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1-Methyl-4-ferrocenylmethyl-3,5-diphenylpyrazole: A versatile ligand for palladium(II) and platinum(II)

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ABSTRACT

The syntheses and characterization of two novel ferrocene derivatives containing 3,5-diphenylpyrazole units of general formula [1-R-3,5-Ph_2-(C_3N_2)-CH_2-Fc] {Fc = (η^5-C_5H_5)Fe(η^5-C_5H_4) and R = H (**2**) or Me (**3**)} together with a study of their reactivity with palladium(II) and platinum(II) salts or complexes under different experimental conditions is described. These studies have allowed us to isolate and characterize *trans*-[Pd{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc]}$_2Cl_2$] (**4a**) and three different types of heterodimetallic complexes: *cis*-[M{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc]}Cl_2(dmso)] {M = Pd (**5a**) or Pt (**5b**)}, the cyclometallated products [M{κ^2-*C*,*N*-[3-(C_6H_4)-1-Me-5-Ph-(C_3N_2)]-CH_2-Fc}Cl(L)] with L = PPh_3 and M = Pd (**6a**) or Pt (**6b**) or L = dmso and M = Pt (**8b**) and the *trans*-isomer of [Pt{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc]}Cl_2(dmso)] (**7b**). In compounds **4a**, **5a**, **5b** and **7b**, the ligand behaves as a neutral N-donor group; while in **6a**, **6b** and **8b** it acts as a bidentate [C(sp^2,phenyl),N(pyrazole)]$^-$ group. A comparative study of the spectroscopic properties of the compounds, based on NMR, IR and UV–Visible experiments, is also reported.

1. Introduction

The synthesis and design of ferrocene derivatives containing heterocyclic systems have attracted great interest in recent years [1–3] because of their physical or chemical properties as well as for their applications in a wide variety of areas including homogeneous catalysis [1,2d,3c] and Biomedicine [2e]. In this sort of compounds, the presence of heterocycles with one or more atoms with good donor abilities is especially interesting in view of their use as ligands for transition metals to give heteropolymetallic complexes [1,2d,4] in which the existence of two or more proximal metal ions may induce a co-operative effect [4].

On the other hand, palladium(II) and platinum(II) complexes with heterocyclic ligands with two potentially donor atoms is one of the research areas that has undergone a fast development during the last years [5–17]. Among all the examples reported so far those containing pyrazole backbones are specially attractive [6–8]. Compounds of this kind exhibiting greater antitumoral activity and lower toxicity than *cis*-[$PtCl_2(NH_3)_2$] or antibacterial activity have been reported [6c,7h]. Furthermore, some examples of their utility in Macromolecular Chemistry [7a,i–k] or in homogeneous catalysis [8a] have also been published.

In addition, when the pyrazole contains substituents in which there is a σ(C–H) bond with the proper orientation, cyclopalladated [9] or platinated [10] complexes can also be isolated. The interest on metallacycles with a σ(M–C) (M = Pd or Pt) bond has increased exponentially due to their properties and applications in different areas [11–17]. Metallomesogens [11], precursors for homogeneous catalysis [13], antitumor drugs [14] and "building blocks" for Supramolecular Chemistry [15] containing pallada- and platinacycles have been reported. In addition, the high reactivity of the σ(M–C) bond in this sort of compounds makes them valuable precursors in organic synthesis [11a,12b,c,16] including the total synthesis of natural products [12b,16]. However, and despite the increasing interest on palladium(II) and platinum(II) complexes with ligands containing simultaneously a ferrocenyl unit and a (N,O) or a (N,S) heterocycle [3,4], parallel studies on related compounds with pyrazole rings are scarce [4c,18,19]. A few palladium(II) complexes containing this type of ligands are known and most of them contain additional allylic ligands [3c,19]. Only one example of a cyclopalladated complex having simultaneously the ferrocenyl and the pyrazolyl units has been described so far [4c], but platinum(II) derivatives are still unknown. In view of these facts, and as a part of a project centred on the synthesis of heterodimetallic complexes with heterocycles having ferrocenyl moieties [3c,d,4,12d], we focused our attention on: (a) the synthesis of novel pyrazolyl containing ferrocene derivatives and (b) the study of their reactivity towards palladium(II) and platinum(II) salts or complexes. In this work, we present the syntheses and characterization of [1-R-3,5-Ph_2-(C_3N_2)-CH_2-Fc] {Fc = (η^5-C_5H_5)Fe (η^5-C_5H_4) and R = H (**2**) or Me (**3**)} (Scheme 1) that contain the

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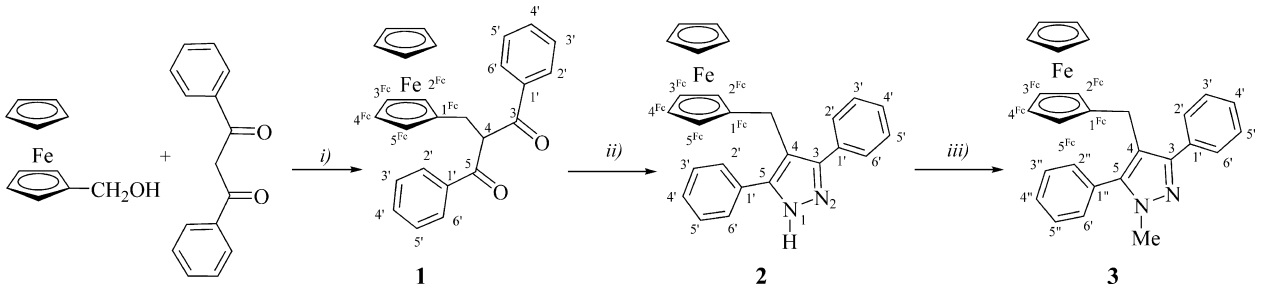


Scheme 1. (i) HBF_4 (40%)/CH_2Cl_2. (ii) N_2H_4, EtOH under reflux. (iii) NaOH (40%), CH_2Cl_2 and MeI.

3,5-diphenylpyrazolyl group in the pendant arm of the ferrocene as well as a variety of palladium(II) and platinum(II) complexes derived from these ligands.

2. Results and discussion

2.1. The ligands

The preparation of the new ferrocenyl ligands [1-R-3,5-Ph_2-(C_3N_2)-CH_2-Fc] (R = H or Me) was achieved following the sequence of reactions presented in Scheme 1. First, 3-ferrocenylmethyl dibenzoylmethane (**1**) was obtained by electrophilic coupling on position 3 of the diketone using ferrocenylmethanol (Fc-CH_2OH) [20] in a two-phase CH_2Cl_2/40% aqueous HBF_4 mixture (Scheme 1, step (i)) [21]. Subsequent treatment with hydrazine in ethanol at reflux temperature (Scheme 1, step (ii)) [4c] followed by purification of the crude product of the reaction by column chromatography gave [1-R-3,5-Ph_2-(C_3N_2)-CH_2-Fc] with R = H (**2**). The subsequent alkylation with methyl iodide (Scheme 1, step (iii)) using the same procedure as described before for indigo [22], gave [1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc] (**3**) in good yield (98%).

Compounds **1**–**3** were characterized by elemental analyses, mass spectrometry, infrared spectra and mono- and two-dimensional NMR experiments. The elemental analyses (Section 3) were consistent with the proposed formulae and their mass spectra showed a peak at *m/z* = 422.1 (for **1**), 419.1 (for **2**) and 433.1 (for **3**) that agree with the values expected for the $\{[M]+H\}^+$ cations.

Proton NMR spectra of **1**–**3** showed the typical patterns of monosubstituted ferrocene derivatives [1,23] and the resonances due to the –CH_2– protons appeared as a doublet (in **1**) or as a singlet (in **2** and **3**) in the range 3.10–4.00 ppm. The signals observed in the $^{13}C\{^1H\}$ NMR spectra of **1**–**3** were assigned with the aid of two-dimensional $\{^1H–^{13}C\}$ HSQC and HMBC experiments. The resonances due to the quaternary carbon nuclei of **1**–**3** were easily identified by comparison of the signals detected in the $^{13}C\{^1H\}$ and in the $\{^1H–^{13}C\}$ HSQC, and the analyses of the cross peaks between the –CH_2– protons allowed to assign the resonances of the *ipso* carbon of the ferrocenyl unit (C^{1Fc}) and of the C^3–C^5 nuclei.

2.2. Palladium(II) complexes

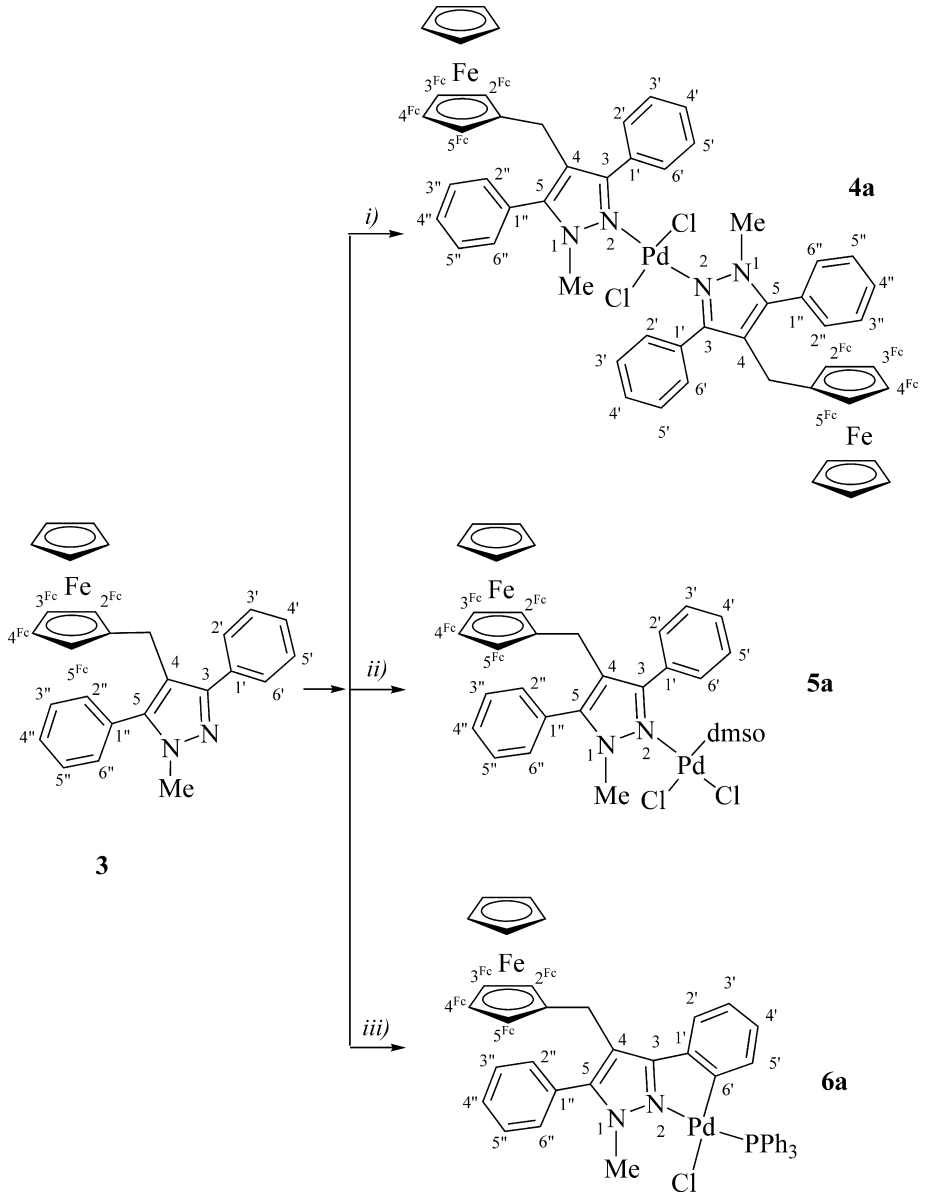
Treatment of [1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc] (**3**) with [$PdCl_2$(dmso)$_2$] [24] (in a 2:1 molar ratio) in refluxing methanol for 3.5 h under reflux produced a pale yellow solid that was identified as the heterotrimetallic complex [Pd{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc}]$_2Cl_2$] (**4a**) (Scheme 2, step (i)). It is well-known that in palladium(II) complexes of the type [Pd(L)$_2Cl_2$] (with L = planar N-donor ligand) the "$PdCl_2$" is nearly orthogonal to the main plane of the N-donor ligand [25,26]. For this arrangement of groups, the use of molecular models reveals that in *cis*-[Pd{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc]}$_2Cl_2$], the steric hindrance is greater than in the *trans*-isomer (**4a**). In addition, the IR spectrum of **4a** in the range of metal–ligand vibrations showed two bands at ν = 498 and 334 cm^{-1}. According to Ref. [27] these absorptions are due to the Pd–N and Pd–Cl stretching vibrations of *trans*-[Pd(N-donor)$_2Cl_2$] complexes. In view of these findings we assume that **4a** is the *trans*-isomer of [Pd{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc]}$_2Cl_2$].

In contrast with these results, when the reaction was carried out using equimolar amounts of **3** and [$PdCl_2$(dmso)$_2$] [24] a different product was obtained. Elemental analyses were consistent with those expected for [Pd{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc]}Cl_2(dmso)] (**5a**) (Scheme 2, step (ii)) and its ^1H NMR spectrum in $CDCl_3$ at 298 K showed an intense singlet at 3.25 ppm assigned to the protons of the dmso ligand; however, no evidence of the existence of NOE peaks between these protons and any of the coordinated ligand **3** were detected in the $\{^1H–^1H\}$ NOESY spectrum. The far IR spectrum of **5a** showed two absorption bands of the Pd–Cl stretching vibrations at 298 and 320 cm^{-1}. Their position is similar to those reported for [$PdCl_2$(dmso)(L)] with L = 5,7-*di*-*ert*butyl-1,2,4-triazolo[1,5-*a*]pyrimidine, for which: (a) the crystal structure confirmed a *cis*-arrangement of the two Cl^- ligands and (b) only one singlet due to the protons of the dmso ligand was also observed in the ^1H NMR spectrum [28]. On these bases, we tentatively postulate that in **5a**, the Cl^- ligands are in a *cis*-disposition.

It is well-known that for N-donor ligands (L), the formation of the palladacycle usually takes place in two steps, first the coordination of two (or one) units of the ligand to give *trans*-[Pd(L)$_2X_2$] {or [Pd(L)X_3]$^-$} species, followed by the subsequent electrophilic attack of the palladium(II) species formed to the carbon atom [11a,29]. Despite the arrangement of ligands in **4a** is identical to those of the *trans*-[Pd(L)$_2X_2$] species formed in the first step of the cyclopalladation process, no evidence of the formation of any palladacycle were detected by ^1H NMR when **4a** was refluxed in toluene for long periods (up to 12 h). In view of these results and since it is well-known that Pd(OAc)$_2$ is a better metallating agent than [$PdCl_2$(dmso)$_2$] [11a,29] we also studied the reactivity of **3** with this salt.

When ligand **3** was treated with Pd(OAc)$_2$ in toluene under reflux for 3.5 h followed by: (a) the addition of PPh_3 first and LiCl later on and (b) a column chromatography on silica gel, the cyclopalladated complex [Pd{κ^2-*C*,*N*-[3-(C_6H_4)-1-Me-5-Ph-(C_3N_2)]-CH_2-Fc}Cl(PPh_3)] (**6a**) (Scheme 2, step (iii)) was isolated in fairly good yield (74%). In this product, the ligand acts as a bidentate [C(sp^2,phenyl),N(pyrazole)]$^-$ group and the phosphine is in a *cis*-arrangement in relation to the metallated carbon atom, in good agreement with the so-called *transphobia effect* [30].

It should be noted that when any of the reactions depicted in Scheme 1, steps (i) and (ii) were performed under identical conditions but using [1-R-(3,5-Ph_2-(C_3N_2)-CH_2-Fc] with R = H (**2**), instead of ligand **3**, the starting materials were recovered unchanged and no evidence of the formation of any palladium(II) complex was detected by NMR. The well-known tautomeric process involving the proton transfer between the two nitrogen atoms



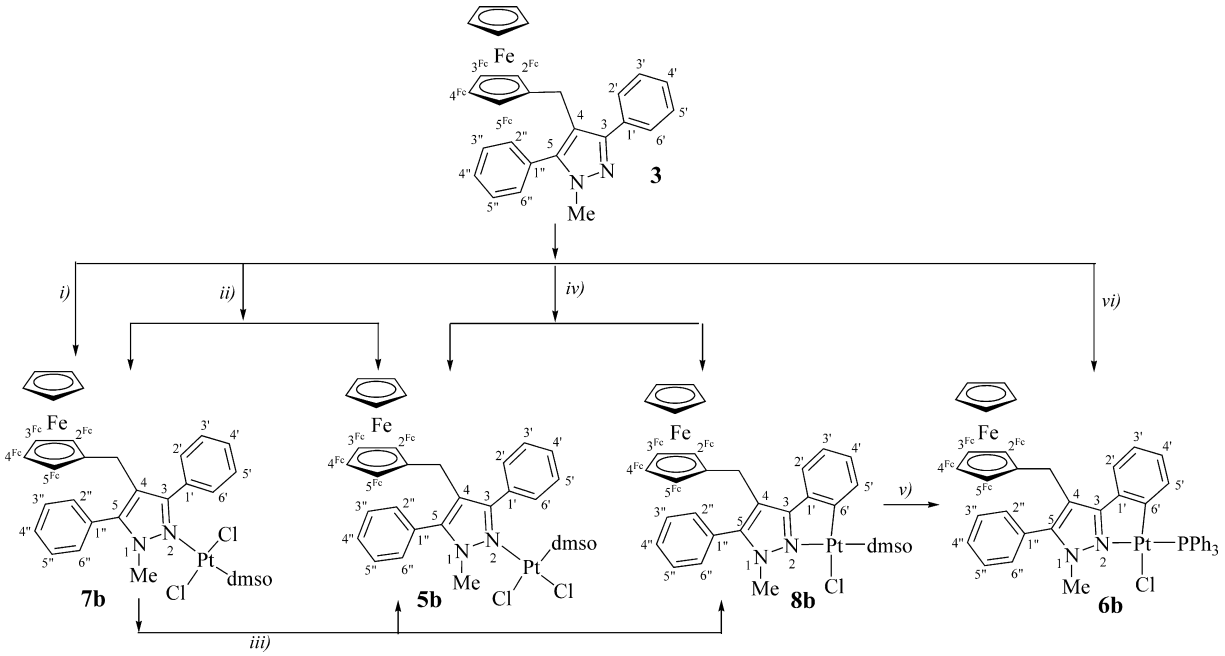
Scheme 2. (i) *Cis*-[$PdCl_2(dmso)_2$] (molar ratio **3**:Pd = 2)/MeOH under reflux. (ii) *Cis*-[$PdCl_2(dmso)_2$] (molar ratio **3**:Pd = 1)/MeOH under reflux. (iii) $Pd(OAc)_2$/toluene under reflux; PPh_3/CH_2Cl_2; LiCl, acetone and SiO_2 column chromatography.

of the pyrazolyl moiety may hinder the coordination of ligand **2** to palladium(II) [31].

2.3. Platinum(II) complexes

The reaction of equimolar amounts of [1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc] (**3**) and *cis*-[$PtCl_2(dmso)_2$] [32] in refluxing methanol for 3.5 h followed by column chromatography on silica gel produced a yellow solid, whose characterization data (see below and Section 3) agreed with those expected for [Pt{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc]}Cl_2(dmso)] (**7b**) (Scheme 3, step (i)).

When the reaction was carried out under identical experimental conditions but using dry toluene as solvent (Scheme 3, step (ii)) the ^{1}H NMR spectrum of the raw material showed two superimposed sets of signals of relative intensities 3.7:1.0 thus indicating the presence of at least two products. The resonances due to the major component were identical to those observed for **7b**; while for the minor one (hereinafter referred to as **5b**), two singlets of identical intensity were observed at δ = 2.47 ($^3J_{Pt-H}$ = 20.6 Hz) and 3.31 ppm ($^3J_{Pt-H}$ = 20.3 Hz)]. This suggested that the two Me groups of the dmso were not equivalent. A column chromatography on silica gel allowed to isolate **7b** and a bright orange microcrystalline product (**5b**). Elemental analyses of **5b** also agreed with those expected for [Pt{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc]}Cl_2(dmso)], thus suggesting that **7b** and **5b** might be two isomers of this compound. The signal detected in the ^{195}Pt{^{1}H} NMR of **5b** (at δ = −2925 ppm) also is consistent with the values of platinum(II) complexes with a "N,Cl_2,S(dmso)" set of donor atoms but it was downfield shifted in relation to that of **7b** (δ = −3015 ppm) and the difference $\Delta\delta = \delta$ (for **5b**) − δ (for **7b**) = 90 ppm, falls in the range reported for the *cis*- and *trans*-isomers of [Pt(N-donor ligand)Cl_2(dmso)] {55 ppm < ($\delta_{cis-}-\delta_{trans-}$ < 128 ppm} [34,35a–c,36]. The analysis of the cross peaks detected in the {^{1}H–^{1}H} NOESY spectrum of **5b** indicated that one of the methyl groups of the dmso ligand (at δ = 2.47 ppm) was close to the *ortho* protons of the phenyl ring, which causes the high field shift of this signal, when compared with that observed for **7b** {δ = 3.44 ppm ($^3J_{Pt-H}$ = 20.4 Hz)}, due to the magnetic anisotropy of the phenyl ring. Furthermore, the far



Scheme 3. (i) *Cis*-[$PtCl_2(dmso)_2$]/MeOH under reflux. (ii) *Cis*-[$PtCl_2(dmso)_2$]/toluene under reflux. (iii) NaOAc/in MeOH under reflux. (iv) *Cis*-[$PtCl_2(dmso)_2$]/NaOAc/toluene:MeOH under reflux; SiO_2 column chromatography. (v) PPh_3/CH_2Cl_2. (vi) *Cis*-[$PtCl_2(dmso)_2$]/NaOAc/toluene:MeOH/reflux; PPh_3/CH_2Cl_2; SiO_2 column chromatography.

IR-spectra of **5b** showed two bands due to the stretching of the Pt–Cl bond (at 348 and 312 cm^{-1}) while that of **7b** exhibited only one (at 355 cm^{-1}). According to Refs. [27,36], all these findings suggested that compounds **5b** and **7b** differed in the relative arrangement of the Cl^- ligands {*cis*-(in **5b**) and *trans*-(in **7b**)}.

In order to confirm the relative arrangement of the Cl^- ligands in **5b** or **7b**, several crystallization procedures were used; however, most of the experiments failed and only when CH_2Cl_2 solutions of **5b** were evaporated at −4 °C small crystals were obtained. Unfortunately, they rapidly degraded upon the X-ray radiation at 298 K. At 243 K unit-cell parameters could be determined (see Section 3) but even in these conditions, and due to the low stability and poor quality of the crystal, the number of reflections collected was (951, R_{int} = 0.1821) too low as to allow the resolution of the structure.[1]

On the other hand, the comparison of the results obtained in the two solvents indicate that the replacement of methanol by toluene as solvent promotes the preferential formation of the *cis*-isomer of [Pt{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc]}Cl_2(dmso)]. This result is in good agreement with those obtained in the reaction of *cis*-[$PtCl_2(dmso)_2$] with the imine 4Cl–C_6H_4–CH=N–(CH_2)-(4′Cl–C_6H_4) and related N-donor ferrocenyl ligands [34,37].

Due to the recent interest in platinacycles with heterocyclic ligands [10], we attempted the synthesis of cycloplatinated complexes. Since it is well-known that some platinum(II) complexes of the type [Pt(N-donor ligand)Cl_2(dmso)] undergo the intramolecular cycloplatination reaction in the presence of a base, such as NaOAc [26,33–35,37], we also explored the reactivity of *trans*-[Pt{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc]}Cl_2(dmso)] (**7b**) with this salt. The reaction between equimolar amounts of **7b** and NaOAc in refluxing methanol for 24 h yielded after work up a mixture of two compounds (Scheme 3, step (iii)). The major component was identified as **5b**. This result is similar to that obtained by Crespo et al. [37] for the imine 4Cl–C_6H_4–CH=N–(CH_2)-(4′Cl–C_6H_4) and is consistent with previous studies on the reactivity of related N-donor ligands with *cis*-[$PtCl_2(dmso)_2$] [35]. Characterization data of the minor component (see Section 3) were consistent with those expected for [Pt{κ²-*C*,*N*-[3-(C_6H_4)-1-Me-5-Ph-(C_3N_2)]-CH_2-Fc}Cl(dmso)], (**8b**) (see below and Section 3) in which the ferrocene derivative **3** behaves as a bidentate {C(sp^2,phenyl),N(pyrazole)}$^-$ ligand and the dmso group is in a *cis*-arrangement to the metallated carbon atom.

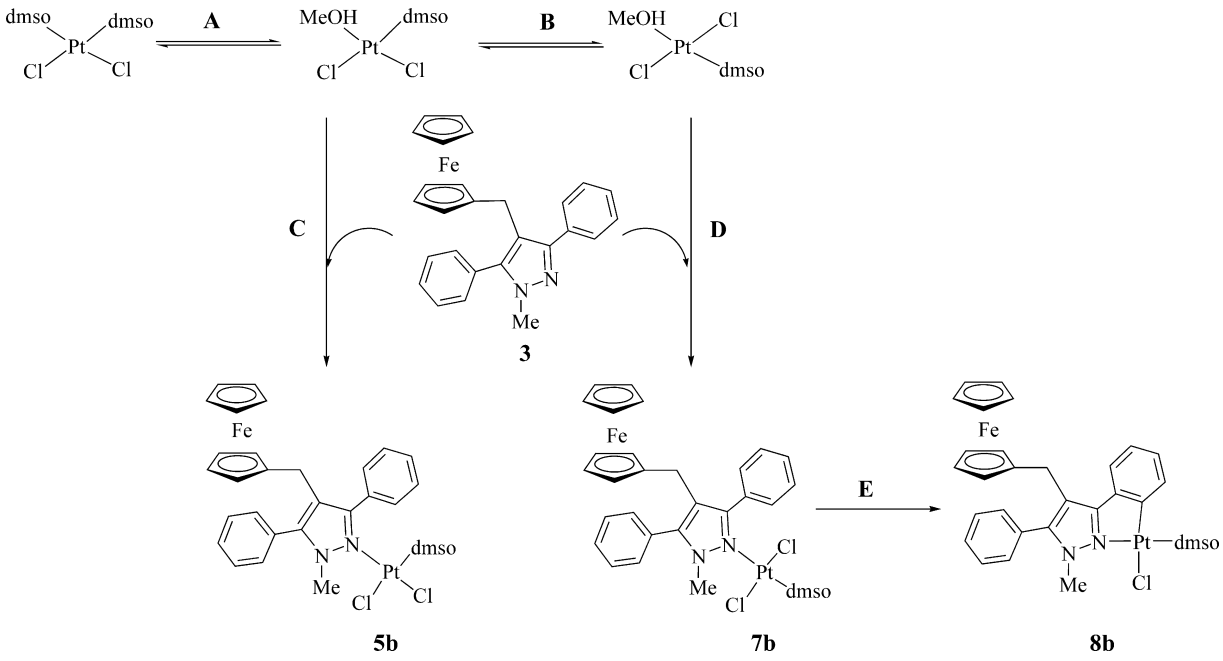
This process (Scheme 3, step (iii)) produced the platinacycle **8b** but the reaction was complex due to the formation of **5b** and the molar ratio **5b**:**8b** was 8.5:1.0. In view of these results and in order to increase the yield of **8b** a different strategy, based on the direct method reported for the synthesis of a few platinacycles with bidentate [C(sp^2,phenyl or ferrocene), N]$^-$ ligands, was used [4b,34,35]. Treatment of equimolar amounts of **3**, *cis*-[$PtCl_2(dmso)_2$] and NaOAc in a mixture toluene/methanol under reflux for 54 h, followed by column chromatography on silica gel, furnished compounds **8b** and **5b** (Scheme 3, step (iv)). It should be noted that the molar ratio **5b:8b** decreased as the refluxing time increased (from 8.5:1.0 for 24 h to 3.7:1.0 for 54 h).

The results obtained in the study of the reactivity of **3** with *cis*-[$PtCl_2(dmso)_2$] suggest that the formation of the platinacycle **8b** is a multistep process (Scheme 4) in which the main reactions involve, the replacement of one of the dmso ligands of the starting material by methanol (Scheme 4, A) to give *cis*-[$PtCl_2$(MeOH)(dmso)] which may isomerize to the *trans*-form (Scheme 4, B). Further coordination of the N-donor ligand **3**, would produce the *cis*- and *trans*-isomers of [Pt{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc]}Cl_2(dmso)] (Scheme 4, steps C and D, respectively) and this may proceed at different rates. Finally, the activation of the σ(C–H) bond of the phenyl ring of compound **7b**, would produce the platinacycle **8b** (Scheme 4, step E).

It should be noted that the set of reactions presented in Scheme 4 agree with: (a) the mechanism postulated for the cycloplatination of aryloximes, [38a] (b) the results obtained recently from a DFT-based theoretical studies of the cycloplatination process [38b] and previous studies on the cyclometallation of N-donor ligands (L) for which it has been demonstrated that *trans*-[$PtCl_2$(L)dmso] complexes are the key intermediates of the process [35a,37].

Further reaction of **8b** with the equimolar amount of PPh_3 produced the replacement of the dmso ligand by the phosphine to give

[1] A minimum of 2421 reflections were required to achieve a resolution of 1 Å.



Scheme 4.

[Pt{κ^2-*C*,*N*-[3-(C_6H_4)-1-Me-5-Ph-(C_3N_2)]-CH_2-Fc}Cl(PPh_3)], (**6b**) (Scheme 3, step (v)). Characterization data of **6b** suggests that this product is formally identical to the palladacycle **6a**, except for the nature of the metal atom {M = Pd (in **6a**) or Pt (in **6b**)}. It should be noted that complex **6b** could also be isolated by direct treatment of **3**, *cis*-[$PtCl_2$(dmso)$_2$] and NaOAc under reflux in a toluene:methanol (5:1) mixture, followed by the reaction of the residue obtained after concentration with an excess (50%) of triphenylphosphine (Scheme 3, step (vi)).

2.4. Characterization of the palladium(II) and platinum(II) complexes

The new complexes were characterized by elemental analyses, mass and infrared spectroscopy and mono-and two-dimensional NMR spectroscopy. In all cases elemental analyses and mass spectra (Section 3) were consistent with the proposed formulae. IR-spectra of the complexes showed the typical bands due to the S-bonded dmso ligand (**5a**, **5b**, **7b** and **8b**) [27] or those due to the PPh_3 (in **6a** and **6b**) [39].

The assignment of the signals detected in the ^{1}H and ^{13}C{^{1}H} NMR spectra (Section 3) of the Pd(II) and Pt(II) complexes was achieved with the aid of two-dimensional NMR [{^{1}H–^{1}H} NOESY, COSY and {^{1}H–^{13}C} HSQC and HMBC] experiments. Proton and ^{13}C{^{1}H} NMR spectra of all the compounds exhibited: (a) the typical pattern of monosubstituted ferrocene derivatives [1,23] and (b) the resonances due to the dmso (in **4a**, **5a**, **5b**, **7b** and **8b**) or the PPh_3 (in **6a** and **6b**) ligands.

For the cyclometallated complexes **6a**, **6b** and **8b** the resonance of the proton in the adjacent position to the metallated carbon ($H^{5'}$), was up-field shifted in comparison with its position for the free ligand and compounds **5a**, **5b** and **7b**, where this ligand behaves as a monodentate N-donor group. This trend, that has also been observed for related [M(C,N)X(L)] complexes with M = Pd(II) or Pt(II), L = pyridine or phosphines and X = AcO^-, Cl^-, Br^- or I^-, has been attributed to anisotropy of the aromatic rings of the ligands L that are close to that proton [15c,33,34,40].

The ^{195}Pt{^{1}H} NMR spectra not only provided convincing evidence for the coordination sphere and structure of the platinum(II) derivatives but also explained the variations produced by: (a) the different mode of binding of ligand **3** {N(pyrazole) (in **5b** and **7b** or [C(sp^2,phenyl),N(pyrazole)]$^-$ (in **6b** and **8b**)} or (b) the relative arrangement of the ligands in **5b** and **7b**. The chemical shift of the signals follows the trend: **5a** < **7b** < **6b** < **8b**. According to the literature [33,36,41], an up-field shift in ^{195}Pt NMR is related to a strong interaction between the platinum and its ligands, and since **6b** and **8b** differ only in the nature of the neutral ligand [PPh_3 (in **6b**) or dmso (in **8b**)], the variations observed in the ^{195}Pt chemical shift of **6b** and **8b** can be ascribed to the different donor abilities of the PPh_3 and dmso ligands.

Due to the ongoing interest of the photophysical properties of multifunctional heterocyclic ligands and their palladium(II) and platinum(II) complexes [8,11,42,43] we also studied the Ultraviolet–Visible spectra of CH_2Cl_2 solutions of all new products (see Section 3). The spectra of ligands **2** and **3** showed an intense [20 000 < ε < 27 000 M^{-1} cm^2] band in the range 230 nm < λ < 260 nm. According to the Ref. [8] this absorption is due to a $\pi \rightarrow \pi^*$ transition of the 3,5-pyrazolyl unit (intraligand transition: IT). The palladium(II) and platinum(II) complexes also exhibited a band in this region and its position did not change appreciably from those of the free ligand, thus suggesting that it corresponds to a metal perturbed intraligand transition (MPILT).

In the UV–Vis spectra of ligands **2** and **3** an additional absorption at 449 nm (ε = 256 M^{-1} cm^2, for **2**) or 438 nm (ε = 269 M^{-1} cm^2 for **3**), due to an electronic *d*–*d* transition of the ferrocenyl unit, was also observed. It has been reported that for ferrocene derivatives, the presence of electron withdrawing substituents produce a decrease of the energy of this transition, while for electron donating groups the effect is opposite [44]. On this basis, the comparison of the position of band for ligands **2**, **3** and for the Fc-CH_2-NMe_2 {λ = 402 nm (ε = 302 M^{-1} cm^2)} [44,45] suggests that the electron donor ability of the CH_2R substituents increases according to the sequence: **2** < **3** < Fc-CH_2-NMe_2.

The UV–Vis spectra of compounds **5a**, **5b**, **6a** and **7b** also showed a band in the range 420 nm < λ < 440 nm (with extinction coefficients in the range 165 < ε < 200 M^{-1} cm^2) and its position does not vary significantly when ligand **3** binds to the palladium(II) and platinum(II), thus suggesting that this absorption can be ascribed to a metal perturbed intraligand transition (MPILT).

Similarly to what happened for the free ligands, for the palladium(II) and platinum(II) complexes presented here this band appears at lower energies than for their analogues containing the Fc-CH_2-NMe_2 as ligand [45].

Finally, it should be noted that for compounds **3**, **5b**, **6b** and **8b**, an additional and poorly defined absorption at 271 nm (for **3**) or in the range 310–320 nm (ε = 1759, 6219, 2338 M^{-1} cm^2 for **5b**, **6b** and **8b**, respectively) was also observed in their UV–Vis spectra.

2.5. Conclusions

The results presented here have allowed us: (a) to prepare and characterize the two novel ferrocene derivatives [1-R-3,5-Ph_2-(C_3N_2)-CH_2-Fc] {Fc = (η^5-C_5H_5)Fe(η^5-C_5H_4) and R = H (**2**) or Me (**3**)} that contain a 3,5-diphenyl pyrazole unit and (b) to evaluate the coordinating abilities of these ligands with Pd(II) and Pt(II). The results obtained have shown that compound **3** is more prone to bind to these ions than the non-methylated derivative **2**. The study of the reactivity of **3** with $Pd(OAc)_2$ or [MCl_2(dmso)$_2$] (M = Pd or Pt) under different experimental conditions has allowed us to establish the best experimental conditions to control selectively the preferential formation of the different sorts of the complexes: *trans*-[Pd{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc}$_2Cl_2$] (**4a**) or the heterodimetallic products *cis*-[M{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc}Cl_2(dmso)] {M = Pd (**5a**) or Pt (**5b**)}, the *trans*-isomer of the platinum(II) complex (**7b**) and the cyclometallated compounds: [M{κ^2-*C*,*N*-[3-(C_6H_4)-1-Me-5-Ph-(C_3N_2)]-CH_2-Fc}Cl(L)] {with L = PPh_3 and M = Pd (**6a**) or Pt (**6b**) or L = dmso and M = Pt (**8b**)} and to tune the mode of binding of **3** in the complexes {(N) in **4a**, **5a**, **5b** and **7b** or [C(sp^2,phenyl),N(pyrazole)]$^-$ in **6a**, **6b** and **8b**}.

Since platinum(II) compounds containing pyrazole ligands have greater antitumoral activity and lower toxicity than *cis*-[$PtCl_2(NH_3)_2$] [6c,7h] and some platinum(II) complexes derived from N-donor ferrocenyl ligands also exhibit antitumoral activity [46], the new platinum(II) derivatives presented in this work containing simultaneously a ferrocenyl- and a pyrazolyl units appear to be specially attractive for further studies as antitumoral drugs.

3. Experimental

3.1. Materials and methods

Compounds [MCl_2(dmso)$_2$] (M = Pd or Pt) were prepared as reported previously [24,32], $FcCH_2OH$ was synthesized from the ferrocenecarboxaldehyde [20] and the remaining reagents were obtained from commercial sources and used as received. Except methanol (which was HPLC-grade), the remaining solvents were dried and distilled before use [47]. Elemental analyses were carried out at the Serveis de Cientifico-Tècnics (Universitat de Barcelona). Mass spectra (ESI^+) were performed at the Servei d'Espectrometria de Masses (Universitat de Barcelona). Infrared spectra in the range 4000–400 cm^{-1} were obtained with a Nicolet 400FTIR instrument using KBr pellets; while far IR-spectra of **4a**, **5a**, **5b** and **7b** (in the range 200–400 cm^{-1}) were registered with a Bomen-DA3 instrument using polyethylene discs. Routine ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Mercury-400 MHz instrument. High resolution ^1H NMR spectra and the two-dimensional [$\{^1H$–$^1H\}$-NOESY and COSY and $\{^1H$–$^{13}C\}$-HSQC and HMBC] experiments were registered with a Varian VRX-500 or a Bruker Avance DMX-500 MHz instruments at 298 K. The chemical shifts (δ) are given in ppm and the coupling constants (*J*) in Hz. $^{195}Pt\{^1H\}$ NMR spectra of compounds **5b**–**8b** were obtained with a Bruker-250 MHz instrument at 298 K. $^{31}P\{^1H\}$ NMR spectra of **6a** and **6b** were recorded with a Varian-Unity-300 instrument. In all cases the solvent for the NMR experiments was $CDCl_3$ (99.9%) and the references were $SiMe_4$ [for ^1H and $^{13}C\{^1H\}$ NMR], $P(OMe)_3$ [$\delta(^{31}P)$ = 140.17 ppm] for ^{31}P NMR and $H_2[PtCl_6]$ [$\delta^{195}Pt\{H_2$-$[PtCl_6]\}$ = 0.0 ppm] for $^{195}Pt\{^1H\}$ NMR experiments. UV–Vis spectra of 1.6×10^{-4} M solutions of the compounds in CH_2Cl_2 were recorded with a Cary 100 scan Varian UV spectrometer. Unit cell parameters of **5b**[2] were determined at 243 K with a MAR345 with an image plate detector diffractometer using 1203 reflections ($3° < \theta < 31°$) and refined by least-squares method.

3.2. Preparation of the compounds

3.2.1. Preparation of [Fc-CH_2-CH{C(O)Ph}$_2$] (**1**)

Dibenzoyl methane (0.68 g, 3.03×10^{-3} mol) and Fc-CH_2OH (0.66 g, 3.03×10^{-3} mol) were dissolved in 60 mL of CH_2Cl_2. Then a solution formed by 12 mL of HBF_4 and 8 mL of H_2O was added dropwise under stirring. The resulting mixture was magnetically stirred at room temperature for 1 h and afterwards it was treated with 150 mL of H_2O. The mixture was extracted with two (50 mL) portions of CH_2Cl_2, the organic layer was then dried over Na_2SO_4 and the filtrate was concentrated to dryness on a rotary evaporator. The solid formed was collected and air-dried for one day. Yield: 1.57 g (84%). *Characterization data*: Anal. Calc. for $C_{26}H_{22}O_2Fe$: C, 73.96; H, 5.22. Found: C, 73.81; H, 5.36%. MS (ESI^+): m/z = 422.1 $[M+H]^+$. $R_f(CH_2Cl_2)$ = 0.62. IR: 1763(w), 1700(s), 1666(s), 1470(s), 1446(w), 1402(w), 1335(s), 1300(s), 1142(s), 1020(s), 990(s), 924(m), 866(m), 821(s), 773(s), 705(s), 645(m), 588(s) and 497(s) cm^{-1}. UV–Vis ($c = 1.6 \times 10^{-4}$ M in CH_2Cl_2): λ in nm (ε in M^{-1} cm^2) = 246(23 150) and 340(1944). ^1H NMR data [48]: δ = 3.17(dd, 2H, *J* = 6.5 and 1.0, –CH_2–), 4.00(s, 2H, H^{3Fc} and H^{4Fc}), 4.09(s, 2H, H^{2Fc} and H^{5Fc}), 4.12(s, 5H, Cp), 5.29(t, 1H, *J* = 6.5, H^4), 7.51(m, 2H, $H^{4'}$), 7.38(m, 4H, $H^{3'}$ and $H^{5'}$) and 7.86(d, 4H, *J* = 7.0, $H^{2'}$ and $H^{6'}$).$^{13}C\{^1H\}$ NMR data [48]: δ = 30.1(–CH_2–), 59.8(C^4), 67.7(Cp), 67.8(C^{3Fc} and C^{4Fc}), 69.0(C^{2Fc} and C^{3Fc}), 86.1(C^{1Fc}), 126.4($C^{4'}$), 128.7($C^{3'}$ and $C^{5'}$), 136.1($C^{1'}$), 139.4($C^{2'}$and $C^{6'}$), and 195.4(>CO).

3.2.2. Preparation of [1-R-3,5-Ph_2-(C_3N_2)-CH_2-Fc] with R = H (**2**)

A solution formed by 1.27 g (3.01×10^{-3} mol) of compound **1** and 35 mL of ethanol was treated with 1.5 mL (30.1×10^{-3} mol) of $N_2H_4 \cdot H_2O$. The resulting solution was refluxed for 3 h and then allowed to cool to room temperature. The subsequent concentration of the solution on a rotary evaporator produced a yellow residue. The solid was dissolved in CH_2Cl_2 (≈15 mL) and passed through a short SiO_2 column (5.0 × 1.0 cm). Elution with CH_2Cl_2 released a yellow band that was collected and concentrated to dryness on a rotary evaporator. The solid formed was collected and dried in vacuum for 2 days. Yield: 0.975 g (98%). *Characterization data*: Anal. Calc. for $C_{26}H_{22}N_2Fe$: C, 74.67; H, 5.27; N, 6.70. Found: C, 74.6; H, 5.4; N, 6.7%. MS (ESI^+): m/z = 419.1 $[M+H]^+$. $R_f(CH_2Cl_2)$ = 0.22. IR: 1724(m), 1641(w), 1493(s), 1445(s), 1409(w), 1293(s), 1162(m), 1104(s), 1072(s), 1021(s), 999(s), 920(m), 833(m), 767(s), 698(s), 568(m), 501(s) and 482(m) cm^{-1}. UV–Vis ($c = 1.6 \times 10^{-4}$ M in CH_2Cl_2): λ in nm (ε in M^{-1} cm^2) = 248(21 919) and 449(256). ^1H NMR data [48]: δ = 3.76(s, 2H, –CH_2–), 3.62(s, 2H, H^{3Fc} and H^{4Fc}), 3.68(s, 2H, H^{2Fc} and H^{5Fc}), 3.87(s, 5H, Cp), 6.50(d, 1H, *J* = 6.5, NH), 7.35(br.m, 2H, $H^{4'}$), 7.40-7.53(br.m, 4H, $H^{3'}$ and $H^{5'}$) and 7.57(d, 4H, *J* = 7.5, $H^{2'}$ and $H^{6'}$). $^{13}C\{^1H\}$ NMR data [48]: δ = 23.8(–CH_2–), 66.8(C^{2Fc}, C^{3Fc}, C^{4Fc} and C^{5Fc}), 68.6(Cp), 88.9(C^{1Fc}), 115.3(C^4), 125.4($C^{4'}$), 128.1($C^{3'}$and $C^{5'}$), 128.6($C^{2'}$ and $C^{6'}$), 132.2($C^{1'}$) and 145.2(br., C^3 and C^5).

[2] Cystal system: triclinic, *a* = 12.210(7) Å, *b* = 15.806(8) Å, *c* = 17.562(5) Å, α = 109.44(3)°, β = 102.79(2)° and γ = 91.07(3)°.

*3.2.3. Preparation of [1-Me-3,5-Ph$_2$-(C$_3$N$_2$)-CH$_2$-Fc] (**3**)*

To a solution containing 800 mg (1.91×10^{-3} mol) of compound **2** and 30 mL of toluene, benzyltriethylammonium chloride (218 mg, 0.95×10^{-3} mol) and 7 mL of an aqueous NaOH (40%) solution were added. Afterwards, 0.24 mL (3.82×10^{-3} mol) of CH_3I were added dropwise in two portions and the resulting mixture was magnetically stirred at 298 K for 24 h. After this period H_2O (50 mL) was added and then the mixture was extracted with two (25 mL) portions of CH_2Cl_2. The organic layers were combined and dried over Na_2SO_4. The resulting filtrate was concentrated to dryness on a rotary evaporator. The residue was then dissolved in the minimum amount of CH_2Cl_2 (≈10 mL) and passed through a short neutral alumina column (5.0×2.0 cm). Elution with CH_2Cl_2 released a yellow band that was collected and concentrated to dryness on a rotary evaporator. The solid formed was then dried in vacuum for 2 days. Yield: 0.811 g (98%). *Characterization data*: Anal. Calc. for $C_{27}H_{24}N_2Fe$: C, 75.03; H, 5.56; N, 6.48. Found: C, 75.2; H, 5.5; N, 6.6%. MS(ESI$^+$): m/z = 433.1[M+H]$^+$. $R_f(CH_2Cl_2)$ = 0.33. IR: 1957(w), 1724(s), 1637(m), 1459(s), 1429(s), 1408(m), 1291(m), 1159(w), 1104(s), 1049(m), 1028(m), 1000(m), 922(w), 828(m), 817(s), 754(s), 700(m), 680(m), 611(w), 494(s) and 478(m) cm^{-1}. UV–Vis ($c = 1.6 \times 10^{-4}$ M in CH_2Cl_2): λ in nm (ε in M^{-1} cm^2) = 242(26 125), 271sh(≈23 019) and 438(269). ^{1}H NMR data [48]: δ = 3.62(s, 2H, –CH$_2$–), 3.76(s, 5H, Cp), 3.88(s, 3H, NMe), 3.98(br.s, 4H, H^{2Fc}, H^{3Fc}, H^{4Fc} and H^{5Fc}), 7.30–7.50(br.m, 6H, H$^{3'}$, H$^{4'}$, H$^{5'}$, H$^{3''}$, H$^{4'}$and H$^{5''}$) and 7.65(d, 4H, J = 7.5, H$^{2'}$, H$^{6'}$, H$^{2''}$and H$^{6''}$). ^{13}C{^{1}H} NMR data [48]: δ = 23.8(–CH$_2$–), 38.9(NMe), 66.7(C^{2Fc}, C^{3Fc}, C^{4Fc} and C^{5Fc}), 68.4(Cp), 88.8(C^{1Fc}), 116.9(C^4), 128.3(C$^{2'}$ and C$^{6'}$), 128.2(C$^{3'}$ and C$^{5'}$), 127.4(C$^{4'}$), 127.6(C$^{4''}$), 128.6(C$^{3''}$and C$^{5''}$), 130.0(C$^{2''}$ and C$^{6''}$), 130.2(C$^{1'}$), 134.2(C$^{1''}$), 142.3(C^5) and 149.3(C^3).

*3.2.4. Preparation of trans-[Pd{1-Me-3,5-Ph$_2$-(C$_3$N$_2$)-CH$_2$-Fc}$_2$Cl$_2$] (**4a**)*

Cis-[PdCl$_2$(dmso)$_2$] (260 mg, 7.8×10^{-4} mol) was suspended in 30 mL of methanol and refluxed until complete dissolution. Then the hot solution was filtered directly on a solution containing 15.6×10^{-4} mol of **3** (672 mg) in 5 mL of methanol. The resulting reaction mixture was refluxed for 2 h. The precipitate formed was collected, washed with (2×5 mL) portions of methanol, air-dried and then dried in vacuum for 2 days. Yield: 640 mg (79%). *Characterization data*: Anal. Calc. for $C_{54}H_{50}Cl_2N_4PdFe_2$: C, 62.12; H, 4.83; N, 5.37. Found: C, 62.20; H, 4.91; N, 5.45%. MS (ESI$^+$): m/z = 1042.0 [M]$^+$. IR: 1636(s), 150(m), 1479(m), 1246(s), 1224(m), 1077(m), 1024(m), 923(s), 827(m), 756(m), 70s0(w) and 498(Pd–N) and 334(Pd–Cl) cm^{-1}. ^{1}H NMR data [48]: δ = 3.41(s, 4H, 2 –CH$_2$–), 3.54(br., 4H, 2H^{3Fc} and 2H^{4Fc}), 3.84(s, 10H, 2 Cp), 3.89(br.s, 4H, 2 NMe), 3.88(br.s, 4H, H^{2Fc} and H^{5Fc}), 3.80(br.s, 4H, H^{2Fc} and H^{5Fc}), 7.09–7.16(br. m, 4H, 2H$^{4'}$ and 2H$^{4''}$) and 7.40–7.62(br. m. 16H, 2H$^{2'}$, 2H$^{3'}$, 2H$^{5'}$, 2H$^{6'}$, 2H$^{2''}$, 2H$^{3''}$, 2H$^{5''}$and 2H$^{6''}$). ^{13}C{^{1}H} NMR data [48]: δ = 23.5(–CH$_2$–), 37.4(NMe), 67.0(C^{3Fc}), 67.2(C^{4Fc}), 68.4(C^{5Fc}), 68.6(C^{2Fc} and Cp), 87.4(C^{1Fc}), 119.5(C^4), 128.1(C$^{5''}$), 128.7(C$^{4''}$), 128.8(C$^{3'}$, C$^{5'}$ and C$^{3''}$), 128.9(C$^{4'}$), 129.6(C$^{1'}$), 129.8(C$^{6''}$), 130.1(C$^{2'}$ and C$^{6'}$), 131.2(C$^{2''}$), 131.9(C$^{1''}$), 144.7(C^5) and 150.9(C^3).

*3.2.5. Preparation of cis-[Pd{1-Me-3,5-Ph$_2$-(C$_3$N$_2$)-CH$_2$-Fc}Cl$_2$(dmso)] (**5a**)*

[PdCl$_2$(dmso)$_2$] (260 mg, 7.8×10^{-4} mol) was suspended in 30 mL of methanol and refluxed until complete dissolution. Then the hot solution was filtered directly on a solution containing 7.8×10^{-4} mol of **3** (337 mg) in 5 mL of methanol. The resulting reaction mixture was refluxed for 2 h and then allowed to cool at room temperature. The precipitate formed was collected by filtration, washed with (2×5 mL) portions of methanol and air-dried for one day. After this period the solid was dissolved in the minimum amount of CH_2Cl_2 (≈15 mL) and passed through a SiO_2 column (8.5 cm × 3.0 cm). Elution with CH_2Cl_2:MeOH (100:1) released a reddish yellow band that was collected and concentrated to dryness on a rotary evaporator. The solid formed (**5a**) was collected and dried in vacuum for 2 days. Yield: 300 mg (56%). *Characterization data*: Anal. Calc. for $C_{29}H_{30}Cl_2N_2OPdFeS$: C, 50.64; H, 4.37; N, 4.07; S, 4.66. Found: C, 50.48; H, 4.52; N, 3.98; S, 4.60%. MS (ESI$^+$): m/z = 710.1 {[M]+Na}$^+$. $R_f(CH_2Cl_2)$ = 0.10. IR: 1636(s), 1501(w), 1444(m), 1373(m), 1297(w), 1105(m), 1076(w), 1022(m), 920(w), 822(w), 755(m), 700(s), 496(Pd-N) and 320 and 298 (Pd–Cl) cm^{-1}. UV–Vis ($c = 1.6 \times 10^{-4}$ M in CH_2Cl_2): λ in nm (ε in M^{-1} cm^2) = 239(26 818) and 421(193). ^{1}H NMR data [48]: δ = 3.25(s, 12H, dmso), 3.41(s, 2H, –CH$_2$–), 3.54(br., 2H, H^{3Fc} and H^{4Fc}), 3.83(br.s, 8H, –NMe and Cp), 3.88(br.s, 2H, H^{2Fc} and H^{5Fc}), 7.10–7.20(br. m, 2H, H$^{4'}$ and H$^{4''}$) and 7.30–7.58(br. m. 8H, H$^{2'}$, H$^{3'}$, H$^{5'}$, H$^{6'}$, H$^{2''}$, H$^{3''}$, H$^{5''}$and H$^{6''}$). ^{13}C{^{1}H} NMR data [48]: δ = 23.5(–CH$_2$–), 38.6(NMe), 37.4(dmso), 66.9(C^{3Fc}), 67.1(C^{4Fc}), 68.2(C^{2Fc}), 68.3(C^{5Fc}), 68.6(Cp), 87.2(C^{1Fc}), 119.6(C^4), 128.5(C$^{5''}$), 128.6(C$^{4''}$), 128.7(C$^{3'}$, C$^{5'}$ and C$^{3''}$), 128.9(C$^{4'}$), 129.4(C$^{1'}$), 129.6(C$^{6''}$), 129.9(C$^{2'}$ and C$^{6'}$), 129.9(C$^{2''}$), 131.8(C$^{1''}$), 144.6(C^5), and 150.9(C^3).

*3.2.6. Preparation of [Pd{κ^2-C,N-[3-(C$_6$H$_4$)-1-Me-5-Ph-(C$_3$N$_2$)]-CH$_2$-Fc}Cl(PPh$_3$)] (**6a**)*

Pd(OAc)$_2$ (156 mg, 6.9×10^{-4} mol) was added to a solution containing 300 mg (6.9×10^{-4} mol) of compound **3** and 20 mL of toluene. The reaction mixture was protected from the light with aluminium foil and refluxed for 3.5 h. During the reflux the deposition of the metallic palladium on the walls of the flask was detected. After this period the resulting hot solution was filtered through a small plug (2.0 cm × 3.5 cm) of Celite. The bright yellow solution was concentrated to dryness and kept for further use. The Celite was allowed to dry overnight and then it was washed with CH_2Cl_2 until nearly colourless washings were obtained. The washings were collected in the same flask containing the residue and the resulting solution was concentrated to dryness on a rotary evaporator. The crude product thus obtained was dissolved in 20 mL of CH_2Cl_2 and treated with PPh_3 (182 mg, 6.9×10^{-4} mol) and the resulting reaction mixture was stirred for 1.5 h at room temperature. It was then filtered and the filtrate was concentrated to dryness on a rotary evaporator giving a brownish residue. This was then suspended in 30 mL of acetone and treated with LiCl (31 mg, 6.9×10^{-4} mol). The resulting suspension was stirred for 2.5 h at room temperature under argon atmosphere. The undissolved materials were removed by filtration and the filtrate was concentrated to dryness on a rotary evaporator and then dried in vacuum. The yellowish-brown residue was dissolved in minimum amount of CH_2Cl_2 and passed through a SiO_2 column (3.0 cm × 9.0 cm) using CH_2Cl_2 as eluant. After the removal of the first band, that contained [PdCl$_2$(PPh$_3$)$_2$], the eluted bands were collected in *ca.* 100 mL portions. Then the bright yellow solutions collected were concentrated to dryness on a rotary evaporator to give **6a** (425 mg, 74%). *Characterization data*: Anal. Calc. for $C_{45}H_{38}ClN_2PFePd$: C, 64.69; H, 4.55; N, 3.35. Found: C, 64.54; H, 4.62; N, 3.31%. MS (ESI$^+$): m/z = 799.1 {[M]−Cl}$^+$. $R_f(CH_2Cl_2)$ = 0.31. IR: 1671(w), 1591(m), 1479(m), 1434(s), 1367(m), 1314(w), 1271(w), 1095(s), 1017(m), 999(m), 818(m), 748(s), 725(m), 709(s), 533(s), 515(s) and 494(m) cm^{-1}. UV–Vis ($c = 1.6 \times 10^{-4}$ M in CH_2Cl_2): λ in nm (ε in M^{-1} cm^2) = 242(25 256) and 437(192). ^{1}H NMR data [48]: δ = 3.80(s, 2H, –CH$_2$–), 3.89(s, 5H, Cp), 3.97(s, 2H, H^{3Fc} and H^{4Fc}), 4.10(s, 2H, H^{2Fc} and H^{5Fc}), 4.33(s, 3H, –NMe), 6.47(td, 2H, J = 7.5 and 1.0, H$^{5''}$), 6.27(td, 1H, J = 7.5 and 1.0, H$^{4''}$), 6.82(d, 1H, J = 7.2, H$^{3''}$), 7.40-7.51 (br.m, 20H, H$^{3'}$, H$^{4'}$, H$^{5'}$, H$^{6'}$, H$^{2''}$ and aromatic protons of the PPh$_3$ ligand) and 7.79(d, 2H, J = 7.6, H$^{2'}$ and H$^{2'}$). ^{13}C{^{1}H} NMR data [48]: δ = 23.8(–CH$_2$–), 39.0(NMe), 66.9(C^{2Fc}, C^{3Fc}, C^{4Fc} and C^{5Fc}), 68.6(Cp), 87.6(C^{1Fc}), 123.9(C^4),

125.8($C^{4''}$), 128.9($C^{3'}$ and $C^{5'}$), 129.4($C^{4'}$), 129.0($C^{3''}$), 129.2($C^{5''}$), 130.2($C^{2''}$), 130.6($C^{2'}$ and $C^{6'}$), 138.7(d, $^3J_{C-P}$ = 14, $C^{6''}$), 140.4($C^{1''}$), 145.9(C^5), 150.0(C^3), 156.0($C^{1'}$), and four additional doublets centred at *ca.* 128.1, 130.7, 131.3 and 135.0 due to due to the four types of non-equivalent carbon-13 nuclei of the PPh_3 ligand). $^{31}P\{^1H\}$ NMR data: δ = 47.6.

3.2.7. Preparation of [Pt{κ²-C,N-[3-(C_6H_4)-1-Me-5-Ph-(C_3N_2)]-CH_2-Fc}Cl(PPh_3)] (**6b**)

This product was obtained using two different procedures {methods (a) and (b)}.

Method (a): In this case compound **6b** was prepared in NMR scale and characterized in solution by ^1H NMR. Compound **8b** (20 mg, 2.7×10^{-5} mol) and PPh_3 (7 mg, 2.7×10^{-5} mol) were introduced in a NMR tube and then 0.7 mL of $CDCl_3$ was added. It was shaken vigorously for 2 min. This produced a bright yellow solution which gave the desired complex **6b** in 84% yield (21 mg) (after evaporation in vacuum).

Method (b): Ligand **3** (256 mg, 5.92×10^{-4} mol) and *cis*-[$PtCl_2(dmso)_2$] (250 mg, 5.92×10^{-4} mol) were suspended in 20 mL toluene. Then, a solution containing 49 mg (5.92×10^{-4} mol) of sodium acetate and 4 mL of methanol was added. The resulting reaction mixture was refluxed for 54 h and then allowed to cool at room temperature. The undissolved materials were removed by filtration and the filtrate was concentrated to dryness on a rotary evaporator. Afterwards, the deep-brown residue was dissolved in 20 mL of CH_2Cl_2 and treated with 280 mg (8.8×10^{-4} mol) of PPh_3. The resulting reaction mixture was magnetically stirred at room temperature for 1.5 h. It was then filtered and the filtrate was concentrated to dryness on a rotary evaporator. The deep-brown residue was dissolved in the minimum amount of CH_2Cl_2 and passed through a SiO_2 column (3.0 cm × 9.0 cm) using CH_2Cl_2 as solvent. The two bright yellow solutions collected were concentrated to dryness on a rotary evaporator to give [$PtCl_2(PPh_3)_2$] (100 mg) and **6b** (275 mg, 50%), respectively.

Characterization data: Anal. Calc. for $C_{45}H_{38}ClN_2PPtFe$: C, 58.48; H, 4.14; N, 3.03. Found: C, 58.31; H, 4.02; N, 3.16%. MS (ESI⁺): *m/z* = 888.1 $\{[M]-Cl\}^+$. $R_f(CH_2Cl_2)$ = 0.71. IR: 1638(s), 1618(s), 1478(m), 1272(w), 1096(m), 1025(w), 999(w), 895(w), 819(m), 745(s), 691(s), 542(s) and 481(m) cm^{-1}. UV–Vis ($c = 1.6 \times 10^{-4}$ M in CH_2Cl_2): λ in nm (ε in $M^{-1}\,cm^2$) = 242(30 150), 312(6219), 347sh(≈2150) and 452broad (≈165). ^1H NMR data [48]: δ = 3.83(s, 2H, $-CH_2-$), 3.89(s, 5H, Cp), 3.96(s, 2H, H^{3Fc} and H^{4Fc}), 4.00(s, 2H, H^{2Fc} and H^{5Fc}), 4.18(s, 3H, –NMe), 6.32(d, 1H, *J* = 7.2, $H^{5''}$), 6.63(td, 1H, *J* = 7.5 and 1.0, $H^{4''}$), 6.84(td, 2H, *J* = 7.5 and 1.0, $H^{3''}$), 7.84(d, 1H, *J* = 7.5, $H^{2'}$), 7.32–7.64(br.m, 18H, $H^{3'}$, $H^{4'}$, $H^{5'}$ and aromatic protons of the PPh_3). $^{13}C\{^1H\}$ NMR data [48]: δ = 23.7($-CH_2-$), 39.4(NMe), 39.8(dmso), 67.0(C^{2Fc}, C^{3Fc},C^{4Fc} and C^{5Fc}), 68.6(Cp), 87.2(C^{1Fc}), 123.2(C^4), 130.7($C^{2'}$ and $C^{6'}$), 120.4($C^{4'}$), 128.7($C^{3'}$ and $C^{5'}$), 124.2($C^{4''}$), 129.5($C^{3''}$), 129.3($C^{5''}$), 130.6($C^{2''}$), 139.8($C^{1''}$), 138.1(d, $^3J_{C-P}$ = 9 and $^1J_{C-Pt}$ = 34, $C^{6''}$), 149.5(C^3), 147.1(C^5), 158.0($C^{1'}$), and four additional doublets centred at *ca.* 128.0, 130.9, 131.0 and 135.1 due to the four types of non-equivalent carbon-13 nuclei of the PPh_3 ligand). $^{31}P\{^1H\}$ NMR data: δ = 25.6($^1J_{Pt-P}$ = 4706). $^{195}Pt\{^1H\}$ NMR data: δ = −4169 ppm ($^1J_{Pt-P}$ = 4706 Hz).

3.2.8. Preparation of cis-[Pt{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc}Cl_2(dmso)] (**5b**)

It is basically the same as that described for compound **6b**, {method (b)}, (see above), except that in this case the refluxing period was decreased to 24 h to increase the yield of **5b**. After the work up of the column the amounts of the isolated compounds were: 37 mg and 302 mg for **6b** and **5b**, respectively. *Characterization data*: Anal. Calc. for $C_{29}H_{30}Cl_2N_2OPtFeS$: C, 44.85; H, 3.87; N, 3.61; S, 4.12. Found: C, 45.10; H, 3.89; N, 3.75; S, 3.92%. MS (ESI⁺): *m/z* = 794.1 $\{[M]+NH_4\}^+$. $R_f(CH_2Cl_2)$ = 0.22. IR: 1637(s), 1502(w), 1445(m), 1379(m), 1311(w), 1147(s), 1105(w), 1023(m), 975(w), 822(s), 755(m), 700(s), 497(m), 440(m) and 348 and 312 (Pt–Cl) cm^{-1}. UV–Vis ($c = 1.0 \times 10^{-4}$ M in CH_2Cl_2): λ in nm (ε in $M^{-1}\,cm^2$) = 435(700), 239(26 656). ^1H NMR data [48]: δ = 2.47(s, 3H, $^3J_{H-Pt}$ = 20.6 Hz, dmso) and 3.31(s, 3H,$^3J_{H-Pt}$ = 20.3 Hz, dmso), 3.62(s, 2H, $-CH_2-$), 3.69(s, 2H, H^{3Fc} and H^{4Fc}), 3.84(s, 5H, Cp), 3.88(s, 2H, H^{2Fc} and H^{5Fc}), 4.11(s, 3H, –NMe), 7.30(dd, 2H, $H^{3''}$and $H^{5''}$), 8.00(d, 2H, $H^{2'}$ and $H^{6'}$), 7.40-7.65(br. m, 6H, $H^{3'}$, $H^{4'}$, $H^{5'}$, $H^{2''}$, $H^{4''}$ and $H^{6''}$) $^{13}C\{^1H\}$ NMR data [48]: δ = 23.7($-CH_2-$), 38.6(NMe), 42.1(dmso), 67.1(C^{3Fc} and C^{4Fc}), 68.3(C^{2Fc} and C^{5Fc}), 68.6(Cp), 87.5 (C^{1Fc}), 119.3(C^4), 126.5($C^{5'}$ and $C^{3'}$), 127.6($C^{3''}$), 128.3($C^{4''}$), 128.9($C^{2''}$ and $C^{6''}$), 129.7($C^{4'}$), 129.9($C^{1'}$), 130.1($C^{2'}$ and $C^{6'}$) 131.1($C^{1''}$, and $C^{5''}$), 145.1(C^5) and 151.0(C^3). $^{195}Pt\{^1H\}$ NMR data: δ = −2925 ppm.

3.2.9. Preparation of trans-[Pt{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc}Cl_2-(dmso)] (**7b**)

This product was synthesized as described above for **5a**, but using 256 mg (5.92×10^{-4} mol) of ligand **3**, and 250 mg (5.92×10^{-4} mol) of *cis*-[$PtCl_2(dmso)_2$]. Yield: 400 mg (87%). *Characterization data*: Anal. Calc. for $C_{29}H_{30}Cl_2N_2OPtFeS$: C, 44.85; H, 3.87; N, 3.61; S, 4.12. Found: C, 44.87; H, 3.91; N, 3.77; S, 3.98%. MS (ESI⁺): *m/z* = 799.0 $\{[M]+Na\}^+$. $R_f(CH_2Cl_2)$ = 0.11. IR: 1636(s), 1504(w), 1447(m), 1379(m), 1312(w), 1294(w), 1246(w), 1142(s), 1105(m), 1023(s), 763(m), 702(s), 494(m), 441(m) and 355 (Pt–Cl) cm^{-1}. UV–Vis ($c = 1.6 \times 10^{-4}$ M in CH_2Cl_2): λ in nm (ε in $M^{-1}\,cm^2$) = 238(25 725), 313sh(1759) and 437(200). ^1H NMR data [48]: δ = 3.44(s, 12H, $^3J_{H-Pt}$ = 20.4 Hz, dmso), 3.46(br., 4H, $-CH_2-$, H^{3Fc} and H^{4Fc}), 3.51(br., 2H, H^{2Fc} and H^{5Fc}), 3.84(s, 5H, Cp), 4.13(s, 3H, –NMe), 7.30–7.48(br.m. 2H, $H^{3'}$ and $H^{5'}$), 7.45–7.62(br. m, 6H, $H^{3'}$, $H^{4'}$, $H^{5'}$, $H^{2''}$, $H^{4''}$, $H^{6'''}$), 7.82(d, 2H, *J* = 7.6, $H^{2'}$ and $H^{6'}$). $^{13}C\{^1H\}$ NMR data [48]: δ = 23.7($-CH_2-$), 38.6(NMe), 42.1(dmso), 67.3(C^{2Fc}, C^{3Fc}, C^{4Fc} and C^{5Fc}), 68.6(Cp), 87.5(C^{1Fc}), 119.3(C^4), 128.2($C^{3'}$, $C^{3''}$ and $C^{5'}$), 128.0($C^{5''}$), 128.5($C^{4'}$), 129.1($C^{4''}$), 129.4($C^{2''}$and $C^{6'}$), 129.6($C^{2''}$ and $C^{6''}$), 130.2($C^{1'}$), 131.3($C^{1'''}$), 148.5(C^5) and 152.0(C^3). $^{195}Pt\{^1H\}$ NMR data: δ = −3015 ppm.

3.2.10. Preparation of [Pt{κ²-C,N-[3-(C_6H_4)-1-Me-5-Ph-(C_3N_2)]-CH_2-Fc}Cl(dmso)] (**8b**)

This product can be isolated by two different methods.

Method (a). Compound **3** (256 mg, 5.92×10^{-4} mol), *cis*-[$PtCl_2(dmso)_2$] (250 mg, 5.92×10^{-4} mol) and 20 mL of toluene were introduced in a 100 mL Erlenmeyer flask. Then, a solution containing 49 mg (5.92×10^{-4} mol) of sodium acetate and 4 mL of methanol was added. The reaction mixture was refluxed for 54 h and then allowed to cool at room temperature. The resulting solution was filtered and the filtrate was concentrated to dryness on a rotary evaporator giving a yellowish-brown residue, which later on was dissolved in the minimum amount of CH_2Cl_2 and passed through a SiO_2 column (3.0 cm × 9.0 cm) using CH_2Cl_2 as solvent, and the eluted bands were collected in *ca.* 100 mL portions. The first bright yellow solutions collected were concentrated to dryness on a rotary evaporator to give **8b** (77 mg) as yellow solid. The orange fractions collected afterwards yielded, compound **7b** (285 mg) (molar ratio **7b:8b** = 3.7:1.0).

Method (b). A mixture of *trans*-[Pt{1-Me-3,5-Ph_2-(C_3N_2)-CH_2-Fc}Cl_2(dmso)] (**7b**) (150 mg, 1.93×10^{-4} mol) and NaOAc (16 mg, 1.93×10^{-4} mol) in dry methanol (15 mL) was heated under reflux for 30 h. The resulting solution was filtered and the filtrate was concentrated to dryness on a rotary evaporator. The residue was dissolved in minimum amount of CH_2Cl_2 and passed through a SiO_2 column (3.0 cm × 9.0 cm) using CH_2Cl_2 as eluant, and the eluted bands were collected in *ca.* 100 mL portions. The bright yellow solutions collected were concentrated to dryness on a rotary evaporator to give compounds **8b** (10 mg) and **5b** (125 mg) in a

molar ratio of **5b**:**8b** = 8.5:1.0. *Characterization data:* Anal. Calc. for $C_{29}H_{29}ClN_2OPtFeS$: C, 47.07; H, 3.95; N, 3.71; S, 4.33. Found: C, 47.24; H, 4.08; N, 3.66; S, 4.24%. MS (ESI^+): m/z = 704.0 $\{[M]-Cl\}^+$. $R_f(CH_2Cl_2)$ = 0.44. IR: 1720(w), 1638(s), 1618(s), 1460(w), 1382(w), 1278(m), 1105(w), 1073(w), 1024(w), 912(w), 764(m), 697(s), 617(w) and 481(m) cm^{-1}. UV–Vis (1.6×10^{-4} M in CH_2Cl_2): λ in nm (ε in $M^{-1}\,cm^2$) = 255(23 050) and 319sh(≈2338). ^1H NMR data [48]: δ = 3.72(s, 2H, $-CH_2-$), 3.83(s, 3H, $^3J_{H-Pt}$ = 20.7 Hz, dmso), 3.97(s, 2H, H^{3Fc} and H^{4Fc}), 3.93(s, 5H, Cp), 3.97(s, 2H, H^{2Fc} and H^{5Fc}), 4.11(s, 3H, –NMe), 5.98(dd, 1H, J = 7.5 and 1.6, $H^{5''}$), 6.77td(1H, J = 7.5 and 1.0, $H^{4''}$), 6.94(td, 1H, 7.5 and 1.0, $H^{3''}$), 7.42–7.60(br. m, 3H, $H^{3'}$, $H^{4'}$ and $H^{5'}$), 7.83(d, 1H, 7.5 and 1.0, $H^{2'}$) and 7.89(dd, 1H, J = 7.5 and 1.0, $H^{2''}$), 7.52(m, 1H). $^{13}C\{^1H\}$ NMR data [48]: δ = 23.3($-CH_2-$), 37.6(NMe), 38.6 and 38.9(dmso), 67.1(C^{2Fc}, C^{3Fc}, C^{4Fc} and C^{5Fc}), 68.5(Cp), 87.5(C^{1Fc}), 119.8(C^4), 128.6($C^{3'}$ and $C^{5'}$), 127.5($C^{5''}$), 127.9($C^{4''}$), 129.6($C^{4'}$), 130.3 ($C^{2''}$), 130.7($C^{2'}$ and $C^{6'}$), 139.2($C^{1''}$), 144.2(C^5), 145.0($C^{6''}$, $^1J_{C-Pt}$ = 31), 151.2(C^3) and 158.4($C^{1'}$). $^{195}Pt\{^1H\}$ NMR data: δ = −3383 ppm.

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References

[1] (a) A. Togni, T. Hayashi (Eds.), Ferrocenes. Homogeneous Catalysis, Organic Synthesis. Materials Science, VCH, Weinheim, Germany, 1995;
(b) P. Stepnicka (Ed.), Ferrocene. Ligands, Materials and Biomolecules, Wiley, Weinheim, Germany, 2008.

[2] (a) For recent reviews on the properties or utility of ferrocene derivatives with heterocycles, see: L.V. Snegur, Y.S. Nekrasov, N.S. Sergeeva, Z.V. Zhilina, V.V. Gumenyuk, Z.A. Starikova, A.A. Simenel, N.B. Morozova, I.K. Sviridova, V.N. Babin, Appl. Organomet. Chem. 22 (2008) 139–147;
(b) G. Fu, Asymmetry Synth. (2007) 186–190;
(c) J. Yoon, S.K. Kim, N.J. Singh, K.S. Kim, Chem. Soc. Rev. 35 (2006) 355–360;
(d) R. Gómez Arrayas, J. Adrio, J.C. Carretero, Angew. Chem., Int. Ed. 45 (2006) 7674–7715;
(e) D.R. van Staveren, N. Metzler-Nolte, Chem. Rev. 104 (2004) 5931–5986.

[3] (a) For latest advances on this field, see: M.E. Weiss, D.F. Fischer, Z. Xin, S. Jautze, W.B. Schweizer, R. Peters, Angew. Chem., Int. Ed. 45 (2006) 5694–5698;
(b) C.E. Anderson, Y. Donde, C.J. Christopher, L.E. Overman, J. Org. Chem. 70 (2005) 648–657;
(c) D. Pou, A.E. Platero-Prats, S. Pérez, C. López, X. Solans, M. Font-Bardía, P.W.N.M. van Leeuwen, G.P.F. van Strijdonck, Z. Freixa, J. Organomet. Chem. 692 (2007) 5017–5025;
(d) S. Pérez, C. López, A. Caubet, X. Solans, M. Font-Bardía, A. Roig, E. Molins, Organometallics 25 (2006) 596–601.

[4] (a) A. Moyano, M. Rosol, R.M. Moreno, C. López, M.A. Maestro, Angew. Chem., Int. Ed. 44 (2005) 1865–1869;
(b) S. Pérez, C. López, A. Caubet, X. Solans, M. Font-Bardía, A. Roig, E. Molins, Organometallics 25 (2006) 596–601;
(c) A. González, C. López, X. Solans, M. Font-Bardía, E. Molins, J. Organomet. Chem. 693 (2008) 2119–2131.

[5] J.J. Li, G.W. Gribble, Palladium in Heterocyclic Chemistry, Pergamon, New York, USA, 2000.

[6] (a) V. Montoya, J. Pons, X. Solans, M. Font-Bardía, J. Ros, Inorg. Chim. Acta 358 (2005) 2312–2318;
(b) V. Montoya, J. Pons, X. Solans, M. Font-Bardía, J. Ros, Inorg. Chim. Acta 358 (2005) 2763–2769;
(c) J. Chakraborty, M.K. Saha, P. Benerjee, Inorg. Chem. Commun. 10 (2007) 671–676.

[7] (a) K. Li, M.S. Mohlala, T.V. Segapelo, P.M. Shumbula, I.A. Guzei, J. Darkwa, Polyhedron 27 (2008) 1017–1023;
(b) R.Y. Mawo, D.M. Johnson, J.L. Wood, I.P. Smoliakova, J. Organomet. Chem. 693 (2008) 33–45;
(c) I. Ara, L.R. Falvello, J. Fornies, R. Lasheras, A. Martin, O. Oliva, V. Sicilia, Inorg. Chim. Acta 359 (2006) 4574–4584;
(d) I. Ara, J. Forniés, R. Lasheras, A. Martin, V. Sicilia, Eur. J. Inorg. Chem. (2006) 948–957;
(e) Y. Han, H.V. Huynh, G.K. Tan, Organometallics 26 (2007) 6581–6585;
(f) F. Churruca, R. SanMartin, I. Tellitu, E. Domínguez, Synlett (2005) 3116–3120;
(g) F. López-Linares, O. Colmenares, E. Catari, A. Karam, React. Kinet. Catal. Lett. 85 (2005) 139–144;
(h) A. Satake, T. Nakata, J. Am. Chem. Soc. 120 (1998) 10391–10396;
(i) E. Budzisz, U. Krajewska, M. Rozalski, A. Szulawska, M. Czyz, B. Nawrot, Eur. J. Pharmacol. 502 (2004) 59–65;
(j) M.C. Torralba, M. Cano, J.A. Campo, J.V. Heras, E. Pinilla, M.R. Torres, Inorg. Chem. Commun. 5 (2002) 887–890;
(k) M.T. Pinillos, C. Tejel, L.A. Oro, C. Foces-Foces, F.H. Cano, J. Chem. Soc., Dalton Trans. (1989) 1133–1138.

[8] (a) S.Y. Chang, J.-L. Chen, Y. Chi, Y.-M. Cheng, G.-H. Lee, C.-M. Jiang, P.-T. Chou, Inorg. Chem. 46 (2007) 11202–11212;
(b) A. Eisenwiener, M. Neuburger, T.A. Kaden, Dalton Trans. (2007) 218–233;
(c) A.V. Khripun, M. Haukka, V.Y. Kukushkin, Russ. Chem. Bull. 55 (2006) 247–255;
(d) A.V. Khripun, S.I. Selivanov, V.Y. Kukushkin, M. Haukka, Inorg. Chim. Acta 359 (2006) 320–326;
(e) E. Ciesielska, A. Szulawska, K. Studzian, J. Ochocki, K. Malinowska, K. Kik, L. Szmigiero, J. Inorg. Biochem. 100 (2006) 1579–1585;
(f) K. Sakai, Y. Tomita, T. Ue, K. Goshima, M. Ohminato, T. Tsubomura, K. Matsumoto, K. Ohmura, K. Kawakami, Inorg. Chim. Acta 297 (2000) 64–71.

[9] (a) E. Tonon de Almeida, A.E. Mauro, A. Martínez Santana, Eclet. Chim. 27 (2002) 201–210;
(b) X. Gai, R. Grigg, M.I. Ramzan, V. Sridharan, S. Collard, J.E. Muir, Chem. Commun. (2000) 2053–2054;
(c) A.J. Canty, J. Patel, B.W. Skelton, A.H. White, J. Organomet. Chem. 607 (2000) 194–202;
(d) C.M. Hartshorn, P.J. Steel, Organometallics 17 (1998) 3487–3496;
(e) A.J. Canty, J.L. Hoare, B.W. Brian, A.H. Allan, G. van Koten, J. Organomet. Chem. 552 (1998) 23–29;
(f) M.T. Alonso, O. Juanes, J. de Mendoza, J.C. Rodriguez-Urbis, J. Organomet. Chem. 484 (1994) 19–26;
(g) J.M. Valk, F. Maassarani, P. van der Sluis, A.L. Spek, J. Boersma, G. van Koten, Organometallics 13 (1994) 2320–2329;
(h) M.T. Alonso, O. Juanes, J. de Mendoza, J.C. Rodríguez-Urbis, J. Organomet. Chem. 430 (1992) 335–347;
(i) S. Chakladar, P. Paul, K. Venkatsubnamanian, K. Nag, Dalton Trans. (1991) 2669–2676;
(j) G.B. Caygill, P.J. Steel, J. Organomet. Chem. 395 (1990) 375–381;
(k) O. Juanes, J. de Mendoza, J.C. Rodríguez-Urbis, J. Organomet. Chem. 363 (1989) 393–399;
(l) G.B. Caygill, P.J. Steel, J. Organomet. Chem. 327 (1987) 115–123;
(m) M. Nonoyama, J. Organomet. Chem. 229 (1982) 287–292;
(n) E.C. Alyea, S.A. Dias, F. Bonati, Transition Met. Chem. 6 (1981) 24–27.

[10] (a) F. Niedermair, K. Waich, S. Kappaun, T. Mayr, G. Trimmel, K. Mereiter, C. Slugovc, Inorg. Chim. Acta 360 (2007) 2767–2777;
(b) C.-K. Koo, Y.-M. Ho, C.-F. Chow, M.H.-W. Lam, T.-C. Lau, W.-Y. Wong, Inorg. Chem. 46 (2007) 3603–3612;
(c) C.-K. Koo, B. Lam, S.-K. Leung, M.H.-W. Lam, W.-Y. Wong, J. Am. Chem. Soc. 128 (2006) 16434–16435;
(d) A.S. Iokin, W.J. Marshall, Y. Wang, Organometallics 24 (2005) 619–627;
(e) H.P. Dijkstra, M.D. Meijer, J. Patel, R. Kreiter, G.P.M. van Klink, M. Lutz, A.L. Spek, A.J. Canty, G. van Koten, Organometallics 20 (2001) 3159–3168;
(f) A.J. Canty, R.T. Honeyman, B.W. Skelton, A.H. White, J. Organomet. Chem. 430 (1992) 245–257.

[11] (a) For a general overview on cyclopallada- and cycloplatinated compounds and their applications, see: J. Dupont, M. Pfeffer, Palladacycles. Synthesis, Characterization and Applications, Wiley-VCH, Weinheim, Germany, 2008;
(b) M. Ghedini, I. Aiello, A. Crispini, A. Golemme, M. La Deda, D. Pucci, Coord. Chem. Rev. 250 (2006) 1373–1390.

[12] (a) For recent advances in pallada- and platinacycles, see: I. Omae, J. Organomet. Chem. 692 (2007) 2608–2632;
(b) K. Godula, D. Sames, Science 312 (2006) 67–72;
(c) J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 2527–2571;
(d) C. López, S. Pérez, X. Solans, M. Font-Bardía, A. Roig, E. Molins, P.W.N.M. van Leeuwen, G.P.F. van Strijdonck, Organometallics 26 (2007) 571–576;
(e) T.-K. Zhang, K. Yuan, X.-L. Hou, J. Organomet. Chem. 692 (2007) 1912–1919;
(f) P.G. Evans, N.A. Brown, G.J. Clarkson, C.P. Newman, J.P. Rourke, J. Organomet. Chem. 691 (2006) 1251–1256.

[13] (a) For applications of palladacycles in homogeneous catalysis, see: A.S. Gruber, D. Zim, G. Ebeling, A.L. Monteiro, Org. Lett. 2 (2000) 1287–1290;
(b) D. Zim, A.S. Gruber, G. Ebeling, J. Dupont, A.L. Monteiro, Org. Lett. 2 (2000) 2881–2884;
(c) J. Dupont, M. Pfeffer, J. Spencer, Eur. J. Inorg. Chem. (2001) 1917–1927. and references cited therein.

[14] (a) For examples of the antitumoral activity of this sort of compounds, see: J.D. Higgins, L. Neely, S. Fricker, J. Inorg. Biochem. 49 (1993) 149–156;
(b) C. Navarro-Ranninger, I. López-Solera, J.M. Pérez, J.R. Massaguer, C. Alonso, Appl. Organomet. Chem. 7 (1993) 57–61;
(c) C. Navarro-Ranninger, I. López-Solera, V.M. González, J.M. Pérez, A. Alvarez-Valdes, A. Martin, P.R. Raithby, J.R. Masaguer, C. Alonso, Inorg. Chem. 35 (1996) 5181–5187;
(d) R.W.-Y. Sun, D.L. Ma, E.L.-M. Wong, C.-M. Che, Dalton (2007) 4883–4892.

[15] (a) For macromolecules containing cyclopalladated or cycloplatinated units: M. López-Torres, A. Fernández, J.J. Fernández, A. Suárez, S. Castro-Juiz, J.M. Vila, M.T. Pereira, Organometallics 20 (2001) 1350–1353;
(b) C. López, A. Caubet, S. Pérez, X. Solans, M. Font-Bardía, J. Organomet. Chem. 681 (2003) 82–90;
(c) A. Fernández, E. Pereira, J.J. Fernández, M. López-Torres, A. Suarez, R. Mosteiro, M.T. Pereira, J.M. Vila, New J. Chem. 26 (2002) 895–901.
[16] (a) For recent examples of the use of palladacycles in organic and organometallic synthesis, see: D. Solé, L. Vallverdú, X. Solans, M. Font-Bardía, J. Bonjoch, Organometallics 23 (2004) 1438–1447;
(b) D. Solé, L. Vallverdú, X. Solans, M. Font-Bardía, J. Bonjoch, J. Am. Chem. Soc. 125 (2003) 1587–1594;
(c) N. Gul, J.H. Nelson, A.C. Willis, A.D. Ross, Organometallics 21 (2002) 2041–2048;
(d) S. Pérez, C. López, A. Caubet, A. Pawelczyk, X. Solans, M. Font-Bardía, Organometallics 22 (2003) 2396–2408.
[17] Y. Donde, L.E. Overman, J. Am. Chem. Soc. 121 (1999) 2933–2934.
[18] (a) M. Zora, A.N. Pinar, M. Odabasoglu, O. Bueyuekguengoer, G. Turgut, J. Organomet. Chem. 693 (2008) 145–154;
(b) M. Zora, M. Görmen, J. Organomet. Chem. 692 (2007) 5026–5032;
(c) L. Gaina, A. Csampai, G. Turos, T. Lovasz, V. Zsoldos-Mady, I.A. Silberg, P. Sohar, Org. Biomol. Chem. 4 (2006) 4375–4386;
(d) W.-C. Shen, Y.-J. Wang, K.-L. Cheng, G.-H. Lee, C.K. Lai, Tetrahedron 62 (2006) 8035–8044;
(e) Y.S. Nekrasov, R.S. Skazov, A.A. Simenel, L.V. Snegur, V.V. Gumenyuk, Russ. Chem. Bull. 54 (2005) 2460–2462;
(f) A.H. Ilkhechi, M. Bolte, H.-W. Lerner, M. Wagner, J. Organomet. Chem. 602 (2005) 1971–1977;
(g) E.I. Klimova, E.A. López, T. Klimova, C.A. Toledano, R.A. Toscano, M. Martínez García, J. Heterocycl. Chem. 42 (2005) 265–271.
[19] (a) A. Magistrato, T.K. Woo, A. Togni, U. Rothlisberger, Organometallics 23 (2004) 3218–3227;
(b) M.C. Carrión, A. Díaz, A. Guerrero, F.A. Jalon, B.R. Manzano, A. Rodriguez, R.L. Paul, J.C. Jeffery, J. Organomet. Chem. 650 (2002) 210–222;
(c) T.K. Woo, G. Pioda, U. Rothlisberger, A. Togni, Organometallics 19 (2000) 2144–2152;
(d) U. Burckhardt, V. Gramlich, P. Hofmann, R. Nesper, P.S. Pregosin, R. Salzmann, A. Togni, Organometallics 15 (1996) 3496–3503.
[20] A.S.J. Stewart, C.N.C. Drey, J. Chem. Soc., Perkin Trans. I 6 (1990) 1753–1756.
[21] (a) V.I. Boev, L.V. Snegur, V.N. Babin, Y.S. Nekrasov, Russ. Chem. Rev. 66 (1997) 613–636;
(b) K. Pagel, A. Werner, W. Friedrichsen, J. Organomet. Chem. 481 (1994) 109–123.
[22] G. Pfeiffer, H. Bauer, Liebigs Ann. Chem. (1980) 564–576.
[23] C. López, J. Sales, X. Solans, R. Zquiak, J. Chem. Soc., Dalton Trans. (1992) 2321–2328.
[24] Z. Szafran, R.M. Pike, M.M. Singh, Microscale Inorganic Chemistry. A Comprehensive Laboratory Experience, John Wiley and Sons, New York, USA, 1991. p. 218.
[25] F.H. Allen, Acta Crystallogr., Sect. B 58 (2002) 380–388.
[26] C. López, R. Bosque, X. Solans, M. Font-Bardía, J. Organomet. Chem. 535 (1997) 99–105.
[27] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., Wiley, New York, USA, 1997.
[28] I. Łakomska, M. Barwiołek, A. Wojtczak, E. Szłyk, Polyhedron 26 (2007) 5349–5354.
[29] (a) S.A. Kurzeev, G.M. Kazankov, A.D. Ryabov, Inorg. Chim. Acta 340 (2002) 192–196;
(b) A.D. Ryabov, Chem. Rev. 90 (1990) 403–424.
[30] J. Vicente, J.A. Abad, A.D. Frankland, M.C. Ramírez de Arellano, Chem. Eur. J. 5 (1999) 3066–3075.
[31] (a) J. Elguero, Pyrazoles and their benzoderivatives, in: A.R. Katritzy, C.W. Rees (Eds.), Comprehensive Heterocyclic Chemistry, Pergamon Press, Oxford, UK, 1984, pp. 167–303 (Chapter 4.04);
(b) J. Elguero, Pyrazoles, in: A.R. Katritzy, W. Rees, E.F.V. Scrivens (Eds.), Comprehensive Heterocyclic Chemistry-II, Pergamon Press, Oxford, 1996, pp. 1–75 (Chapter 3.01).
[32] J.H. Price, A.N. Williamson, R.F. Schramm, B.B. Wayland, Inorg. Chem. 11 (1972) 1280–1284.
[33] (a) X. Riera, A. Caubet, C. López, V. Moreno, X. Solans, M. Font-Bardía, Organometallics 19 (2000) 1384–1390;
(b) X. Riera, C. López, A. Caubet, V. Moreno, X. Solans, M. Font-Bardía, Eur. J. Inorg. Chem. (2001) 2135–2141;
(c) A. Caubet, C. López, X. Solans, M. Font-Bardía, J. Organomet. Chem. 669 (2003) 164–171.
[34] S. Pérez, C. López, A. Caubet, X. Solans, M. Font-Bardía, Eur. J. Inorg. Chem. (2008) 1599–1612.
[35] (a) Y. Wu, S. Huo, J. Gong, X. Cui, L. Ding, K. Ding, C. Du, Y. Liu, M. Song, J. Organomet. Chem. (2001) 637–639. 27–46 and references therein;
(b) L. Ding, Y.J. Wu, D.P. Zhou, Polyhedron 17 (1998) 1725–1728;
(c) Y.J. Wu, L. Ding, H.X. Wang, Y.H. Liu, H.Z. Yuan, X.A. Mao, J. Organomet. Chem. 535 (1997) 49–58;
(d) A. Capapé, M. Crespo, J. Granell, A. Vizcarro, J. Zafrilla, M. Font-Bardía, X. Solans, Chem. Commun. (2006) 4128–4130.
[36] (a) E. Szłyk, I. Lakomska, A. Surdykowski, T. Glowiak, L. Pazderski, J. Sitkowski, L. Kokerski, Inorg. Chim. Acta 333 (2002) 93–99;
(b) N. Nédélec, F.D. Rochon, Inorg. Chem. 40 (2001) 5236–5244;
(c) N. Nédélec, F.D. Rochon, Inorg. Chim. Acta 319 (2001) 95–108;
(d) A. Cornia, A.C. Fabretti, M. Bonivento, L. Cattalini, Inorg. Chim. Acta 255 (1997) 405–409.
[37] M. Crespo, R. Martín, T. Calvet, M. Font-Bardía, X. Solans, Polyhedron 27 (2008) 2603–2611.
[38] (a) A.D. Ryabov, S. Otto, P.V. Samuleev, V.A. Polyakov, L. Alexandrova, G.M. Kazankov, S. Shova, M. Revenko, J. Lipkowski, M.H. Johansson, Inorg. Chem. 41 (2002) 4286–4294;
(b) S. Otto, A. Chanda, P.V. Samuleev, A.D. Ryabov, Eur. J. Inorg. Chem. (2006) 2561–2565.
[39] H.D. Kaesz, F.G.A. Stone, Spectrochim. Acta 15 (1959) 360–377.
[40] J. Albert, R.M. Ceder, M. Gómez, J. Granell, J. Sales, Organometallics 11 (1992) 1536–1541.
[41] B.M. Still, P.G.A. Kumar, J.R. Aldrich-Wright, W.S. Price, Chem. Soc. Rev. 36 (2007) 665–686.
[42] (a) J.R. Berenguer, E. Lalinde, J. Torroba, Inorg. Chem. 46 (2007) 9919–9930;
(b) A. Díez, J. Forniés, S. Fuertes, E. Lalinde, C. Larraz, J.A. López, A. Martín, M.T. Moreno, V. Sicilia, Organometallics 28 (2009) 1705–1718;
(c) S.W. Lai, H.W. Lam, W. Lu, K.K. Cheung, C.M. Che, Organometallics 21 (2002) 226–234.
[43] (a) C.-K. Koo, K.-L. Wong, C.W.-Y. Man, Y-W. Lam, L.K.-Y. So, H.-L. Tam, S.-W. Tsao, K.W. Cheah, K.-C. Lau, Y.-Y. Yang, J.-C. Chen, M.H.-W. Lam, Inorg. Chem. 48 (2009) 872–878;
(b) F-Q. Bai, X. Zhou, T. Liu, G.-J. Zhao, J.-P. Zhang, H.-X. Zhang, Int. J. Quant. Chem. 109 (2008) 308–319.
[44] M.E.N. Silva, A.J.L. Pombeiro, M.E.N.P. Rodríguez, I. Ugi, Port. Electrochim. Acta 2 (1984) 57–65.
[45] C. López, R. Bosque, X. Solans, M. Font-Bardía, New J. Chem. (1998) 977–982.
[46] R.W. Mason, K. McGrouther, P.R.R. Ranatunge-Bandarage, B.H. Robinson, J. Simpson, Appl. Organomet. Chem. 13 (1999) 163–173.
[47] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 4th ed., Butterworth-Heinemann, Oxford, UK, 1996.
[48] Labelling of the atoms corresponds to those shown in Schemes 1 (for compounds **1**–**3**), 2 (for **4a**, **5a** and **6a**) and **3** (for **5b**–**8b**).