess of MeI to an acetone solution of **3** did not produce any chemical change, even when the reaction periods were increased up to 24 h. These results are in sharp contrast with those reported for [Pt{($C_6H_{4-n}R_n$)–CH=N–$(CH_2)_2$–NMe_2}X][7d] and suggest that **3** is less prone to undergo the formation of the corresponding six-coordinated platinum(IV) derivative.

Characterisation of the compounds

Except for **4** and **5**, which were isolated in a extremely low yield, the remaining platinum(II) compounds described in this work were characterised by elemental analyses, infrared as well as mono- and two-dimensional NMR spectra; the molecular structures of **2a** and **3** have also been resolved by X-ray diffraction. In all cases the elemental analyses are consistent with the proposed formulae (see Experimental). The infrared spectra of **2**–**6** show a sharp and intense band in the range of 1150–1610 cm^{-1}, which is ascribed to the stretching of the >C=N– group. In all cases, this band appears at lower frequencies than for the free ligand (1640 cm^{-1}),[16] indicating the binding of the imine nitrogen to the platinum.[24,25] Comparison of IR data also indicates that the position of this band is sensitive not only to the mode of binding of the ligand but also to its conformation because ν(>C=N–) decreased according to the sequence: **1** > **2b** > **2a** > **6** > **3**.

In all cases the assignment of the signals detected in the ^{1}H and ^{13}C{^{1}H}-NMR spectra has been carried out with the aid of two-dimensional (HSQC and HMBC) NMR experiments. Proton-NMR data permit the elucidation of the conformation of the ligand in the platinum complexes and its mode of binding. According to the literature,[26,27] for cycloplatinated and cyclopalladated compounds derived from aldimines, the variations of the chemical shift due to the imine proton in the metal complexes when compared with the free ligand allows to elucidate the conformation of the aldimine. If the ligand adopts the *Z* (*syn*) form, this signal is strongly shifted to lower fields, due to the proximity of the imine proton and the metal,[27] but if the conformation of the ligand in the complexes is *E* (*anti*), then the resonance appears at higher fields. On this basis, we can conclude that the ligand has the *Z* (*syn*) conformation in **2a** and the *E* (*anti*) conformation in **2b**, **3** and **6**. Besides this, the coupling between the imine proton and the ^{195}Pt nucleus [^3J(H–Pt)] increased according to the sequence: **2a** < **6** < **2b** < **3**. Since the environment around the platinum in **2a** and **2b** is identical this trend reflects the influence of the conformation of the ligand [*syn*-(*Z*) in **2a** and *anti*-(*E*) in **2b**] upon the magnitude of the interaction between these two nuclei.

The high-field shift of the signal due to the H^3 proton in **6**, when compared with that of the free ligand or of **3**, agrees with the results reported for related metallacycles, where the ligand acts as a [C(sp^2, ferrocene),N]$^-$.[28] This fact was rationalised on the basis of the proximity of the phenyl rings of the PPh$_3$ ligand.

One of the most relevant features observed in the ^{13}C{^{1}H}-NMR spectra was the low-field shift of the signals due to the carbon-13 nuclei of the >C=N– and –NMe$_2$ groups when compared with the free ligand (δ = 160.3 ppm[16]). This trend is consistent with those reported for [Pd{(η^5-C$_5$H$_5$)Fe[(η^5-C$_5$H$_4$)–CH=N–(CH$_2$)$_n$–NMe$_2$]}Cl$_2$] and [Pd{[(η^5-C$_5$H$_3$)–CH=N–(CH$_2$)$_n$–NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] (with *n* = 2 or 3).[16] For **6** the signal due to the metallated carbon is also low-field shifted by *ca.* 16 ppm. The sign and magnitude of this shift agrees with previous ^{13}C-NMR studies of cyclopallada- and cycloplatinated complexes.[10a,b,16]

^{195}Pt{^{1}H}-NMR spectra of **2a** and **3** show one signal at δ = −2120 ppm (for **2a**) and at δ = −3326 ppm (for **3**). The positions of these resonances are similar to those of *cis*-[Pt{C$_6$H$_5$–CH=N–(CH$_2$)$_2$–SEt}Cl$_2$] (δ = −2927 ppm[10a]), [Pt{C$_6$H$_4$–CH=N–(CH$_2$)$_2$–SEt}Cl] (δ = −3716 ppm[10a]) and related complexes having "Pt(N,N′)Cl$_2$" or "Pt(C,N,N′)Cl" cores. The ^{195}Pt{^{1}H}-NMR spectrum of **6** exhibits a signal centred at δ = −4184 ppm [^1J(Pt–P) = 4146 Hz], its position as well as the value of the coupling constant fall in the range expected for cycloplatinated complexes containing a PPh$_3$ ligand and a [C,N]$^-$ bidentate group such as [Pt{C$_6$H$_4$–CH=N–CH$_2$–CH$_2$–SEt}Cl(PPh$_3$)].[10a]

The ^{31}P{^{1}H}-NMR spectrum of **6** showed one signal centred at δ = 16.0 ppm [^1J(P–Pt) = 4147 Hz]. The chemical shift suggests, according to the literature,[7d,10a] that the PPh$_3$ and the imine nitrogen are in a trans arrangement.

As mentioned above, cycloplatinated complexes having terdentate [C,N,N′] or [N,C,N]$^-$ ligands have attracted much interest in recent years due to their potential luminescence.[11,12] In the view of this we were prompted to elucidate whether **3** could also exhibit this property in solution. The ultraviolet-visible spectrum of **2a** and **3** in CH$_2$Cl$_2$ exhibited two intense bands in the 270–400 nm range, which are typical of ferrocenylimines and their transition metal complexes.[29] For **3** the spectrum showed an additional band at 530 nm, which shifts to higher energies when the platinum(II) is replaced by palladium(II). This absorption was attributed, according to the literature,[11h] to a 5d(Pt) → π*(C,N,N′) transition. Unfortunately, no emission spectrum was obtained when the excitation wavelengths $\lambda_{exc.}$ = 366 or 560 nm were used, thus indicating that **3** is not luminescent in solution.

Description of the crystal structures

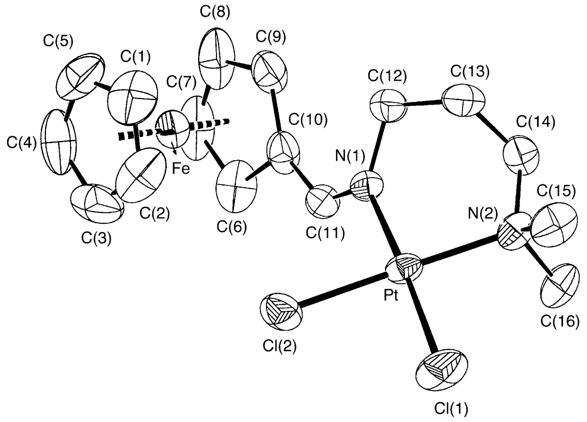


Fig. 2 Molecular structure and atom numbering scheme of *cis*-[Pd{[(η^5-C$_5$H$_4$)–CH=N–(CH$_2$)$_3$–NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl$_2$], **2a**.

The molecular structure of **2a** and the atom labelling scheme are presented in Fig. 2. The structure consists of discrete molecules of *cis*-[Pt{(η^5-C$_5$H$_5$)Fe[(η^5-C$_5$H$_4$)–CH=N–(CH$_2$)$_3$–NMe$_2$]}Cl$_2$] separated by van der Waals contacts. In each molecule the platinum is bound to the two nitrogen atoms [N(1) and N(2)] of **1** and to two chlorides [Cl(1) and Cl(2)], in a slightly distorted square-planar environment,† thus confirming the mode of binding of the ligand.

The Pt–N and Pt–C bond lengths (Table 1) fall in the range described for related cycloplatinated compounds, and the variations detected in the Pt–Cl(1) [2.3112(17) Å] and Pt–Cl(2) [2.2911(19) Å] bond lengths may be attributed to the different influence of the atom in the trans position.[30] The six-membered chelate ring has a boat-conformation‡ in which the platinum and the C(13) atoms deviate by *ca.* −0.674 and −0.623 Å from the plane defined by the remaining atoms.

In **2a** the ligand adopts the syn conformation, in good agreement with the conclusions reached by the NMR studies. For this arrangement of groups the separation between the imine proton [H(11)] and the Cl(2) atom is shorter than the sum of the van der Waals radii [Cl, 1.75 Å and H, 1.20 Å][31] of these atoms, thus suggesting a weak C(11)–H···Cl(2) interaction. The Cl(1) atom is also involved in a similar type of interaction with the H(15) hydrogen of the methyl group. Similar situations have also been described for a wide variety of palladium and platinum complexes.[32]

The molecular structure of **3** together with the atom labelling scheme is depicted in Fig. 3 and a selection of bond lengths and angles is presented in Table 1. The structure consists of discrete molecules of: [Pt{[(η^5-C$_5$H$_3$)–CH=N–(CH$_2$)$_3$–NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] separated by van der Waals contacts. In each molecule the platinum is bound to a chloride, the two nitrogen atoms of the ligand and the ortho carbon of the C$_5$H$_3$ ring of the ferrocenyl unit [C(1)] in a slightly distorted square-planar environment.§ Bond lengths and angles around the platinum center do not differ significantly from those reported for related platinacycles having [Csp^2,N,N′]$^-$ cores.[33] 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 nitrogen atoms to the platinum, a five-membered platinacycle and the 1,2-disubstituted pentagonal ring of the ferrocenyl moiety. The metallacycle,

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† The least-squares equation of the plane defined by the atoms N(1), N(2), Cl(1) and Cl(2) is: (0.0290)XO + (0.4472)YO + (0.8430)ZO = 1.6513 [deviations from the plane: N(1), 0.0022; N(2), −0.022; Cl(1), 0.020 and Cl(2), −0.021 Å].

‡ The least-squares equation of the plane defined by the atoms N(1), N(2), C(12) and C(13) is: (0.9060)XO + (0.7761)YO + (0.6232)ZO = 1.5952.

§ The least-squares equation of the plane defined by Cl, N(1), N(2) and C(6) is: (0.3345)XO + (−0.7039)YO + (0.6266)ZO = 5.2240 [deviations from the plane: Cl, 0.028; N(1), 0.034; N(2), −0.023 and C(6), −0.034 Å].

Table 1 Selected bond lengths (Å) and bond angles (deg.) for *cis*-[Pt{[(η^5-C_5H_4)–CH=N–$(CH_2)_3$–NMe_2]Fe(η^5-C_5H_5)}Cl_2] (**2a**) and [Pt{[(η^5-C_5H_3)–CH=N–$(CH_2)_3$–NMe_2]Fe(η^5-C_5H_5)}Cl] (**3**). Standard deviation parameters are given in parentheses

2a		**3**	
Pt–N(1)	2.024(5)	Pt–N(1)	2.020(7)
Pt–N(2)	2.075(6)	Pt–N(2)	2.182(7)
Pt–Cl((1)	2.3112(17)	Pt–C(6)	1.939(8)
Pt–Cl(2)	2.2911(19)	Pt–Cl	2.327(2)
N(1)–C(11)	1.268(8)	N(1)–C(11)	1.317(10)
N(1)–C(12)	1.475(8)	N(1)–C(12)	1.460(11)
N(2)–C(14)	1.487(9)	N(2)–C(14)	1.430(12)
N(2)–C(15)	1.504(9	N(2)–C(15)	1.433(11)
N(2)–C(16)	1.496(8)	N(2)–C(16)	1.464(11)
C(12)–C(13)	1.516(10)	C(12)–C(13)	1.550(14)
C(13)–C(14)	1.504(10)	C(13)–C(14)	1.600(15)
N(1)–Pt–N(2)	91.8(2)	N(1)–Pt–N(2)	95.9(3)
N(1)–Pt–Cl(1)	90.75(16)	N(1)–Pt–Cl	91.9(3)
N(2)–Pt–Cl(2)	88.65(15)	N(2)–Pt–Cl	90.28(19)
Cl(2)–Pt–Cl(1)	88.76(9)	C(6)–Pt–N(1)	81.9(3)
N(1)–C(11)–C(10)	131.2(6)	N(1)–C(11)–C(10)	114.1(7)

formed by the atoms Pt, N(1), C(11), C(10) and C(6), has an envelope-like conformation¶ in which the platinum(II) is displaced by *ca.* 0.105 Å out of the main plane in the opposite direction of the iron(II).

The six-membered chelate ring has a chair-like conformation in which the N(1), C(12), C(14) and N(2) atoms are nearly co-planar and the platinum deviates by *ca.* −0.352 Å towards the Fe atom group and the C(13) is displaced *ca.* 0.724 Å in the opposite direction.‖ The imine group forms an angle of 6.92° with the C_5H_3 ring, the >C=N– bond length [1.317(10) Å] is slightly greater than that found for **2a** [1.268(8) Å] and the ligand has an anti conformation (*E*-form). The distance between the Cl and the H(16) atoms (2.625 Å) suggests a weak intramolecular C(16)–H(16)···Cl interaction similar to that found for **2a**. In both structures, the separation between the two metals (Fe and Pt: 5.5449 Å in **2a** and 3.3636 Å in **3**) precludes the existence of a direct interaction. Besides this, bond lengths and angles of the ferrocenyl units are consistent with the values reported for most of ferrocene derivatives. The two pentagonal rings are planar, nearly parallel (tilt angles = 0.83° for **2a** and 3.82° for **3**) and they deviate by *ca.* 5.20° (for **2a**) or 2.60° (for **3**) from the ideal eclipsed conformation.

Conclusions

The results presented here provide (a) a useful method to prepare platinum(II) compounds in which **1** acts as a neutral bidentate (N,N′) ligand (in **2a**, **2b**, **4** and **5**), as a monoanionic bidentate [C(sp^2, ferrocene),N]$^-$ ligand (in **6**), or even as a terdentate [C(sp^2, ferrocene),N,N′]$^-$ group (in **3**), which to the best of our knowledge is the first example of a platinum(II) compound having this sort of terdentate ligand, and (b) conclusive evidence of the importance of the conformation of the ligand in **2a** or **2b** and the presence of sodium acetate in the cycloplatination process.

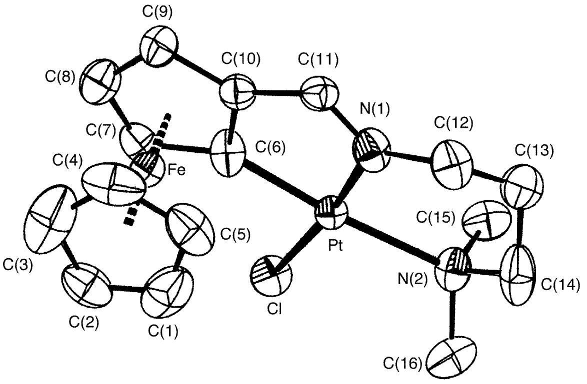

Fig. 3 Molecular structure and atom numbering scheme for [Pd{[(η^5-C_5H_3)–CH=N–$(CH_2)_3$–NMe_2]Fe(η^5-C_5H_5)}Cl], **3**.

Cycloplatination of [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–R′}], (with R = phenyl group) using equimolar amounts of *cis*-[$PtCl_2(dmso)_2$] and sodium acetate in refluxing methanol have been described by Wu *et al.*[13a,b] and for these substrates the formation of the platinacycle is achieved faster than for **1**. These findings indicate that the incorporation of a "–$(CH_2)_3$–NMe_2" moiety on the R′ group may play a crucial role in the process, that is it may hinder the isomerisation of the ligand in the coordination compound, which appears to control the progress of the reaction.

In addition, the two isomeric forms **2a** and **2b** are particularly interesting from the point of view of their potential antitumoural activity, since in them the environment around to the platinum(II) is similar to that of cisplatin. The cytotoxic activity of platinacycles having a (Csp^2, ferrocene,N)$^-$ ligand, such as **C**, shown in Fig. 1, has also been reported. Thus, **2a** and **2b** appear to be excellent candidates for further studies of their interactions with DNA as well as their antitumoural activity. In addition, **3** may also be useful as a precursor in organic or organometallic synthesis. Further work in these areas is currently under way.

Experimental

General comments

The ligand [(η^5-C_5H_5)Fe{(η^5-C_5H_4)–CH=N–$(CH_2)_3$–NMe_2}] (**1**) and *cis*-[$PtCl_2(dmso)_2$] were prepared as described previously.[16,17] Elemental analyses (C, H, and N) were carried out at the Institut de Quimica Bio-organica (C.S.I.C., Barcelona) or at the Serveis de Recursos Cientifics i Tècnics (Univ. Rovira i Virgili, Tarragona). Mass (FAB+ and MALDI-TOF) spectra were acquired at the Departament de Química Orgànica, Univ. de Barcelona, using 3-nitrobenzyl alcohol, (NBA) and 2,5-dihydroxybenzoic acid (DHB) as the respective matrices.

Infrared spectra were obtained with a Nicolet-Impact 400 instrument. Routine ^{1}H-NMR spectra were run with a Gemini-200 MHz instrument using $CDCl_3$ as solvent and and $SiMe_4$ as the reference. The ^{31}P{^{1}H}-NMR spectrum of **6** was registered on a Bruker DXR-250 instrument using $CDCl_3$ as solvent and $P(OMe)_3$ [$\delta^{31}P$ = 140.17 ppm] as reference. High resolution proton NMR spectra as well as the {^{1}H–^{13}C} NMR experiments [heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond coherence (HMBC)] were obtained with either Varian-VXR-500 or Bruker Avance 500DMX-500 instruments. The solvent used for the NMR spectra was $CDCl_3$ (99.9%). ^{195}Pt{^{1}H}-NMR spectra of **2a** and **3**–**6** were recorded with a Bruker DXR-250 instrument and the chemical shifts given are refered to a $Na_2[PtCl_6]$ solution in D_2O as external standard. The low

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¶ The least-squares of the plane defined by N(1), C(6), C(10) and C(11) is: (0.4317)XO + (−0.6198)YO + (0.6181)ZO = 6.8202 [deviations from the plane: N(1), −0.003; C(6), 0.003; C(10), −0.005 and C(11), 0.005 Å].

‖ The least-squares equation of the plane defined by N(1), N(2), C(12) and C(14) is: (0.4088)XO + (−0.7910)YO + (0.4552)ZO = 4.4762 [deviations from the plane: N(1), 0.03; N(2), −0.032; C(12), −0.036 and C(14), 0.036 Å].

solubility of **2b** in $CDCl_3$ did not allow its $^{195}Pt\{^1H\}$-NMR spectrum to be recorded. In all cases the labelling of the atoms corresponds to those shown in Scheme 1, the chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz.

The UV-vis spectra of 10^{-5} M solutions of **2a** and **3** in CH_2Cl_2 were recorded at 25 °C with a Shimadzu-160A spectophotometer, and an Aminco–Bowman spectrofluorimeter was used to try to elucidate if **3** was luminescent in solution.

Preparation of the compounds

***cis*-Pt{[(η^5-C_5H_4)–CH=N–$(CH_2)_3$–NMe_2]Fe(η^5-C_5H_5)}Cl_2] (2a and 2b).** *cis*-[$PtCl_2(dmso)_2$] (100 mg, 2.37×10^{-4} mol) was suspended in 40 ml of methanol and refluxed until complete dissolution. Then the hot solution was filtered and the filtrate was poured into an Erlenmeyer flask containing 71 mg (2.37×10^{-4} mol) of **1**. The resulting mixture was refluxed for 1 h and filtered. The filtrate was then concentrated to dryness on a rotary evaporator. The residue was passed though a short SiO_2 column (5 cm × 2 cm). The use of CH_2Cl_2 as eluant produced the release of an orange band that lead, after work-up, to ferrocenecarboxaldehyde. Once this band was collected, 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 orange solid, **2a**, formed was collected, air-dried and then dried in vacuum (yield: 45 mg, 34%). Once this band was collected, a CH_2Cl_2–MeOH (100:0.3) mixture was used as eluant and small amounts of **2b** (≈10 mg) were isolated after work-up of the band released.

2a. Anal (%) calcd. for $C_{16}H_{22}N_2Cl_2FePt$ (found): C, 34.06 (34.0); H, 3.94 (4.1) and N, 4.97 (4.5). MS (FAB$^+$): $m/z = 563$ {[M]$^+$}, 528 {[M − Cl]}$^+$. $R_f = 0.21$ [in CH_2Cl_2–MeOH (100:0.1)]. IR: 1606 cm^{-1} [ν(>C=N–). ^{1}H-NMR: 4.40 (s, 5H, C_5H_5); 4.62 (s, 2H, H^2 and H^5]); 4.60 (s, 2H, H^3 and H^4); 8.86 [s, 1H, –CH=N–, ^3J(Pt–H) = 61]; 3.70 (m, 2H, =N–CH_2–); 2.24 (m, 2H, –CH_2–); 2.50 (m, 2H, –CH_2–N–); 3.00 [s, 6H, 2Me, ^3J(Pt–H) = 33]. $^{13}C\{^1H\}$-NMR:** 70.8 (C_5H_5), 73.6 (C^2), 72.1 (C^3), 72.1 (C^4), 73.6 (C^5), 173.7 (–CH=N–), 51.8 (=N–CH_2–), 26.3 (–CH_2–), 62.6 (–CH_2–N–) and 53.5 (Me). $^{195}Pt\{^1H\}$ NMR: −2120. UV-vis: λ_{max}/nm (ε/dm^{-3} mol^{-1} cm^{-1}): 280 (9664), 312 (10 114) and 471 (1786).

2b. Anal (%) calcd. for $C_{16}H_{22}N_2Cl_2FePt\cdot1.5CH_2Cl_2$ (found): C, 30.39 (30.73); H, 3.64 (3.52) and N, 4.05(4.26). MS (MALDI-TOF): $m/z = 528$ {[M − Cl]}$^+$. IR: 1624 cm^{-1} [ν(>C=N–)]. ^{1}H-NMR: 4.31 (s, 5H, C_5H_5); 5.76 (s, 1H, H^2); 4.69 (s, 1H, H^3); 4.72 (s, 2H, H^4); 5.93 (s, 1H, H^5); 8.17 [s, 1H, –CH=N–, ^3J(Pt–H) = 120]; 3.98 and 4.53 (m, 2H, =N–CH_2–); 1.89 and 2.40 (m, 2H, –CH_2–); 2.66 and 2.99 (m, 2H, –CH_2–N–); 2.94 and 2.85 [s, 6H, 2Me, ^3J(Pt–H) = 33]. $^{13}C\{^1H\}$-NMR:** 70.2 (C_5H_5), 73.3 (C^2), 73.1 (C^3), 73.8 (C^4), 72.6 (C^5), 169.5 (–CH=N–), 61.4 (=N–CH_2–), 29.8 (–CH_2–), 62.4 (–CH_2–N–) and 53.2 and 53.7 (Me).

[Pt{[(η^5-C_5H_3)–CH=N–$(CH_2)_3$–NMe_2]Fe(η^5-C_5H_5)}Cl], 3. This complex was prepared using the same methodology as described for **2**, but in this case a stoichiometric amount of sodium acetate (19 mg, 2.37×10^{-4} mol) was added to the initial mixture and the resulting solution was refluxed for 6 days. After this period the solution was filtered and the filtrate was concentrated to dryness on a rotary evaporator. The gummy residue was passed through a SiO_2 column (4.5 cm × 2 cm) using CH_2Cl_2 as eluant. The first eluted band led, after work-up, to ferrocenecarboxaldehyde. The deep purple band collected afterwards was concentrated to dryness on a rotary evaporator to give a purple solid, which was collected, air-dried and then dried in vacuum for 3 days (yield: 32 mg). Further use of CH_2Cl_2–MeOH mixtures (100:0.2 and 100:0.3) as eluant led to small amounts of **2a** (13.7 mg) and traces of **2b**, respectively. Anal (%) calcd. for $C_{16}H_{21}N_2ClFePt$ (found): C, 36.41 (36.5); H, 4.01 (4.2) and N, 5.31 (5.3). MS (FAB$^+$): $m/z = 528$ {[M]$^+$}. $R_f = 0.45$ (in CH_2Cl_2). IR: 1564 cm^{-1} [ν(>C=N–)]. ^{1}H-NMR: 4.27 (s, 5H, C_5H_5); 4.54 (s, 1H, H^3); 4.60 (s, 1H, H^4); 4.99 (s, 1H, H^5); 8.24 [s, 1H, –CH=N–, ^3J(Pt–H) = 125]; 3.61 and 3.50 (m, 2H, =N–CH_2–); 1.90 (m, 2H, –CH_2–); 2.81 (m, 2H, –CH_2–N); 2.66 and 2.82 (s, 6H, 2Me). $^{13}C\{^1H\}$-NMR: 70.3 (C_5H_5), 86.6 (C^1), 66.6 (C^3), 71.1 (C^4), 75.6 (C^5), 175.0 (–CH=N–), 58.2 (=N–CH_2–), 27.9 (–CH_2)–, 64.5 (–CH_2–N–), 49.8 and 50.1 (Me), the signal due to the C^2 atom was not observed. $^{195}Pt\{^1H\}$ NMR: −3326. UV-vis: λ_{max}/nm (ε/dm^{-3} mol^{-1} cm^{-1}): 278 (14300), 366 (3998) and 530 (1970).

***cis*-[Pt{[(η^5-C_5H_4)–CH=N–$(CH_2)_3$–NMe_2]Fe(η^5-C_5H_5)}(AcO)-Cl] (4 and 5).** A mixture containing **2a** (72 mg, 1.28×10^{-4} mol), Na(CH_3COO) (11 mg, 1.24×10^{-4} mol) and 20 ml of methanol was refluxed for 6 days and then filtered. The filtrate was concentrated to dryness and the residue was passed through a SiO_2 column. Elution with CH_2Cl_2 gave, after work-up, **3**; elution with a CH_2Cl_2–MeOH (100:0.5) mixture allowed to collect traces of unreacted **2a**, and finally elution with a CH_2Cl_2–MeOH (100:2) mixture produced the release of two orange bands, which led after concentration to **4** (10 mg) and **5** (4 mg).

4. MS (FAB$^+$): $m/z = 587$ {[M$^+$]}, 552 {[M − Cl]$^+$}, 529 {[M − (CH_3COO)]$^+$} and 493 {[MH − Cl − CH_3COO]$^+$}. IR: 1603 cm^{-1} [br. ν(>C=N– and ν(COO)]. ^{1}H-NMR: 4.37 (s, 5H, C_5H_5); 4.59 (s, 2H, H^2 and H^5); 4.56 (s, 2H, H^3 and H^4); 8.77 [s, 1H, –CH=N–, ^3J(H–Pt) = 52]; 3.67 (dt, 2H, =N–CH_2–); 2.15 (m, 2H, –CH_2–); 2.67 (m, 2H, –CH_2–N–); 2.83 (s, 6H, NMe_2); 2.06 [s, 3H, CH_3 (acetate)]. $^{13}C\{^1H\}$-NMR: 173.6 (–CH=N–), 70.8 (C_5H_5), 71.8 (C^2 and C^5), 73.3 (C^3 and C^4), 52.4 (=N–CH_2–), 26.5 (–CH_2–), 63.1 (–CH_2–N–), 52.8 (–NMe_2), 23.8 [CH_3 (acetate)], 178.4 [–COO (acetate)], the signal due to the C^1 carbon was not detected. $^{195}Pt\{^1H\}$-NMR: −1820.

5. IR: 1707 cm^{-1} [ν(COO)} and 1631 cm^{-1} [ν(>C=N–)]. ^{1}H-NMR: 4.30 (s, 5H, C_5H_5); 4.61 (br m, 4H, H^2, H^3, H^4 and H^5); 8.65 [s, 1H, –CH=N–, ^3J(H–Pt) = 60]; 3.72 (dt, 2H, =N–CH_2–); 2.25 (m, 2H, –CH_2–); 2.39 (m, 2H, –CH_2–N–); 2.95 (s, 6H, NMe_2); 2.07 [s, 3H, CH_3 (acetate)]. $^{13}C\{^1H\}$-NMR: 172.3 (–CH=N–), 70.3 (C_5H_5), 72.1 (C^2 and C^5), 73.5 (C^3 and C^4), 52.2 (=N–CH_2–), 26.4 (–CH_2–), 63.2 (–CH_2–N), 54.2 (–NMe_2), 23.9 (CH_3 (acetate)], 178.1 [–COO (acetate)], the signal due to the C^1 carbon was not detected. $^{195}Pt\{^1H\}$-NMR data: −2127.

[Pt{[(η^5-C_5H_3)–CH=N–$(CH_2)_3$–NMe_2]Fe(η^5-C_5H_5)}Cl(PPh_3)], 6. Compound **3** (18 mg, 3.41×10^{-5} mol) was dissolved in 0.7 ml of $CDCl_3$ and then a stoichiometric amount of PPh_3 (9.1 mg, 3.47×10^{-5} mol) was added. The initial colour of the solution changed from deep purple to red upon addition of the phosphine. The reaction mixture was shaken for 5 min at *ca.* 20 °C. Slow evaporation of the solvent yielded a red solid, which was washed with small amounts of *n*-hexane, air-dried and then dried in vacuum for 3 days (yield: 18 mg, 67%). Anal (%) calcd. for $C_{34}H_{36}N_4ClFePPt$ (found): C, 51.69 (52.57); H, 4.60 (4.84) and N, 3.54 (3.39). MS (FAB+): $m/z = 755$ [M − Cl]$^+$; IR: 1584 cm^{-1} [ν(>C=N–)]. ^{1}H-NMR: 3.82 (s, 5H, C_5H_5); 4.16 [t, 2H, H^3 and H^4, J(H–H) = 2.2]; 4.39 [d, 1H, H^5, J(H–H) = 2.2]; 8.23 [d, 1H, –CH=N–, ^3J(Pt–H) = 86, ^4J(P–H) = 9.2]; 3.79 and 4.15 (m, 2H, =N–CH_2–); 2.40 and 2.45 (m, 2H, –CH_2–); 1.88 and 2.20 (m, 2H, –CH_2–N); 2.26 (s, 6H, 2Me); 7.34–7.80 (m, 15H, aromatic protons of the PPh_3). $^{13}C\{^1H\}$-NMR: 70.0 (C_5H_5), 87.2 (C^1), 85.0 [d, C^2, ^2J(C–P) = 9.1], 76.0 (C^3), 71.0 (C^4), 66.4 (C^5), 174.1(–CH=N–), 59.1

** The signal due to the C^1 carbon was not observed in the $^{13}C\{^1H\}$-NMR spectrum.

(=N–CH$_2$–), 29.5 (–CH$_2$)–, 56.8 (–CH$_2$–N–), 45.6 (Me). ^{31}P{^{1}H}-NMR: 16.40 [^1J(Pt–P) = 4146]. ^{195}Pt{^{1}H}-NMR : −4186 [d, ^1J(Pt–P) = 4146].

Crystallography

A prismatic crystal of **2a** (or **3**) was selected and mounted on a MAR345 diffractometer with a image plate detector (for **2a**) or on a Enraf–Nonius CAD4 four-circle diffractometer (for **3**). For **2a**, unit cell parameters were determined from 10581 reflections in the range $3° < \Theta < 31°$, while for **3**, they were determined from automatic centring of 25 reflections in the range $12° < \Theta < 21°$ and refined by least-squares methods. Intensities were collected with graphite monochromated Mo–Kα radiation using the $\omega/2\Theta$ scan technique. Three reflections were measured every 2 h as orientation and intensity controls and no significant intensity decay was observed. Lorentz polarisation and absorption corrections were performed in the two cases.

The structures were solved by direct methods, using the SHELXS97 computer programme,[34] and refined by full-matrix least-squares methods with the SHELX97 computer program.[35] The function minimised was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0636P)^2 + 6.8520P]^{-1}$ (for **2a**) or $w = [\sigma^2(I) + (0.0701P)^2]^{-1}$ (for **3**) and $P = (|F_o| - 2|F_c|^2)/3$; f, f' and f'' were obtained from the literature.[36] For **2a** four hydrogen atoms (H11, H15, H15A and H15B) were located from a difference synthesis and refined with an overall isotropic temperature factor while 18 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 to which it is linked. For **3** 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 linked atom. The final *R* indices as well as further details concerning the resolution and refinement of the crystal structures of **2a** and **3** are presented in Table 2.

CCDC reference numbers 196563 and 196564. See http://www.rsc.org/suppdata/nj/b2/b211346e/ for crystallographic files in CIF or other electronic format.

Table 2 Crystallographic data for *cis*-[Pt{[(η^5-C$_5$H$_4$)–CH=N–(CH$_2$)$_3$–NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl$_2$] (**2a**) and [Pt{[(η^5-C$_5$H$_3$)–CH=N–(CH$_2$)$_3$–NMe$_2$]Fe(η^5-C$_5$H$_5$)}Cl] (**3**). Standard deviation parameters are given in parentheses

	2a	**3**
Empirical formula	$C_{16}H_{22}Cl_2FeN_2Pt$	$C_{16}H_{21}ClFeN_2Pt$
M	564.20	527.74
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	11.2560(10)	11.109(5)
b/Å	12.7750(10)	12.596(12)
c/Å	13.9752(8)	12.484(5)
α/deg.	90.0	90.0
β/deg.	117.408(5)	110.81(4)
γ/deg.	90.0	90.0
U/Mg × m^{-3}	1784.0(2)	1632.9(18)
Z	4	4
Abs. coeff./mm^{-1}	8.942	9.604
Reflections collected	13 047	4741
Unique reflections	4271	4741
R_{int}	0.0346	0.0569
Obs. reflections [$I > 2\sigma(I)$]	3766	3215
R_1 [$I > 2\sigma(I)$]	0.0392	0.0442
wR_2 [$I > 2\sigma(I)$]	0.1049	0.1023
R_1 (all data)	0.0483	0.0796
wR_2 (all data)	0.1166	0.1169

Acknowledgements

This work was supported by the Ministerio de Ciencia y Tecnología of Spain (Grants: BQU2000-0652 and PB98-1236) and by the Generalitat de Catalunya (Grant: 2001-SGR-00045). S.P. is also grateful to the Generalitat de Catalunya for a pre-doctoral fellowship.

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