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New Heterodimetallic Platinum(II) Complexes Potentially Useful as Molecular Switches

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Four types of platinum(II) complexes of general formulae [Pt(FcCH=NC_6H_4OH-2)Cl_2(L)] [Fc = (η^5-C_5H_5)Fe(η^5-C_5H_4), L = dmso (**2**) or PhCN (**3**)], [Pt(FcCH=NC_6H_4O-2)Cl(dmso)] (**4**), [Pt{(η^5-C_5H_3CH=NC_6H_4O-2)Fe(η^5-C_5H_5)}(L)] [L = dmso (**5**) or PPh_3 (**6**)] or [Pt{(η^5-C_5H_3CH=NC_6H_4OH-2)Fe(η^5-C_5H_5)}Cl(L)] [L = dmso (**7**) or PPh_3 (**8**)] have been prepared. These compounds differ in the mode of binding of the ligand: (N) (in **2** and **3**), $(N,O)^-$ (in **4**), $[C(sp^2, ferrocene),N,O]^{2-}$ (in **5** and **6**) or $[C(sp^2, ferrocene),N]^-$ (in **7** and **8**). NMR, UV/Vis and electrochemical studies of **2** and **4**–**8** reveal that these products can be grouped in three pairs [(**2c**, **4b**), (**5**, **7**) and (**6**, **8**)], and one of the compounds of each pair can be easily converted into its partner by a H^+/OH^- chemical input. The results obtained revealed that these transformations, that affect the spectroscopic and electrochemical properties, are reversible and robust. A study of the relevancy of the mode of binding of compounds **2** and **4**–**8** upon their potential utility of the new platinum(II) complexes as molecular switches is reported.

Introduction

The design and development of molecular devices based on coordination or organometallic complexes is of great importance nowadays due to their applied interest in different fields.[1–3] Among all types of molecular devices (i.e. clips, rotors, scissors, switches, twisters, etc.) with different architectures reported so far, molecular switches are targets of increasing interest for electronics and optical memory devices.[3] In this type of devices, an external stimulus (i.e. light, electrons, pH, etc.) produces intra- or intermolecular changes that affect a characteristic physical or chemical property of the molecule.[3] To allow their use in the development of sensors, information and storage materials, these transformations should be reversible, to permit the "switch on" and "switch off" of that property, and fast.

On the other hand, and mainly promoted by the crucial role of platinum(II) in cancer therapy,[4] several research groups have foccused their attention in molecular switches based on platinum(II) complexes.[5,6] A few articles showing the utility of such compounds as sensors for amino acids and proteins have been published recently,[6] but examples of acid/base-based molecular switches are scarce. In addition, ferrocene and its derivatives contain a redox-active centre, and this property,[7] which is specially interesting in view of their applications in different areas[8,9] including bio-organometallic chemistry, bio-technology and medicine,[9] has also been used to prepare electrochemical devices for gene sensors and glucose detection as well as molecular switches for non-linear optical properties (NLO) or for the fluorescence of ferrocene derivatives.[9–11]

Despite of these facts, examples of platinum(II) complexes containing ferrocenyl units potentially useful as molecular switches are still unknown. In this paper we present several types of platinum(II) complexes where the ferrocenylimine [FcCH=NC_6H_4OH-2] (**1**)[12] (Scheme 1) adopts four different coordination modes, together with a comparative study showing the relevancy of the mode of binding of **1** in the potential utility of the new products as molecular devices.

Results and Discussion

Synthesis, Characterization and Study of the Reactivity of the Platinum(II) Complexes

In a first attempt to evaluate the potential coordination abilities of the ferrocenyl Schiff base [FcCH=NC_6H_4OH-2] (**1**)[12] to platinum(II), its reactivity with the platinum(II) complexes *cis*-[$PtCl_2(L)_2$] (L = dmso[13] or PhCN) was studied under different experimental conditions. Due to the variety of compounds isolated and the number of reactions

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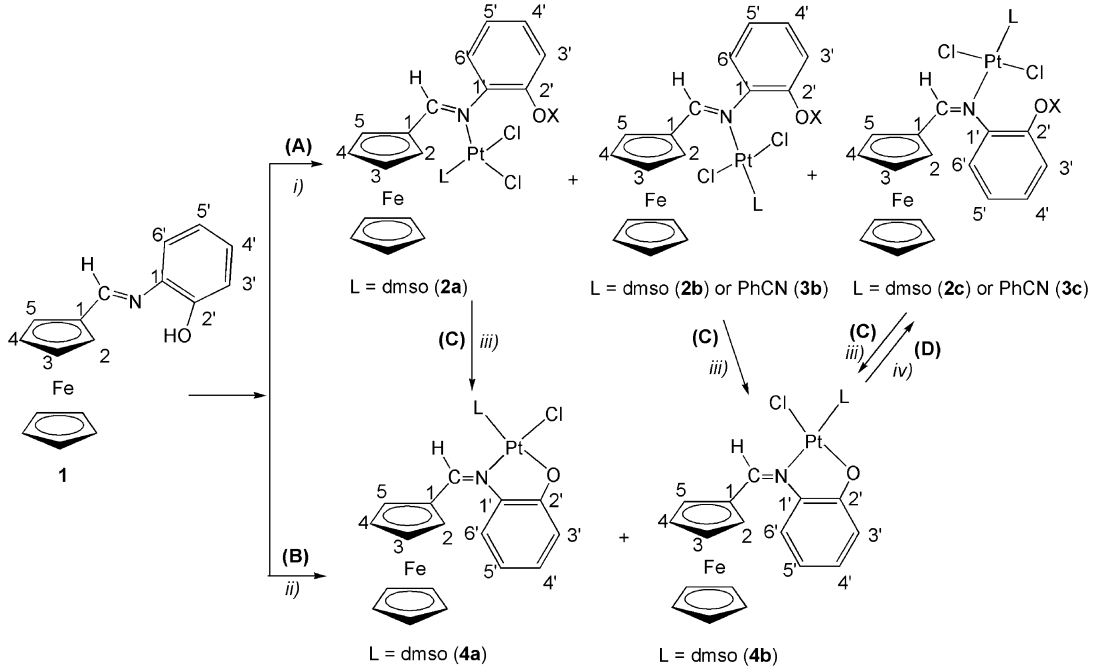


Scheme 1. (i) X = H. Equimolar amount of *cis*-$[PtCl_2(L)_2]$ (with L = dmso or PhCN) (for compounds **2** and **3**, respectively) in refluxing methanol (for **2**) or toluene (for **3**). (ii) Equimolar amounts of *cis*-$[PtCl_2(dmso)_2]$ and NaOAc in refluxing methanol (see text). (iii) For L = dmso, NaOD in $[D_4]$methanol in a molar ratio NaOD/**2** = 0.7. (iv) For L = dmso and X = D, addition of DCl (in a molar ratio Pt^{II}/DCl = 1.0:0.7) in $[D_4]$methanol at 298 K (see text).

studied the most relevant results are presented in Table 1 and Scheme 1.

When **1** was treated with an equimolar amount of *cis*-$[PtCl_2(dmso)_2]$ in refluxing methanol for 2.5 h [Table 1, Entry I; Scheme 1, step (**A**)], the ^1H NMR spectrum of the crude product of the reaction showed the presence of three platinum(II) complexes (**2a**–**2c**) and a small amount of ferrocenecarbaldehyde (hereinafter referred to as FcCHO). Examples of partial hydrolysis of related Schiff bases induced by the presence of platinum(II) complexes have been reported.[14,15] The use of column chromatography allowed us to separate these products. Elemental analyses of **2a**–**2c** are consistent with those expected for $[Pt(FcCH{=}NC_6H_4OH\text{-}2)Cl_2(dmso)]$ (**2**) in which the ligand acts as an N-donor group, and their $^{195}Pt\{^1H\}$ NMR spectra show a singlet centred at δ = –2868, –2991 and –3009 ppm (for **2a**–**2c**, respectively). The positions of these signals are consistent with the values reported for other complexes where the platinum(II) atom has a "$Pt(N)Cl_2(S_{dmso})$" environment.[16,17]

Several isomeric species of **2** could be expected in principal, these may differ in the conformation of the Schiff base [*anti*-(*E*) or *syn*-(*Z*)] or relative arrangement of the two chlorido ligands (*cis* or *trans*). Previous ^1H NMR spectroscopic studies of platinum(II) and palladium(II) complexes derived from imines have shown that the chemical shift of the methine proton signal is indicative of the conformation of the ligand in the complexes.[18–20] If the imine is in the

Table 1. Summary of the experimental conditions [reagents, solvents, temperature (*T*) and reaction time (*t*)] used to prepare the platinum(II) complexes containing the imino alcohol **1** acting as an (N), $(N,O)^-$ or $[C(sp^2,ferrocene),N,O]^{2-}$ donor ligand.

Entry	Reagent (molar ratio)	Solvent	*T*	*t*	Final products (molar ratio)[a]
I	**1** and *cis*-$[PtCl_2(dmso)_2]$ (1:1)	methanol	reflux	2.5 h	**2a/2b/2c/4b** (0.4:0.8:1.0[b])
II	**1** and *cis*-$[PtCl_2(dmso)_2]$ (1:1)	methanol	reflux	16 h	**2a/2b/2c/4b** (0.1:0.5:1.0[b])
III	**1** and *cis*-$[PtCl_2(PhCN)_2]$ (1:1)	toluene	reflux	1.5 h	**3b/3c** (1.0:2.6)
IV	**1** and *cis*-$[PtCl_2(PhCN)_2]$ (2:1)	toluene	reflux	1.5 h	**3b/3c** (1.0:3.1)
V	**1** and *cis*-$[PtCl_2(dmso)_2]$ and NaOAc (1:1:1)	methanol	reflux	16 h[c]	**2a/2b/2c/4a/4b**[d]
VI	**2a** and NaOD (1:0.7)	$CDCl_3$/$[D_4]$methanol	298 K	[e]	**4a**
VII	**2b** (or **2c**) and NaOD (1.0:0.7)	$CDCl_3$/$[D_4]$methanol	298 K	[e]	**4b**
VIII	**1** and *cis*-$[PtCl_2(dmso)_2]$ and NaOAc (1:1:2)	methanol	reflux	24 h[d]	**4a/4b/5** (1.0:1.0[f])
IX	**1** and *cis*-$[PtCl_2(dmso)_2]$ and NaOAc (1:1:2)	toluene/methanol[g]	reflux	72 h[d]	**4a/4b/5** (1.0:1.0:5.5)

[a] In all the experiments ferrocenecarbaldehyde (FcCHO) was also isolated as a by-product. [b] The presence of traces of **4b** was also detected by NMR spectroscopy. [c] When the reaction time decreased to 8 h, the reaction gave **2a/2b/2c/4a/4b** in a relative abundance of 0.4:0.1:0.1:0.6:1.0. [d] Under these experimental conditions **2a**, **2b** and **2c** were isolated as the minor components (ca. 8 mg), and the molar ratio **4a/4b** was 1:1. [e] This reaction is instantaneous. [f] Only traces of **5** (ca. 5 mg) were isolated. [g] 4:1 mixture.

anti-(*E*) form the resonance of the methine proton is high-field-shifted when compared with that of the free ligand, and the value of the coupling constant $^3J_{Pt,H}$ is larger than if the ligand adopts the *syn*-(*Z*) form in the complex.[17,19,20]

The analyses of the signals detected in the ^{1}H NMR spectra of **2** show that for **2a** and **2b** (i) the resonance due to the imine proton [signal at δ = 8.18 ppm (for **2a**) and 8.22 ppm (for **2b**)] appears at higher field than for the free imine (δ = 8.58 ppm[12]) and complex **2c** (δ = 8.56 ppm) and (ii) the values of the coupling constants $^3J_{Pt,H}$ (113.0 Hz and 86.0 Hz for **2a** and **2b**, respectively) are larger than that of **2c** (40.2 Hz). These findings suggest, according to the bibliography,[19,20] that in **2a** and **2b** the ligand adopts an *anti*-(*E*) conformation, while in **2c** it has the *syn*-(*Z*) form. The existence of NOE peaks between the imine proton and the 6′-H proton of the aryl ring of **2a** and **2b** confirm these findings.

In addition, the [^{1}H-^{1}H] NOESY spectrum of **2a** shows NOE contacts between the methyl group of the dmso ligand and the 2-H and 3-H protons of the C_5H_4 ring. These NOE peaks were not detected for any of the two isomers **2b** and **2c**. This indicates that in **2a** this ring is close to the dmso ligand and consequently the two Cl^- ligands should be in *cis* arrangement. Furthermore, since no evidence of the existence of NOE peaks between the signals due to the methyl protons and those of the Fc or Ph groups were detected in the NOESY spectra of **2b** and **2c**, we assume that in these products the relative disposition of the Cl^- ligands is *trans*.

Crystals of **2b**·CH_2Cl_2 and **2c** suitable for X-ray analyses could be also obtained. ORTEP plots of the heterodimetallic units [Pt(FcCH=NC_6H_4OH-2)Cl_2(dmso)] contained in the unit cells, together with a selection of bond lengths and angles are depicted in Figures 1 and 2.

In the [Pt(FcCH=NC_6H_4OH-2)Cl_2(dmso)] molecules, the platinum(II) atom is bound to the imine nitrogen atom, the sulfur atom of the dmso ligand and two chlorido ligands [Cl(1) and Cl(2)] in a *trans* arrangement, as reflected in the value of the bond angle Cl(1)–Pt–Cl(2) [176.18(5)° (**2b**), 175.59(13)° (**2c**)].

In the two complexes the bond lengths around the platinum(II) atom fall in the range reported for related complexes where the platinum(II) atom has a similar environment.[17,21,22] The C(11)–N bond of **2b** [1.285(6) Å] is longer than that in **2c** [1.266(14) Å], and the imine group forms an angle of 15.5° (**2b**) and 13.9° (**2c**) with the C_5H_4 unit of the ferrocenyl moiety. The value of the torsion angles C(10)–C(11)–N(1)–C(12) of **2b** (179.97°) and C(10)–C(11)–N–C(12) of **2c** (3.86°) indicate that the imine adopts the *anti*-(*E*) conformation in **2b** and the *syn*-(*Z*) form in **2c**, in good agreement with the results obtained from the NMR experiments. The phenyl ring is planar, and its mean plane forms an angle of 72.1° (**2b**) and 69.6° (**2c**) with the coordination plane of the platinum atom.

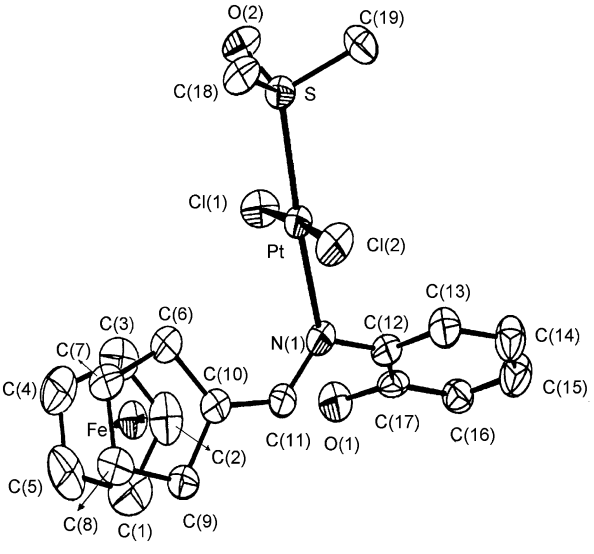


Figure 1. ORTEP plot of *trans*-[Pt(FcCH=NC_6H_4OH-2)Cl_2(dmso)]·CH_2Cl_2 (**2b**·CH_2Cl_2). Hydrogen atoms and the CH_2Cl_2 molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt–N(1) 2.026(4), Pt–S 2.2135(11), Pt–Cl(1) 2.2828(12), Pt–Cl(2) 2.2986(13), C(10)–C(11) 1.436(7), C(11)–N(1) 1.285(6), N(1)–C(12) 1.439(6), C(12)–C(13) 1.393(7), C(13)–C(14) 1.405(8), C(14)–C(15) 1.378(8), C(15)–C(16) 1.400(8), C(16)–C(17) 1.384(7), C(17)–O(1) 1.351(6), S–C(18) 1.763(5), S–C(19) 1.779(6), S–O(2) 1.456(4); S–Pt–Cl(1) 92.05(4), Cl(1)–Pt–N(1) 87.44(11), N(1)–Pt–Cl(2) 89.36(11), Cl(2)–Pt–S 91.31(5), C(10)–C(11)–N(1) 128.7(4), C(11)–N(1)–C(12) 116.8(4), O(1)–C(17)–C(12) 117.4(4), O(1)–C(17)–C(16) 123.0(4).

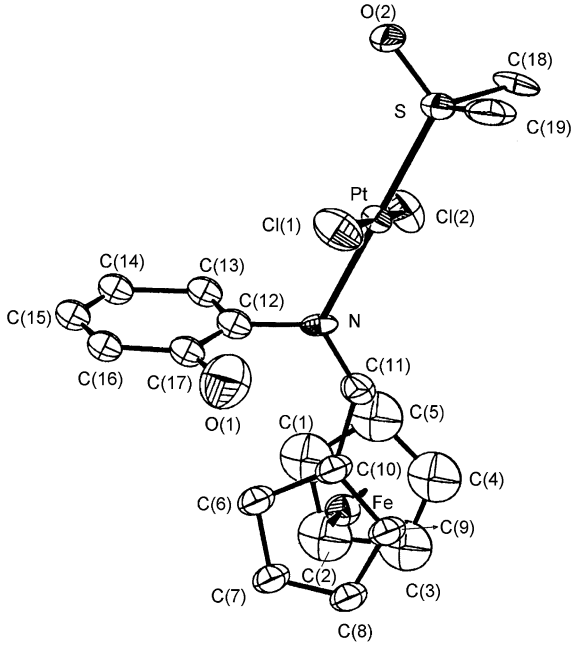


Figure 2. ORTEP plot of the isomer **2c** of *trans*-[Pt(FcCH=NC_6H_4OH-2)Cl_2(dmso)]. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt–N 2.064(9), Pt–S 2.223(3), Pt–Cl(1) 2.287(4), Pt–Cl(2) 2.290(4), C(10)–C(11) 1.442(16), C(11)–N 1.266(14), C(12)–C(13) 1.424(17), C(13)–C(14) 1.503(15), C(14)–C(15) 1.385(16), C(15)–C(16) 1.327(16), C(16)–C(17) 1.394(17), C(17)–O(1) 1.346(16), S–C(18) 1.773(12), S–C(19) 1.707(12), S–O(2) 1.441(8); S–Pt–Cl(1) 90.26(14), Cl(1)–Pt–N 87.7(3), N–Pt–Cl(2) 89.2(3), Cl(2)–Pt–S 92.92(14), C(10)–C(11)–N 132.6(13), C(11)–N–C(12) 121.1(12), O(1)–C(17)–C(12) 117.2(14), O(1)–C(17)–C(16) 123.3(17).

Bond lengths and angles of the ferrocenyl moiety in **2b**·CH_2Cl_2 and **2c** agree with the values reported for other monosubstituted ferrocene derivatives.[21] The two pentagonal rings are planar, nearly parallel [tilt angles: 2.23° (**2b**) and 2.16° (**2c**)], and they deviate by ca. 2.7° (**2b**) and 6.1° (**2c**) from the ideal eclipsed conformations. The separation between the platinum(II) and the iron(II) atoms [4.691 Å (**2b**) and 5.601 Å (**2c**)] clearly exceeds the sum of the van der Waals radii[23] of these atoms, thus precluding the existence of any direct interaction.

In the crystal of **2b** the separation between the O(1) atom of one of the molecules of [Pt(FcCH=NC_6H_4OH-2)-Cl_2(dmso)] and the O(2) atom of a neighbouring molecule suggest the existence of an O(1)–H···O(2) interaction that connects the molecules forming a chain along the *b*-axis (Figure 3).

Data presented in Table 1 (Entries I and II) indicate that the molar ratio **2a**/**2b**/**2c** is time-dependent and show that longer refluxing times favour the formation of **2c**, where the ligand has the *syn*-(*Z*) conformation.

The reaction between equimolar amounts of **1** and *cis*-[$PtCl_2$(PhCN)$_2$] in toluene under reflux [Table 1, Entries III and IV; Scheme 1, step (**B**)] produced two isomers of compound [Pt(FcCH=NC_6H_4OH-2)Cl_2(PhCN)] (**3**) that differ in the conformation of the ligand [*anti*-(*E*) in **3b** and *syn*-(*Z*) in **3c**], and the molar ratios **3c**/**3b** did not change when the molar ratio **1**/Pt^{II} was 2:1. Unfortunately, attempts to separate the two isomers of **3** failed, and the use of column chromatography allowed us to isolate only the major component **3c**.

Since previous studies on the reactivity of *cis*-[$PtCl_2$(dmso)$_2$] with N-donor ligands have shown that the presence of a base such as NaAcO in the reaction medium may induce the formation of the platinacycles,[24] we also studied the effect produced by this salt on the reaction. Treatment of equimolar amounts of **1**, *cis*-[$PtCl_2$(dmso)$_2$] and NaAcO in refluxing methanol for 16 h (Table 1, Entry V) gave after workup a brown residue. Further SiO_2 column chromatography, using CH_2Cl_2 as eluant, yielded traces of FcCHO and **2**, but the subsequent elution with a CH_2Cl_2/MeOH (100:0.2) mixture produced the release of an additional band that gave after concentration a red solid of **4**.

Elemental analyses and mass spectra of **4** are consistent with those expected for [Pt(FcCH=NC_6H_4O-2)Cl(dmso)] where **1** behaves as a bidentate $(N,O)^-$ ligand. The $^{195}Pt\{^1H\}$ NMR spectrum of **4** shows two singlets at δ = –2760 and –2818 ppm suggesting the presence of two species (hereinafter referred to **4a** and **4b**) in solution with a similar environment around the platinum(II) atom. Two sets of superimposed signals of relative intensities 1:1 can also be observed in the ^1H and $^{13}C\{^1H\}$ spectra of **4**. Longer reaction times (*t*) produced a decrease of the molar ratio **2**/**4**. The $\{^1H$-$^1H\}$ NOESY spectrum revealed that the two species (i) did not interchange in solution and (ii) contained the imine in the *syn*-(*Z*) conformation.

Besides, for one of the isomers (**4a**) the existence of an NOE peak between the protons of the >CH=N– and Me(dmso) units indicate that these protons are close. In the $^{13}C\{^1H\}$ NMR spectrum the signal due to the C-2′ atom of the two isomers appears at lower field [δ = 167.7 (**4a**), 168.3 ppm (**4b**)] than for compounds **2** [148.4 (**2a**), 149.5 (**2b**), 148.6 ppm (**2c**)], wheras the resonance of the imine carbon atom is shifted in the opposite direction [δ = 163.5 (**4a**), 168.3 (**4b**), 175.7, 175.4, 176.0 (**2a**, **2b**, **2c**, respectively)]. All these findings suggest that in **4a** and **4b** the ligand behaves as a bidentate $(N,O)^-$ group and that the two isomers differ in the relative arrangement of the Cl^- ligand and the imine nitrogen atom [*trans*-(Cl,N) in **4a** and *cis*-(Cl,N) in **4b**]. Unfortunately, attempts to separate the two isomers by either column chromatography or fractional crystallization failed, and it was only possible to obtain fractions enriched in ca. 95% in each one of the isomers.

Comparison of the chemical formulae of **2a**–**2c** and those of **4a** and **4b** prompted us to elucidate whether the addition of a base could induce the deprotonation of the OH group on the pendant arm of **2** and the formation of compounds **4**. Thus, we studied the action of NaOD ([D_4]methanol) on $CDCl_3$ solutions of **2a**–**2c** and monitored the changes by NMR spectroscopy (Table 1, Entries VI and VII; Figure 4, **A**–**I**). In all cases the addition of NaOD (molar ratios NaOD/**2** in the range 0.4–0.7) produced a change of the color of the solution and the ^1H NMR spectra indicate the complete transformation of **2** into **4** (Figure 4).

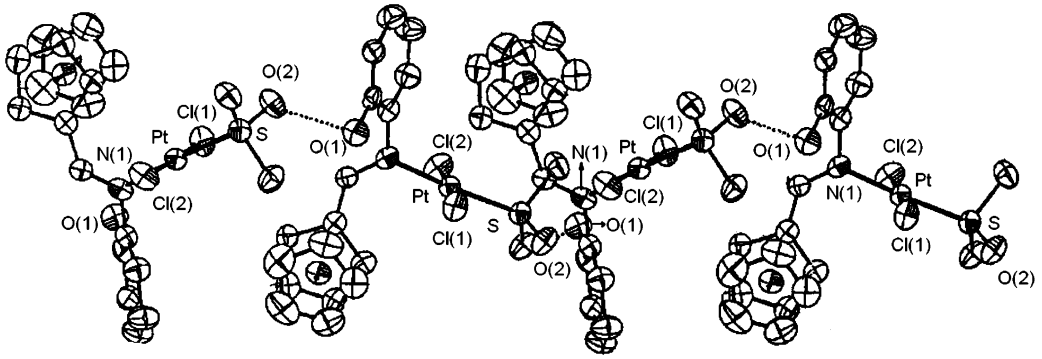


Figure 3. Simplified view of the assembly of the heterodimetallic molecules of *trans*-[Pt(FcCH=NC_6H_4OH-2)Cl_2(dmso)] in the isomer **2c** through O(1)–H···O(2) forming a chain along the *b*-axis.

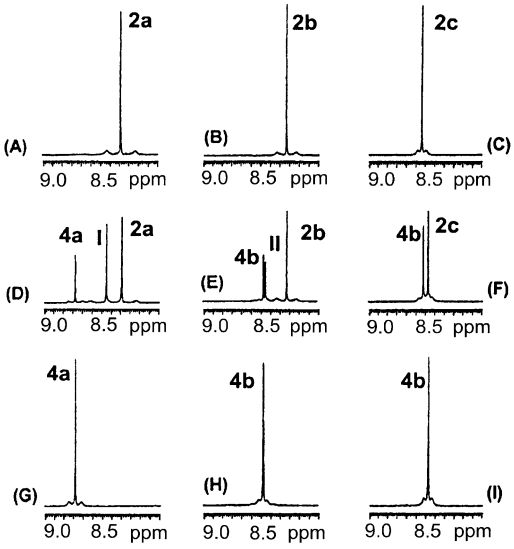


Figure 4. Partial views of the ^{1}H NMR spectra (400 MHz) of **2a**, **2b** and **2c** before (**A**, **B** and **C**, respectively) and after the addition of NaOD (in [D_4]methanol) in a molar ratio NaOD/**2** = 0.4 (**D**–**F**) or 0.7 (**G**–**I**).

For **2c** the conversion was fast and proceeded in one step (Figure 4, **C**, **F** and **I**); but the reactions of **2a** and **2b** [where the ligand has the *anti*-(*E*) form] were more complex than the process **2c** → **4b** and took place in two steps [Figure 4, **A**, **D** and **G** (**2a**) or **B**, **E** and **H** (**2b**)]. When the molar ratio NaOD/[**2a** (or **2b**)] is 0.4 the ^{1}H NMR spectra (Figure 4, **D** and **E**) indicate the presence of new platinum(II) complexes [hereinafter referred to as **I** (**2a**) and **II** (**2b**), Figure 5] which could be transformed into **4a** and **4b**, respectively by an additional supply of NaOD [molar ratio NaOD/Pt^{II} = 0.7 (Figure 4, **G** and **H**) or 1.0].

NMR spectroscopic data of **I** and **II**, suggest that these intermediate species (i) are isomeric forms of **4** containing the imine in the *anti*-(*E*) form and (ii) differ in the relative arrangement between the imine nitrogen atom and the Cl^- ligand [*trans* (**I**) and *cis* (**II**)] (Figure 5). These results suggest that **2a** and **2b** could be easily transformed into their partners (**4a** and **4b**, respectively). The reactions presented in Scheme 1, [steps (**C**)] constitute an alternative and more effective path to obtain separately **4a** and **4b**.

In order to evaluate the potential reversibility of the reactions **2** → **4**, the action of DCl on $CDCl_3$ solutions of **4a** and **4b** was also studied. The addition of DCl (in [D_4]methanol) to solutions of **4b** (in $CDCl_3$) gave **2c**, and no evidence of the presence of **2b** was detected by NMR spectroscopy, even when the molar ratio DCl/**4b** increased. Besides that, subsequent cycles exposing **2c** to basic (or **4b** to acidic) conditions showed that the transformations **2c** ⇄ **4b** are reproducible and robust, suggesting that these systems may be potentially useful as a simple molecular switch[3] (we will return to this point later on).

In order to compare the reactivity of **4a** and **4b**, we treated a $CDCl_3$ solution containing equimolar amounts of **4a** and **4b** with DCl (in [D_4]methanol) (Figure 6). As expected, the addition of DCl produced the conversion of **4b** into **2c**, but the behaviour of **4a** was markedly different since it evolved into **2a** and the new intermediate species **III** (Figure 5) in a molar ratio **2a**/**III** = 0.4:1.0. NMR spectroscopic data suggest that **III** is a new isomeric form of [Pt(FcCH=NC_6H_4OH-2)Cl_2(dmso)] (**2**) in which the ligand adopts the *syn*-(*Z*) conformation and the two Cl^- ligands are in a *cis* arrangement. The comparison of the results obtained indicate that the isomerization process **III** → **2a** is more favoured than the transformation **2c** → **2b**.

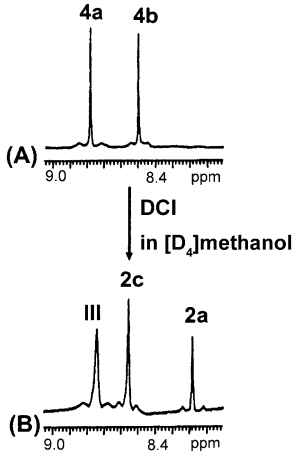


Figure 6. Partial view of the ^{1}H NMR spectra (in the range δ = 8.02–9.02 ppm) of an equimolar solution of compounds **4a** and **4b** (**A**) and after the addition of DCl (in [D_4]methanol) in a molar ratio DCl/Pt^{II} = 0.7 (**B**).

Due to the increasing interest of platinacycles containing pincer ligands,[15a,25–28] and since it has been reported that the formation of metallacycles with $(C,N,E)^-$ or $(C,N)^-$ ligands is often favoured in the presence of a slight excess of

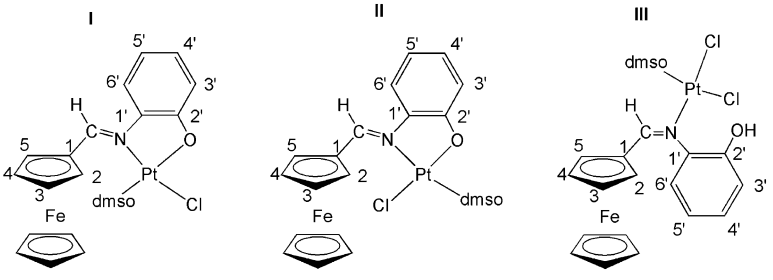
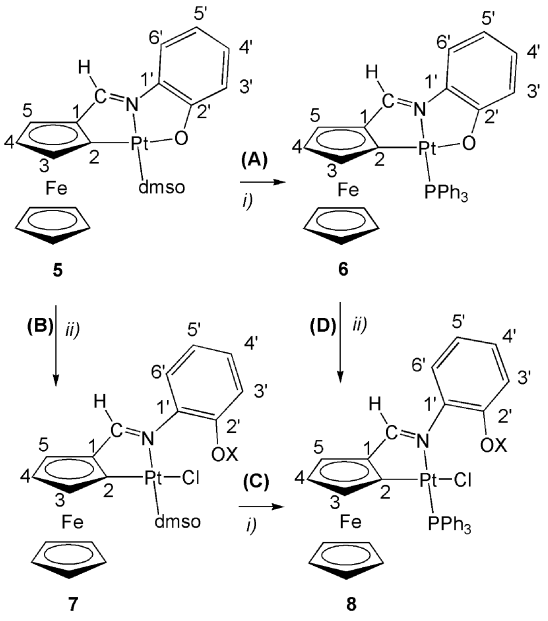


Figure 5. Intermediate species **I**–**II** detected in the reaction of compounds **2a** or **2b** with NaOD (in [D_4]methanol) and the product **III** formed when **4a** was treated with DCl in [D_4]methanol.

a base,[15,17,26a,26b,27–29] we also studied the reactions of **1**, *cis*-[$PtCl_2(dmso)_2$] and NaAcO in amolar ratio of 1:1:2 (Table 1, Entries VIII and IX). When the reaction was performed in methanol (Table 1, Entry VIII), four different products were isolated. Three of them were FcCHO, **4a** and **4b** (in a 1.6:1.0:1.0 molar ratio). The minor component (**5**) was a purple solid whose elemental analysis is consistent with that expected for the platinacycle [Pt{(η^5-$C_5H_3CH{=}NC_6H_4O$-2)Fe(η^5-C_5H_5)}(dmso)] (**5**) (Scheme 2). This compound arises from the activation of the σ-[C(sp^2,ferrocene)–H] and the σ-(O–H) bond of **1**.



Scheme 2. (i) Equimolar amount of PPh_3 in benzene at 343 K for 1 h, followed by SiO_2 column chromatography. (ii) X = D if the reaction is performed on an NMR scale using $CDCl_3$ as solvent and DCl (in [D_4]MeOH) or X = H if non-deuterated solvents and reagents were used. The molar ratios (DCl or HCl)/Pt^{II} were 0.8 and 0.7 for **5** and **6**, respectively.

The replacement of the methanol by a mixture toluene/methanol (4:1) (Table 1, Entry IX) produced **5** (in higher yield), and traces of compounds **4** were detected by NMR spectroscopy of the crude product of the reaction. The comparison of data presented in Table 1 (Entries VIII and IX) shows that in methanol the formation of compounds **4** is preferred over that of complex **5**, whereas a decrease of the polarity of the reaction medium favours the cycloplatination of the ligand and inhibits the formation of **4**, indicating that the proper selection of the solvents permits to control selectively the formation of the two types of platinum(II) complexes (**4** or **5**). Besides that since in **4** the ligand is in the *syn*-(*Z*) form, none of the two *ortho*-σ-[C(sp^2,ferrocene)–H] bonds of the ferrocenyl unit have the proper orientation in relation to the platinum(II) atom as to allow the cycloplatination. Thus, the transformation **4** → **5** is unlikely to occur, unless a complex process [involving (i) the decoordination of the oxygen atom and (ii) the isomerization of the ligand] takes place.

Characterization data of **5** agree with the proposed formulae. In the ^{1}H NMR spectrum of **5** the resonance of the imine proton appears as a singlet at δ = 7.94 ppm and shows the typical satellites due to the ^{195}Pt nucleus ($^3J_{Pt,H}$ = 163.2 Hz), suggesting the coordination of the imine nitrogen atom. In addition, the presence of a group of four signals of relative intensities 5:1:1:1 in the range δ = 4.20–4.90 ppm indicates the existence of a σ-[Pt–C(sp^2,ferrocene)] bond. The comparison of the ^{13}C{^{1}H} NMR spectrum of **5** and that of the free ligand reveals that the resonances due to the C-2 and the C-2′ atoms are shifted to the low-field region. This trend has also been observed for other pallada- and platinacyles containing terdentate $(C,N,O)^{2-}$ ligands.[28b,28c,28f] The ^{195}Pt{^{1}H} NMR spectrum shows a singlet at higher fields (δ = –4031 ppm) than that of **2** and **4**.

One of the main interests of pallada- and platinacycles containing terdentate $(C,N,E)^-$ ligands arises from the potential hemilability[30] of the σ-(M–E) bond and the study of the factors that may induce the formation and cleavage of this bond. These processes may play an important role in view of their applications in homogeneous catalysis.[26c,31] In view of this and in order to study the lability of the Pt–O bond of **5**, additional experiments were performed. The first one [Scheme 2, step (**A**)] consisted of the treatment of **5** with an equimolar amount of PPh_3 in benzene. This reaction gave after workup [Pt{(η^5-$C_5H_3CH{=}NC_6H_4O$-2)-Fe(η^5-C_5H_5)}(PPh_3)] (**6**), which arises from **5** by replacement of the dmso ligand by the phosphane ligand. It should be noted that (i) the formation of **6** does not modify the coordination mode of the ligand and (ii) the presence of a larger excess of PPh_3 did not produce the cleavage of the Pt–O bond. This suggests that the Pt–O bond exhibits a low lability. This finding has also been detected for related pallada- and platinacycles with dianionic $(C,N,O)^{2-}$ ligands.[28b–28d,28f]

On the other hand and in view of the results obtained in the reactions of **4** with DCl, we decided to explore whether the mode of binding of the ligand in **5** could be affected by the acidity of the medium. In a first stage, this process was studied on an NMR scale by treatment of a $CDCl_3$ solution of **5** with DCl (in [D_4]methanol). The addition of DCl produced a change of the color of the solution (from deep-purple to reddish) and of the ^{1}H NMR spectrum. The analysis of the ^{1}H, ^{13}C{^{1}H}, ^{195}Pt{^{1}H} NMR spectra as well as the cross-peaks detected in the {^{1}H-^{1}H} NOESY and {^{1}H-^{13}C} HSQC and HMBC spectra suggest that the DCl produced the protonation of the alkoxido unit, the cleavage of the Pt–O bond with the subsequent opening of the five-membered chelate and the binding of the Cl^- ligand to the platinum(II) atom, suggesting the formation of [Pt{(η^5-$C_5H_3CH{=}NC_6H_4OD$-2)Fe(η^5-C_5H_5)}Cl(dmso)] [Scheme 2, step (**B**)]. When this reaction was carried out on a larger scale and using non-deuterated reagents and solvents, complex [Pt{(η^5-$C_5H_3CH{=}NC_6H_4OH$-2)Fe(η^5-C_5H_5)}Cl(dmso)] (**7**) was isolated.

Further treatment of **7** with an equimolar amount of PPh_3 yielded [Pt(η^5-$C_5H_3CH{=}NC_6H_4OH$-2)Fe(η^5-C_5H_5)-

Cl(PPh$_3$)] (**8**) [Scheme 2, step (**C**)]. This product and its analogue with a deuterated hydroxy group can also be obtained by reaction of **6** with HCl (in MeOH) or DCl (in [D$_4$]methanol) [Scheme 2, step (**D**)]. Characterization data of **8** indicate that the ligand behaves as a monoanionic and bidentate [C(sp^2,ferrocene),N]$^-$ group, and the phosphane is in a *trans* arrangement to the imine nitrogen atom, in good agreement with the "transphobia effect".[32]

Spectroscopic and Electrochemical Studies

In order to elucidate the effects induced by the mode of coordination of the Schiff base to the platinum(II) atom on the electronic environment of the iron(II) atom, we decided (i) to compare the UV/Vis spectra of **1**, **2**, and **4**–**8** in CH_2Cl_2 solutions and (ii) to perform electrochemical studies of these products.

A summary of the results obtained from the spectroscopic studies of 10^{-4} M solutions of **1**, **2**, **4**, **5** and **7** or 5×10^{-5} M solutions of **6** and **8** in CH_2Cl_2 at 298 K is presented in Table 2. The UV/Vis spectrum of the free ligand **1** shows two intense bands at 344 (ε = 11940) and 467 (ε = 1718) nm. Their positions fall in the range reported for ferrocenylketimines of general formula [FcCH=NR^1] (R^1 = substituted phenyl ring) and have been attributed to intraligand transitions (ILT) [3d(Fe)→π* and π→π*, respectively].[26b,33]

The UV/Vis spectra of the platinum(II) complexes where the imine behaves as an (N)-donor group (**2**) or as a bidentate [(N,O)$^-$ (**4**) or (C,N)$^-$ (**7** and **8**)] ligand exhibit two bands in good agreement with the results reported for related metal complexes derived from ferrocenyl Schiff bases for which these bands have been assigned to metal-perturbed intraligand π→π* transitions (MPILCT).[33] Parallel studies on cyclopalladated derivatives of general formulae [Pd{(η^5-C$_5$H$_3$CH=NR^1)Fe(η^5-C$_5$H$_5$)}X(L)] with [C(sp^2,ferrocene),N]$^-$ ligands have shown that the positions of these bands are sensitive to the changes of the nature of the remaining ligands (X and L) bound to the Pd^{II} atom,[34] as occurs for compounds **7** and **8** that differ in the neutral ligand [dmso (**7**) or PPh$_3$ (**8**)]. The spectra of the platinacycles **5** and **6** where the ligand acts as a (C,N,O)$^-$ terdentate group show a band at ca. 582 nm. According to previous studies on pallada- and platinacycles with a terdentate [C(sp^2,ferrocene),N,O]$^-$ or a terdentate [C(sp^2,ferrocene),N,S] ligand such as [Pd{(η^5-C$_5$H$_3$CH=NC$_6$H$_4$CH$_2$O-2)Fe(η^5-C$_5$H$_5$)}(L)] or [Pd{(η^5-C$_5$H$_3$CH=NC$_6$H$_4$SMe-2)-Fe(η^5-C$_5$H$_5$)}Cl] (Figure 7),[28c,28d] this band is due to a metal-to-ligand charge-transfer transition [5d(Pt)→π*].

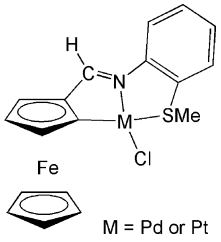


Figure 7. Pallada- and platinacycles of general formula [M{(η^5-C$_5$H$_3$CH=NC$_6$H$_4$SMe-2)Fe(η^5-C$_5$H$_5$)}Cl] reported previously.[26b]

In order to elucidate the effect induced by the mode of coordination of **1** and the nature and relative arrangement of the ligands bound to the platinum(II) atom on the redox properties of the iron(II) atom in **2** and **4**–**8**, we also performed electrochemical studies based on cyclic voltammetry. In all cases, the cyclic voltammograms of freshly prepared solutions (10^{-3} M) of **2**, and **4**–**8** in acetonitrile[35] using (Bu$_4$N)[PF$_6$] as supporting electrolyte were recorded. Cyclic voltammograms are presented in Figures 8 and 9, and the most relevant electrochemical parameters obtained for the complexes and those reported for the free ligand under identical experimental conditions are summarized in Table 2.

As shown in Figures 8 and 9 the cyclic voltammograms show one anodic peak with a directly associated reduction peak in the reverse scan. For the compounds under study the ΔE values depart appreciably from the constant value of 59 mV (theoretically expected for an electrochemically reversible one-electron-step oxidation-reduction process) suggesting that a structural reorganization takes place upon

Table 2. UV/Vis spectroscopic data (wavelengths, λ_i [nm], extinction coefficients, ε_i [M^{-1}cm^{-1}] together with the assignment of the bands[a]) and electrochemical data {anodic (E_{pa}) and cathodic (E_{pc}) potentials, and separation of the peaks (ΔE) [mV] at a scan speed v = 100 mV/s}[b] for the free ligand **1** and compounds **2** and **4**–**8**.

Complex	Binding mode	UV/Vis spectroscopical data			Electrochemical data		
		λ_i (ε_i)	λ_2 (ε_2)	λ_3 (ε_3)	E_{pa}	E_{pc}	ΔE
1[c]	–	344 (11940), ILT	467 (1718), ILT	–	258	178	80
2a	(N)	363 (3060), MPILCT	489 (2249), MPILCT	–	415	294	121
2b	(N)	364 (2273), MPILCT	488 (17163), MPILCT	–	474	323	151
2c	(N)	359 (2671), MPILCT	488 (1890), MPILCT	–	448	316	132
4a	(N,O)$^-$	391 (5361), MPILCT	498 (4051), MPILCT	–	396	228	168
4b	(N,O)	366 (3900), MPILCT	494 (3215), MPILCT	–	416	265	200
5	(C,N,O)$^{2-}$	354 (6250), MPILCT	516 (4579), MILCT	584 (3400), 5d(Pt)→π*	67	–32	95
6	(C,N,O)$^{2-}$	368 (10000)[d], MPILCT	522 (5155), MPILCT	582 (3690)[d], 5d(Pt)→π*	12	–92	104
7	(C,N)$^-$	381 (2570), MPILCT	541 (2008), MPILCT	–	116	15	101
8	(C,N)$^-$	387 (3020), MPILCT	525 (2535), MPILCT	–	151	–3	155

[a] ILT = Intraligand transitions 3d(Fe)→π* and π→π*; MPILCT = metal-perturbed intraligand charge-transfer transition and 5d(Pt)→π* = metal-to-ligand charge-transfer transition. [b] In all cases the E_{pa} and E_{pc} values are referenced to the Fc/Fc$^+$ couple. [c] Data from ref.[12] [d] This band appears as a shoulder.

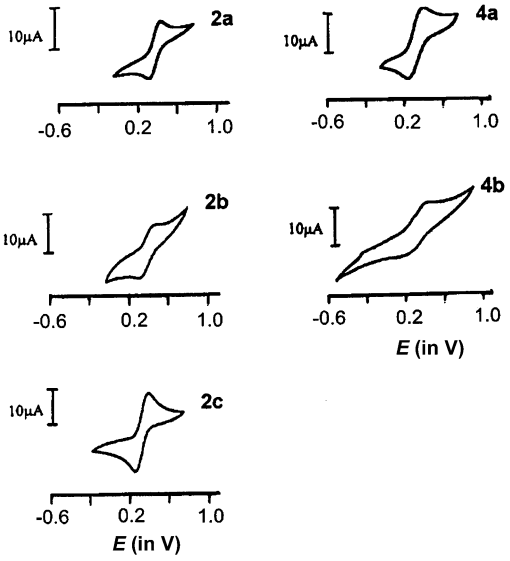


Figure 8. Cyclic voltammograms of compounds **2a**–**2c** and **4a**,**b** in acetonitrile at 298 K and at a scan speed v = 100 mV/s.

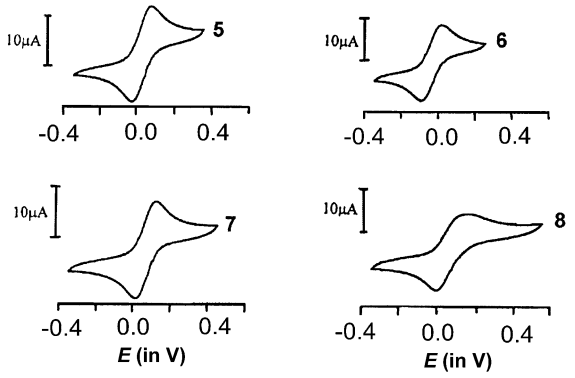


Figure 9. Cyclic voltammograms of compounds **5**–**8** in acetonitrile at 298 K and at a scan speed v = 100 mV/s.

oxidation.[36] According to the general rules established for ferrocene derivatives, the presence of electron-withdrawing groups inhibits the oxidation of the iron(II) atom in contrast to electron-donor groups that facilitate the oxidation.[37]

The comparison of the plots depicted in Figures 8 and 9 shows that for **1**, **2**, **4**, **7** and **8**, the E_{pa} values are larger than that of ferrocene, thus suggesting that the effect induced by the CH=NC$_6$H$_4$OH-2 unit in **1** or its binding of the Pt^{II} atom reduces the proclivity of the iron(II) atom to be oxidized. Besides that, the shift of the position of the peaks to the more anodic region is strongly affected by the mode of binding of the ligand. In general the E_{pa} values increase according to the sequence **6** < **5** < **7** < **8** < **1** < **4a** < **4b** ≈ **2a** < **2c** < **2b** [in the range 12 mV (**6**) to 474 mV (**2b**)]. This trend is closely related to the coordination mode of the ligand (N) (**2**), (N,O)$^-$ (**4**), [C(sp^2,ferrocene),N]$^-$ (**7** and **8**) or [C(sp^2,ferrocene),N,O]$^{2-}$ (**5** and **6**) and indicates that in compounds without a σ-[Pt–C(sp^2,ferrocene)] bond (**2** and **4**) the Fe^{II} atom is less prone to be oxidized than in the free ligand. This agrees with the results reported for related palladium(II) and platinum(II) complexes containing a monodentate (N) or bidentate (N,E) (E = N′, O or S) ferrocenyl ligand.[38] In contrast with these results, the cycloplatinated derivatives **5**–**8** are less resistant to undergo oxidation. This trend is similar to those described for other metallacycles with a σ-[M–C(sp^2,ferrocene)] bond (M = Pd^{II} or Pt^{II}).[26b,39] Furthermore, the comparison of the E_{pa} values for the pairs of compounds (**5**,**6** and **7**,**8**) indicate that changes of the nature of the remaining ligands bound to the Pt^{II} atom at a three-bond-length distance from the iron(II) atom also affect the electrochemical properties of the ferrocenyl unit.

In order to clarify the effect induced by the H$^+$/OH$^-$ chemical input on the electrochemical properties of the new products, we performed some additional studies. First of all, and once the cyclic voltammogram of the solutions of **4b**, **5** and **6** had been recorded, we added an equimolar amount of HCl and studied the electrochemistry of the solution obtained inmediately after the addition of the acid. In all cases the shape of the voltammograms and the position of the peaks coincided with those obtained from their corresponding partners (**2c**, **7** and **8**, respectively). Besides that, the transformations **2c** → **4b**, **5** → **7** or **6** → **8** were easily reverted upon the addition of NaOH in in the range of molar ratios platinum(II) complex/NaOH = 0.7–1.0.

In order to confirm the reversibility of the protonation/deprotonation process, titrations with HCl were carried out and monitored by UV/Vis spectroscopy and cyclic voltammetry. Once the spectrum of a freshly prepared solution of **5** or **6** in CH_2Cl_2 had been recorded, aliquots containing HCl [in a molar ratio HCl/(**5** or **6**) = 0.2] were succesively added. The UV/Vis spectra were registered after each addition, and the comparison of the spectra obtained reveals that the band due to the 5d(Pt)→π* transition vanishes gradualy. After the fourth addition the spectrum obtained is superimbosable with those of compounds **7** and **8**, respectively. Afterwards, we investigated the effect induced by the addition of aliquots of a base; thus, we repeated the whole process but replaced the aliquots of HCl by aliquots of NaOH. In these cases the spectrum obtained after four additions of the NaOH aliquots was also superimposable to those of **5** and **6**. It should be noted that the comparison of the sets of spectra obtained after one cycle (**5** → **7** → **5**) reveals the existence of an isostbestic point at λ = 410 nm, whereas for the process **6** → **8** → **6** two isosbestic points are found.[40] These transformations were also monitored by cyclic voltammetry, and the comparison of the voltammograms along the whole process (Supporting Information) also provides conclusive proof of the reversibility of the reactions **5** ⇄ **7** or **6** ⇄ **8** in acetonitrile. It should be noted that subsequent additions of HCl an NaOH did not produce significant variations in the cyclic voltammograms of the complexes. This indicates that the reactions **5** ⇄ **7** or **6** ⇄ **8** are reversible and robust.

Unfortunately, a similar study with ligand **1** could not be carried out because of its low stability in the presence of HCl and NaOH. When a $CDCl_3$ solution of **1** was treated with NaOD or DCl (in MeOD) [in molar ratios (NaOD or

DCl)/**1** = 0.2]. In both cases, the ^{1}H NMR spectra of the resulting mixtures reveal the formation of ferrocenecarbaldehyde (Supporting Information). In addition, when DCl was used the color of the initially orange solution turned purple, the signals became broader and the peak due to the imine proton of **1** could not be detected. This suggests that in this case hydrolysis of the ligand took place.

Conclusions

The results presented here have allowed us to establish the best experimental conditions to selectively control the mode of binding {(N), (N,O)$^-$, [C(sp^2,ferrocene),N]$^-$ or [C(sp^2,ferrocene),N,O]$^{2-}$} of ligand **1** to a platinum(II) atom and the formation of several different isomers of the heterodimetallic complexes *trans*-[Pt(FcCH=NC$_6$H$_4$OH-2)Cl$_2$(dmso)] (**2**) and [Pt(FcCH=NC$_6$H$_4$O-2)Cl(dmso)] (**4**) that differ in the conformation of the ligand (**2a**–**2c**) or in the relative arrangement of the imine nitrogen atom and the dmso ligand (**2** and **4**).

The study of the reactivity of **2** and **4**–**8** in the presence of H$^+$ or OH$^-$ indicates that the interconversion between the two compounds of each one of the sets of products (**2c**,**4b**), (**5**,**7**) or (**6**,**8**) can be easily achieved by a simple and reversible chemical reaction. The transformations **2c** ⇄ **4b**, **5** ⇄ **7** and **6** ⇄ **8** are instantaneous and clearly faster than the time required to register the ^{1}H NMR or UV/Vis spectra.

On the other hand, electrochemical studies provide a method for fine-tunning the oxidation potential of the ferrocenyl unit in a wide range [from 12 mV (**6**) to 474 mV (**2b**)] by modifying the mode of binding of the ligand in the complexes. In addition, the results obtained from UV/Vis spectroscopy and the electrochemical studies of the pairs of complexes (**2c**,**4b**), (**5**,**7**) or (**6**,**8**) in the presence of NaOH or HCl, indicate that the reactions **2c** ⇄ **4b**, **5** ⇄ **7** and **6** ⇄ **8** (i) affect the proclivity of the iron(II) atom to be oxidized and (ii) are reversible and can be performed for several cycles without a significant variation of the electronic spectra or the intensity of the anodic or cathodic peaks detected in the cyclic voltammograms (Supporting Information), thus indicating that they are robust from an electrochemical point of view. These findings are particularly outstanding since examples of heterodimetallic complexes containing simultaneously Pt^{II} atoms and ferrocenyl units with a similar behaviour have not been reported so far and are especially relevant in view of their potential utility as molecular switches.

Among the three pairs of compounds, those involving the platinacycles containing a bi- (**7** and **8**) or a terdentate (**5** and **6**) ligand appear to be the most relevant for different reasons. First, the H$^+$/OH$^-$ chemical input produces more spectacular variations in their UV/Vis spectra which involve the presence or absence of an additional band at $\lambda \approx 583$ nm which is characteristic of compounds **5** and **6** with a terdentate [C(sp^2,ferrocene),N,O]$^{2-}$ group. In addition, the changes of the mode of binding of the ligands from [C(sp^2,ferrocene),N,O]$^{2-}$ to [C(sp^2,ferrocene),N]$^-$ produced a greater variation of the E_{pa} values [49 mV for the couple (**5**,**7**) or 139 mV for the pair (**6**,**8**)]. Consequently, these studies constitute the first step of a further work centred on (i) the synthesis and the study of the properties of the chemical products formed in the oxidation of **5**–**8** and (ii) the investigation of their practical utility as molecular switches.

Moreover, since it is well known that cyclopallada- and cycloplatinated complexes containing bi- or terdentate ligands are useful precursors in organometallic synthesis and in homogeneous catalysis,[41,42] compounds **5**–**8** are particularly interesting in view of their potential applications in this field.

Experimental Section

General: *cis*-[PtCl$_2$(dmso)$_2$] and ligand [FcCH=NC$_6$H$_4$OH-2] (**1**) were prepared as described,[12,13] and the remaining reagents were obtained from Aldrich and used as received. The methanol was HPLC-grade,[43] and the remaining solvents used, except benzene, were dried and distilled before use.[44] Elemental analyses were carried out at the Serveis Científico-Tècnics (Universitat de Barcelona) and Servei de Recursos Científics i Tècnics (Univ. Rovira i Virgili, Tarragona). Infrared spectra were obtained with a Nicolet Impact 400 instrument using KBr discs. ^{1}H and the two-dimensional NMR ({^{1}H-^{1}H} COSY and NOESY and the {^{1}H-^{13}C} HSQC and HMBC) experiments were run at 500 MHz with either a Varian 500 or a Bruker Avance 500DMX instrument. Except where quoted, the solvent used for the ^{1}H NMR experiments was $CDCl_3$ (99.9%), and $SiMe_4$ was the internal reference. ^{195}Pt{^{1}H} NMR spectra as well as ^{31}P{^{1}H} NMR spectra, were recorded with a Bruker 250DXR instrument using $CDCl_3$ (99.9%) as solvent and H$_2$[PtCl$_6$] {δ^{195}Pt(H$_2$[PtCl$_6$]) = 0.0 ppm} and P(OMe)$_3$ {δ^{31}P[P(OMe)$_3$] = 140.17 ppm} as references, respectively. In order to evaluate the stability of compounds **2** and **4**–**8** in the solvent used for the electrochemical studies, the ^{1}H NMR spectra of these compounds in CD_3CN (99.8%) were also recorded at 298 K. In all cases the chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz. Mass spectra (FAB$^+$, MALDI-TOF$^+$ or electrospray) were registered at the Servei de Espectrometria de Masses (Universitat de Barcelona) with a VG-Quattro, Voyager DE-RP or Waters Micromass instrument, respectively. The matrix used for FAB$^+$ and MALDI-TOF$^+$ mass spectra were 3-nitrobenzyl alcohol (NBA) and 2-hydroxybenzoic acid (DHB), respectively. The UV/Vis spectra of 10^{-4} M solutions of **2**, **4**, **5** and **7** or 5.0×10^{-5} M of **6** and **8** in CH_2Cl_2 were recorded at 298 K with a Shimadzu 160A spectrophotometer.

Preparation of the Compounds

***trans*-[Pt(FcCH=NC$_6$H$_4$OH-2)Cl$_2$(dmso)] (2):** Three isomeric forms of this product (**2a**, **2b** and **2c**) were isolated. These isomers differ in the conformation of the ferrocenyl ligand [*anti*-(*E*) (**2a** and **2b**) or *syn*-(*Z*) (**2c**)] or in the relative arrangement of the two Cl$^-$ ligands [*cis* (**2a**) or *trans* (**2b** and **2c**)]. *cis*-[PtCl$_2$(dmso)$_2$] (250 mg, 5.92×10^{-4} mol) was suspended in methanol (40 mL) and the mixture refluxed until complete dissolution. The hot and yellow solution was filtered, and the filtrate was added to a solution containing **1** (189 mg, 5.92×10^{-4} mol) and methanol (10 mL). The resulting mixture was protected from light with aluminium foil, refluxed for 2.5 h and filtered. The filtrate was concentrated in a rotary evaporator to dryness, and the residue obtained was dissolved in the minimum amount (ca. 5 mL) of CH_2Cl_2/*n*-hexane (100:5) and passed

through an SiO_2 column (5.0 cm × 2.0 cm) using the same solution as eluant. The first band released gave after concentration FcCHO (ca. 10 mg), and the second band produced after workup compound **2a** (15 mg). Once these bands were collected, a CH_2Cl_2/*n*-hexane (100:2) solution was used as eluant. This produced the release of a wide orange band that was collected in ca. 25-mL portions. Concentration of the first portions gave **2b** (28 mg), the following two fractions produced a solid containing a mixture of **2b** and **2c**, while the final portions gave isomer **2c** (36 mg). The subsequent elution with CH_2Cl_2/MeOH (100:0.2) allowed to isolate traces of complex **4b**. **2a:** $C_{19}H_{21}Cl_2FeNO_2PtS$ (649.3): calcd. C 35.15, H 3.25, N 2.16, S 4.93; found C 35.1, H 3.3, N 2.1, S 4.9. MS (ESI$^+$): *m*/*z* = 614 [M – Cl]$^+$. IR: $\tilde{\nu}$ = 1590 [ν(>C=N–)], 3260 [ν(–OH)] cm^{-1}. ^{1}H NMR:[45] $CDCl_3$: δ = 3.37 (s, $^3J_{Pt,H}$ = 20.5 Hz, 3 H, Me, dmso), 3.39 (s, $^3J_{Pt,H}$ = 20.2 Hz, 3 H, Me, dmso), 4.49 (s, 5 H, C_5H_5), 6.97 (s, 1 H, 2-H), 4.98 (s, 1 H, 3-H), 4.82 (s, 1 H, 4-H), 4.86 (s, 1 H, 5-H), 7.05 (dd, ^3J = 8.0 and, ^4J = 1.5 Hz, 1 H, 3′-H), 7.24 (td, ^3J = 8.0, ^4J = 1.5 Hz, 1 H, 4′-H), 6.95 (td, ^3J = 8.0, ^4J = 1.5 Hz, 1 H, 5′-H), 7.57 (dd, ^3J = 8.0, ^4J = 1.5 Hz, 1 H, 6′-H), 7.68 (s, 1 H, OH), 8.28 (s, $^3J_{Pt,H}$ = 113.0 Hz, 1 H, CH=N) ppm; [D$_3$]acetonitrile: δ = 3.37 (s, $^3J_{Pt,H}$ = 19.2 Hz, 3 H, Me, dmso), 3.30 (s, $^3J_{Pt,H}$ = 20.8 Hz, 3 H, Me, dmso), 4.50 (s, 5 H, C_5H_5), 6.51 (s, 1 H, 2-H), 5.31 (s, 1 H, 3-H), 4.92 (s, 1 H, 4-H), 5.03 (s, 1 H, 5-H), 7.02 (d, ^3J = 7.8 Hz, 1 H, 3′-H), 7.25 (t, ^3J = 7.8 Hz, 1 H, 4′-H), 6.99 (d, ^3J = 7.8 Hz, 1 H, 5′-H), 7.52 (d, ^3J = 7.8 Hz, 1 H, 6′-H), 7.73 (s, 1 H, OH), 8.45 (s, $^3J_{Pt,H}$ = 120.0 Hz, 1 H, CH=N). ^{13}C{^{1}H} NMR:[45] $CDCl_3$: δ = 44.8, 44.7 (2 Me, dmso), 71.1 (C_5H_5), 74.3 (C-1), 70.1 (C-2), 75.6 (C-3), 72.5 (C-4), 76.2 (C-5), 139.8 (C-1′), 148.4 (C-2′), 119.6 (C-3′), 129.5 (C-4′), 121.1 (C-5′), 125.7 (C-6′), 175.7 (CH=N) ppm. ^{195}Pt{^{1}H} NMR: $CDCl_3$: δ = –2868 ppm. **2b:** $C_{19}H_{21}Cl_2FeNO_2PtS$ (649.3): calcd. C 35.15, H 3.25, N 2.16, S 4.93; found C 35.3, H 3.5, N 2.1, S 4.9. MS (FAB$^+$): *m*/*z* = 649 [M]$^+$. IR: $\tilde{\nu}$ = 1589 [ν(>C=N–)], 3300 [ν(–OH)] cm^{-1}. ^{1}H NMR:[45] $CDCl_3$: δ = 3.36 (s, $^3J_{Pt,H}$ = 20.0 Hz, 6 H, 2 Me, dmso), 4.44 (s, 5 H, C_5H_5), 5.75 (t, ^3J = 1.8 Hz, 2 H, 2-H, 5-H), 4.86 (t, ^3J = 1.8 Hz, 2 H, 3-H, 4-H), 7.02 (d, ^3J = 7.0 Hz, 1 H, 3′-H), 7.22 (t, ^3J = 7.0 Hz, 1 H, 4′-H), 6.91 (t, ^3J = 7.0 Hz, 1 H, 5′-H), 7.23 (d, ^3J = 7.0 Hz, 1 H, 6′-H), 7.19 (s, 1 H, OH), 8.22 (s, $^3J_{Pt,H}$ = 86.0 Hz, 1 H, CH=N) ppm; [D$_3$]acetonitrile: δ = 3.32 (s, $^3J_{Pt,H}$ = 15.2 Hz, 6 H, 2 Me, dmso), 4.48 (s, 5 H, C_5H_5), 5.81 (s, 2 H, 2-H, 5-H), 4.92 (s, 2 H, 3-H, 4-H), 7.00 (dd, ^3J = 7.6, ^4J = 1.6 Hz, 1 H, 3′-H), 7.27 (td, ^3J = 7.6, ^4J = 1.6 Hz, 1 H, 4′-H), 6.96 (td, ^3J = 7.0, ^4J = 1.6 Hz, 1 H, 5′-H), 7.37 (dd, ^3J = 7.0, ^4J = 1.6 Hz, 1 H, 6′-H), 7.34 (s, 1 H, OH), 8.39 (s, $^3J_{Pt,H}$ = 81.6 Hz, 1 H, CH=N) ppm. ^{13}C{^{1}H}:[45] $CDCl_3$: δ = 43.8 (2 Me, dmso), 71.0 (C_5H_5), 73.8 (C-2, C-5), 75.5 (C-3, C-4), 138.7 (C-1′), 149.5 (C-2′), 118.8 (C-3′), 129.3 (C-4′), 121.1 (C-5′), 126.1 (C-6′), 175.4 (CH=N) ppm. The signal due to C-1 was not observed. ^{195}Pt{^{1}H} NMR: $CDCl_3$: δ = –2991 ppm. **2c:** $C_{19}H_{21}Cl_2FeNO_2PtS$ (649.3): calcd. C 35.15, H 3.25, N 2.16, S 4.93; found C 35.1, H 3.5, N 2.2, S 4.9. MS (FAB$^+$): *m*/*z* = 649 [M]$^+$. IR: $\tilde{\nu}$ = 1594 [ν(>C=N–)], 3313 [ν(–OH)] cm^{-1}. ^{1}H NMR:[45] $CDCl_3$: δ = 3.35 (s, $^3J_{Pt,H}$ = 20.0 Hz, 6 H, 2 Me, dmso), 4.36 (s, 5 H, C_5H_5), 4.55 (s, 1 H, 2-H), 4.52 (s, 1 H, 3-H), 4.03 (s, 1 H, 4-H), 3.65 (s, 1 H, 5-H), 7.09 (dd, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 3′-H), 7.29 (td, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 4′-H), 6.93 (td, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 5′-H), 7.13 (dd, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 6′-H), 6.95 (s, 1 H, OH), 8.53 (s, $^3J_{Pt,H}$ = 40.2 Hz, 1 H, CH=N) ppm; [D$_3$]acetonitrile: δ = 3.29 (s, $^3J_{Pt,H}$ = 19.2 Hz, 6 H, 2 Me, dmso), 4.38 (s, 5 H, C_5H_5), 4.62 (t, ^3J = 2.0 Hz, 2 H, 2-H, 5-H), 3.91 (s, ^3J = 2.0 Hz, 2 H, 3-H, 4-H), 7.04 (dd, ^3J = 8.0, ^4J = 1.6 Hz, 1 H, 3′-H), 7.33 (td, ^3J = 8.0, ^4J = 1.6 Hz, 1 H, 4′-H), 7.00 (td, ^3J = 8.0, ^4J = 1.6 Hz, 1 H, 5′-H), 7.17 (dd, ^3J = 8.0, ^4J = 1.6 Hz, 1 H, 6′-H), 6.93 (s, 1 H, OH), 8.62 (s, $^3J_{Pt,H}$ = 39.2 Hz, 1 H,CH=N) ppm. ^{13}C{^{1}H} NMR:[45] $CDCl_3$: δ = 43.7, 44.0 (2 Me, dmso), 71.1 (C_5H_5), 71.9 (C-1), 75.0 (C-2), 74.7 (C-3), 73.6 (C-4), 71.4 (C-5), 134.4 (C-1′), 148.6 (C-2′), 118.6 (C-3′), 129.5 (C-4′), 121.2 (C-5′), 125.3 (C-6′), 176.0 (CH=N) ppm. ^{195}Pt{^{1}H} NMR: $CDCl_3$: δ = –3009 ppm.

***trans*-[Pt(FcCH=NC$_6$H$_4$OH-2)Cl$_2$(PhCN)] (3):** A suspension of *cis*-[$PtCl_2(PhCN)_2$] (200 mg, 4.23×10^{-4} mol) in toluene (25 mL) was refluxed until complete dissolution of the platinum(II) complex. The hot solution was then filtered, and ligand **1** (129 mg, 4.23×10^{-4} mol) was added. The reaction mixture was protected from light with aluminium foil and refluxed for 1.5 h. After this period, the undissolved materials were removed by filtration and discarded, and the filtrate was concentrated to dryness in a rotary evaporator. The ^{1}H NMR spectrum of the solid formed revealed the coexistence of the two isomeric forms **3b** and **3c** {which differ in the conformation of the ligand [*anti*-(*E*) (**3b**) and *syn*-(*Z*) (**3c**)]} in a molar ratio **3c/3b** = 2.6. Attempts to separate the two isomers by fractional crystallization failed. When a solution of the mixture containing **3b** and **3c** was passed through an SiO_2 column (3.5 cm × 2.3 cm) using CH_2Cl_2 as eluant two colored bands were collected. The first one contained FcCHO and the second one gave, after concentration to dryness, **3c** (70 mg). **3c:** $C_{24}H_{20}Cl_2FeN_2OPt$ (674.3): calcd. C 42.75, H 2.99, N 4.15; found C 42.3, H 2.9, N 4.21. MS (FAB$^+$): *m*/*z* = 639 [M – Cl]$^+$, 535 [M – Cl – PhCN]$^+$. IR: $\tilde{\nu}$ = 1595 [ν(>C=N–)] cm^{-1}. ^{1}H NMR:[45] $CDCl_3$: δ = 4.37 (s, 5 H, C_5H_5), 4.11 (s, 1 H, 2-H), 4.52 (t, ^3J = 2.8 Hz, 1 H, 3-H), 4.50 (t, ^3J = 2.8 Hz, 1 H, 4-H), 3.64 (s, 1 H, 5-H), 7.10 (dd, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 3′-H), 7.29 (td, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 4′-H), 6.94 (td, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 5′-H), 7.16 (dd, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 6′-H), 7.14 (s, 1 H, OH), 8.58 (s, $^3J_{Pt,H}$ = 40.2 Hz, 1 H, CH=N), 7.50–7.80 (m, 5 H, aromatic protons of PhCN) ppm. ^{13}C{^{1}H} NMR:[45] $CDCl_3$: δ = 71.5 (C_5H_5), 72.7 (C-1), 73.7 (C-2), 74.7 (C-3), 75.1 (C-4), 71.6 (C-5), 135.4 (C-1′), 148.9 (C-2′), 119.2 (C-3′), 129.8 (C-4′), 121.6 (C-5′), 125.5 (C-6′), 177.1 (CH=N), 110.4, 129.8, 133.9, 135.3 (four types of aromatic carbon atoms of the PhCN ligand) ppm. ^{195}Pt{^{1}H} NMR: $CDCl_3$: δ = –2144 ppm.

[Pt(FcCH=NC$_6$H$_4$O-2)Cl(dmso)] (4): Two different isomers of this product (**4a** and **4b**) were obtained. In both cases the ligand exhibits *syn*-(*Z*) conformation, but they differ in the relative arrangement between the imine nitrogen atom and the dmso ligand (*cis* in **4a** and *trans* in **4b**). These complexes could be isolated using two different procedures [Methods (a) and (b), respectively]. Method (a) gave an equimolar mixture of the two isomers (**4a** and **4b**), whereas Method (b) allowed to isolate **4a** and **4b** separately. **Method (a):** *cis*-[$PtCl_2(dmso)_2$] (200 mg, 4.73×10^{-4} mol) was suspended in methanol (40 mL) and the mixture refluxed until complete dissolution. The resulting hot solution was filtered, and then equimolar amounts of **1** (147 mg) and NaAcO (39 mg) were added. The flask was then protected from light with aluminium foil, and the mixture was refluxed for 16 h. After this period, the deep-red solution was filtered, and the filtrate was concentrated to dryness in a rotary evaporator. The residue was dissolved in the minimum amount of CH_2Cl_2 and passed through an SiO_2 column (4.5 cm × 2.5 cm). Elution with CH_2Cl_2 produced the release of two orange bands which gave after concentration FcCHO (20 mg) and traces (8 mg) of a solid containing **2a**, **2b** and **2c** (in a molar ratio **2a/2b/2c** = 0.3:0.3:0.2). The subsequent elution with CH_2Cl_2/MeOH (100:0.2) produced a red band that was concentrated to dryness in a rotary evaporator to give 75 mg of **4**. $C_{19}H_{21}Cl_2FeNO_2PtS{\cdot}1/2CH_2Cl_2$ (634.3): calcd. C 36.47, H 3.26, N 2.21, S 5.05; found C 36.8, H 3.2, N 2.2, S 4.8. MS (FAB$^+$): *m*/*z* = 613 [M]$^+$. IR: $\tilde{\nu}$ = 1560 [ν(>C=N–)] cm^{-1}. **Method (b). Synthesis of 4a: 2a** (8.6 mg, 1.32×10^{-5} mol) was dissolved in $CDCl_3$ (0.7 mL), then an NaOD

solution (0.265 M in [D$_4$]methanol) (35 μL) was added. The reaction mixture was stirred at 298 K for ca. 10 min and then filtered. Concentration of the filtrate in a rotary evaporation produced an red oil that was later treated with *n*-hexane to give **4a** as a red solid that was collected and dried in vacuo for 3 d (yield: 7 mg, 86%). $C_{19}H_{20}ClFeNO_2PtS{\cdot}1/4C_6H_{14}$ (634.3): calcd. C 38.72, H 3.53, N 2.20, S 5.05; found C 38.6, H 3.6, N 2.2, S 4.9. MS (FAB$^+$): *m*/*z* = 613 [M]$^+$. IR: $\tilde{\nu}$ = 1560 [ν(>C=N–)] cm^{-1}. ^{1}H NMR:[45] CDCl$_3$: δ = 3.59 (s, $^3J_{Pt,H}$ = 22.0, 6 H, 2 Me, dmso), 4.32 (s, 5 H, C_5H_5), 4.61 (s, 2 H, 2-H, 5-H), 4.65 (s, 2 H, 3-H, 4-H), 7.00 (m, 1 H, 3′-H), 6.99 (m, 1 H, 4′-H), 6.29 (m, 1 H, 5′-H), 7.30 (d, ^3J = 7.0, 1 H, 6′-H), 8.78(s, $^3J_{Pt,H}$ = 58.2, 1 H, CH=N) ppm; [D$_3$]acetonitrile: δ = 3.52 (s, $^3J_{Pt,H}$ = 18.0, 6 H, 2 Me, dmso), 4.37 (s, 5 H, C_5H_5), 4.75(t, ^3J = 2.0, 2 H, 2-H, 5-H), 4.62(t, ^3J = 2.0, 2 H, 3-H, 4-H), 6.77(d, ^3J = 8.0, 1 H, 3′-H), 7.00(t, ^3J = 8.0, 1 H, 4′-H), 6.33 (t, ^3J = 8.0, 1 H, 5′-H), 7.35 (d, ^3J = 8.0, 1 H, 6′-H), 8.83 (s, $^3J_{Pt,H}$ = 56.0, 1 H, CH=N) ppm. ^{13}C{^{1}H} NMR:[45] CDCl$_3$: δ = 46.3 (2 Me, dmso), 71.8 (C_5H_5), 76.6 (C-1), 72.4 (C-2, C-5), 74.0 (C-3, C-4), 138.5 (C-1′), 167.7 (C-2′), 121.1 (C-3′), 130.3 (C-4′), 114.8 (C-5′), 118.6 (C-6′), 163.5 (CH=N) ppm. ^{195}Pt{^{1}H} NMR: CDCl$_3$: δ = –2760 ppm.

Synthesis of 4b: Prepared according to the same procedure but using **2c** (8.2 mg, 1.26×10^{-5} mol) and an NaOD solution (0.252 M in [D$_4$]methanol) (35 μL) (yield: 6.6 mg, 85%). $C_{19}H_{20}ClFeNO_2PtS{\cdot}1/4C_6H_{14}$ (634.3): calcd. C 38.72, H 3.53, N 2.20, S 5.04; found C 39.4, H 3.7, N 2.3, S 4.7. MS (FAB$^+$): *m*/*z* = 613 [M]$^+$. IR: $\tilde{\nu}$ = 1560 [ν(>C=N–)] cm^{-1}. ^{1}H NMR:[45] CDCl$_3$: δ = 3.48 (s, $^3J_{Pt,H}$ = 22.0 Hz, 6 H, 2 Me, dmso), 4.37 (s, 5 H, C_5H_5), 4.68 (br., 4 H, 2-H–5-H), 6.87 (d, ^3J = 7.0 Hz, 1 H, 3′-H), 6.94 (t, ^3J = 7.0 Hz, 1 H, 4′-H), 6.32 (t, ^3J = 7.0 Hz, 1 H, 5′-H), 7.42 (d, ^3J = 7.0 Hz, 1 H, 6′-H), 8.47 (s, $^3J_{Pt,H}$ = 40.2 Hz, 1 H, CH=N) ppm; [D$_3$]acetonitrile: δ = 3.37 (s, $^3J_{Pt,H}$ = 14.4 Hz, 6 H, 2 Me, dmso), 4.40 (s, 5 H, C_5H_5), 4.79 (t, ^3J = 2.0 Hz, 2 H, 2-H, 5-H), 6.74 (t, ^3J = 2.0 Hz, 2 H, 3-H, 4-H), 6.77 (d, ^3J = 8.0 Hz, 1 H, 3′-H), 6.96 (t, ^3J = 8.0 Hz, 1 H, 4′-H), 6.36 (t, ^3J = 8.0 Hz, 1 H, 5′-H), 7.47 (d, ^3J = 8.0 Hz, 1 H, 6′-H), 8.52 (s, $^3J_{Pt,H}$ = 36.4 Hz, 1 H, CH=N) ppm. ^{13}C{^{1}H}:[45] CDCl$_3$: δ = 43.9 (Me, dmso), 71.9 (C_5H_5), 72.6 (C-2, C-5), 74.2 (C-3, C-4), 143.3 (C-1′), 168.3 (C-2′), 121.7 (C-3′), 129.8 (C-4′), 115.0 (C-5′), 118.2 (C-6′), 163.8 (CH=N) ppm; the signal due to C-1 was not observed. ^{195}Pt{^{1}H} NMR: CDCl$_3$: δ = –2818 ppm.

[Pt{(η^5-C_5H_3CH=NC_6H_4O-2)Fe(η^5-C_5H_5)}(dmso)] (5): Ligand **1** (181 mg, 5.92×10^{-4} mol) and an equimolar amount of *cis*-[PtCl$_2$(dmso)$_2$] were dissolved in toluene (20 mL). Then a solution of NaAcO (97 mg, 1.18×10^{-3} mol) and methanol (5 mL) was added. The resulting mixture was protected from light and refluxed for 3 d. After this period, the hot solution was filtered, and the filtrate was concentrated to dryness in a rotary evaporator. The nearly black residue was dissolved in the minimum amount of CH_2Cl_2 and passed through an SiO_2 column (4.5 cm × 2.0 cm). Elution with CH_2Cl_2 produced a band that gave after concentration FcCHO. Afterwards, a CH_2Cl_2/MeOH (100:0.2) mixture produced the release of a red band that gave after workup a small amount (ca. 28 mg) of a solid containing the two isomers of **4** in a molar ratio of 1:1. Once this band was collected, the polarity of the solvent was increased, and the use of CH_2Cl_2/MeOH (100:1.0) gave a deep-purple band that was collected and concentrated to dryness to give **5** (144 mg). $C_{19}H_{19}FeNO_2PtS$ (575.0): calcd. C 39.95, H 3.33, N 2.43, S 5.56; found C 40.1, H 3.4, N 2.3, S 6.3. MS (FAB$^+$): *m*/*z* = 576 [M]$^+$. IR: $\tilde{\nu}$ = 1544 [ν(>C=N–)] cm^{-1}. ^{1}H NMR:[46] CDCl$_3$: δ = 3.48 (s, $^3J_{Pt,H}$ = 22.0 Hz, 6 H, 2 Me, dmso), 4.35 (s, 5 H, C_5H_5), 4.79 (s, 1 H, 3-H), 4.47 (t, ^3J = 2.8 Hz, 1 H, 4-H), 4.81 (s, 1 H, 5-H), 6.65 (dd, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 3′-H), 7.02 (td, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 4′-H), 6.42 (td, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 5′-H), 7.10 (dd, ^3J = 8.0, ^4J = 2.0 Hz, 1 H, 6′-H), 7.94 (s, $^3J_{Pt,H}$ = 163.2 Hz, 1 H, CH=N) ppm; [D$_3$]acetonitrile: δ = 3.38 (s, $^3J_{Pt,H}$ = 29.5, 6 H, 2 Me, dmso), 4.33 (s, 5 H, C_5H_5), 4.53 (d, ^3J = 2.5, 1 H, 3-H), 4.77 (t, ^3J = 2.5, 1 H, 4-H), 4.63 (d, ^3J = 2.5, 1 H, 5-H), 6.47 (dd, ^3J = 8.0, ^4J = 1.0, 1 H, 3′-H), 6.95 (td, ^3J = 8.0, ^4J = 1.0, 1 H, 4′-H), 6.37 (td, ^3J = 8.0, ^4J = 1.0, 1 H, 5′-H), 7.20 (dd, ^3J = 8.0, ^4J = 1.0, 1 H, 6′-H), 8.13 (s, $^3J_{Pt,H}$ = 103.52, 1 H, CH=N). ^{13}C{^{1}H} NMR:[46] CDCl$_3$: δ = 46.5, 47.2 (2 Me, dmso), 71.1 (C_5H_5), 78.0 (C-1), 91.4 (C-2), 72.1 ($^2J_{C,Pt}$ = 45.7 Hz, C-3), 69.5 (C-4), 77.0 (C-5), 137.1 (C-1′), 170.5 (C-2′), 121.3 ($^3J_{C,Pt}$ = 33.1 Hz, C-3′), 130.3 (C-4′), 115.6 (C-5′), 115.4 (C-6′), 161.4 ($^2J_{C,Pt}$ = 72.2 Hz, CH=N) ppm. ^{195}Pt{^{1}H} NMR: CDCl$_3$: δ = –4031 ppm.

[Pt{(η^5-C_5H_3CH=NC_6H_4O-2)Fe(η^5-C_5H_5)}(PPh$_3$)] (6): Compound **5** (62 mg, 1.01×10^{-4} mol) was suspended in benzene (10 mL), then an equimolar amount of PPh_3 was added. The reaction mixture was stirred at 343 K for 1 h and then filtered. The filtrate was concentrated to dryness in a rotary evaporator, and the residue was dissolved in the minimum amount of CH_2Cl_2 and passed through a short SiO_2 column (2.0 cm × 2.3 cm). Elution with CH_2Cl_2/MeOH (100:0.01) produced a violet band that was collected and concentrated to dryness. The solid formed was collected and dried (yield: 57 mg, 71%). $C_{35}H_{28}FeNOPPt$ (760.5): calcd. C 55.27, H 3.71, N 1.84; found C 55.2, H 4.0, N 2.0. MS (FAB$^+$): *m*/*z* = 760 [M]$^+$. IR: $\tilde{\nu}$ = 1561 [ν(>C=N–)] cm^{-1}. ^{1}H NMR:[46] CDCl$_3$: δ = 4.07 (s, 5 H, C_5H_5), 3.08 (d, ^3J = 2.2 Hz, 1 H, 3-H), 4.41 (t, ^3J = 2.2 Hz, 1 H, 4-H), 4.38 (d, ^3J = 2.2 Hz, 1 H, 5-H), 6.67 (dd, ^3J = 8, ^4J = 1.0 Hz, 1 H, 3′-H), 6.99 (td, ^3J = 8, ^4J = 1.0 Hz, 1 H, 4′-H), 6.39 (dd, ^3J = 8, ^4J = 1.0 Hz, 1 H, 5′-H), 7.14 (dd, ^3J = 8, ^4J = 1.0 Hz, 1 H, 6′-H), 8.14 (d, $^4J_{P,H}$ = 10.8, $^3J_{Pt,H}$ = 86.8 Hz, 1 H, CH=N), 7.30–7.80 (m, 15 H, aromatic protons of PPh_3) ppm; [D$_3$]acetonitrile: δ = 4.06 (s, 5 H, C_5H_5), 3.06 (d, ^3J = 2.0, 1 H, 3-H), 4.43 (t, ^3J = 2.0, 1 H, 4-H), 4.46 (d, ^3J = 2.0, 1 H, 5-H), 6.45 (dd, ^3J = 8, ^4J = 1.5, 1 H, 3′-H), 6.93 (td, ^3J = 8, ^4J = 1.5, 1 H, 4′-H), 6.37 (dd, ^3J = 8, ^4J = 1.5, 1 H, 5′-H), 7.26 (dd, ^3J = 8.0, ^4J = 1.5, 1 H, 6′-H), 8.33 (d, $^4J_{P,H}$ = 11.5, $^3J_{Pt,H}$ = 88.7, 1 H, CH=N), 7.30–7.85 (m, 15 H, aromatic protons of PPh_3). ^{13}C{^{1}H} NMR:[46] CDCl$_3$: δ = 70.8 (C_5H_5), 75.9 (C-1), 92.7 (C-2), 76.8 (C-3), 71.4 (C-4), 68.2 ($^3J_{Pt,C}$ = 41.2 Hz, C-5), 137.2 (C-1′), 172.6 (C-2′), 121.9 (C-3′), 130.2 (C-4′), 114.7 (C-5′), 115.5 (C-6′), 159.2 (CH=N) ppm and four additional doublets centred at δ = 128.0, 130.9, 131.0, 135.1 ppm due to the aromatic carbon atoms of the PPh_3 ligand. ^{31}P{^{1}H} NMR: CDCl$_3$: δ = 15.5 (s, $^1J_{Pt,P}$ = 3974 Hz). ^{195}Pt{^{1}H}: CDCl$_3$: δ = –3955 (d, $^1J_{Pt,P}$ = 3974 Hz) ppm.

[Pt{(η^5-C_5H_3CH=NC_6H_4OH-2)Fe(η^5-C_5H_5)}Cl(dmso)] (7): [Pt{(η^5-C_5H_3CH=NC_6H_4O-2)Fe(η^5-C_5H_5)}(dmso)] (**5**) (54 mg, 9.37×10^{-5} mol) was dissolved in $CHCl_3$ (5 mL). Then a 0.145 M solution of HCl in methanol (0.52 mL) was added. The resulting mixture was stirred at room temperature for 1 h. The undissolved materials were removed by filtration and discarded, and the filtrate was concentrated to dryness in a rotary evaporator to give a purple solid which was collected and dried (yield: 50 mg, 94%). $C_{19}H_{20}ClFeNO_2PtS{\cdot}3/4CHCl_3$ (702.3): calcd. C 33.77, H 2.98, N 1.99, S 4.56; found C 33.5, H 3.2, N 2.1, S 4.8. MS (ESI): *m*/*z* = 577 [M – Cl]$^+$. IR: $\tilde{\nu}$ = 1563 [ν(>C=N–)], 3275 [ν(–OH)] cm^{-1}. ^{1}H NMR:[46] CDCl$_3$: δ = 3.59 (s, $^3J_{Pt,H}$ = 24.0 Hz, 3 H, Me, dmso), 3.56 (s, $^3J_{Pt,H}$ = 20.8 Hz, 3 H, Me, dmso), 4.38 (s, 5 H, C_5H_5), 4.63 (d, ^3J = 2.4 Hz, 1 H, 3-H), 4.79 (t, ^3J = 2.4 Hz, 1 H, 4-H), 5.41 (d, ^3J = 2.4 Hz, 1 H, 5-H), 7.04 (d, ^3J = 8.0 Hz, 1 H, 3′-H), 7.22–7.26 (m, 2 H, 4′-H, 5′-H), 6.99 (br. s, 1 H, 6′-H), 5.62 (br. s, 1 H, OH), 8.23 (s, $^3J_{Pt,H}$ = 95.2 Hz, 1 H, CH=N) ppm; [D$_3$]acetonitrile: δ = 3.52 (s, $^3J_{Pt,H}$ = 16.0 Hz, 6 H, 2 Me, dmso), 4.46 (s, 5 H, C_5H_5), 4.76 (s, 1 H, 3-H), 4.83 (s, 1 H, 4-H), 5.31 (s, 1 H, 5-H), 7.15 (d,

^3J = 8.0 Hz, 1 H, 3′-H), 6.90 (m, 2 H, 4′-H, 5′-H), 7.03 (d, ^3J = 8.0 Hz, 1 H, 6′-H), 6.13 (s, 1 H, OH), 8.26 (s, $^3J_{Pt,H}$ = 93.6 Hz, 1 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR:[46] $CDCl_3$: δ = 47.2, 47.0 (2 Me, dmso), 70.9 (C_5H_5), 85.8 (C-1), 103.4 (C-2), 69.0 (C-3), 73.7 (C-4), 77.9 (C-5), 138.8 ($^2J_{Pt,C}$ = 76.2 Hz, C-1′), 149.2 (C-2′), 118.9 (C-3′), 129.1 (C-4′), 121.9 (C-5′), 123.7 (C-6′), 180.6 (CH=N) ppm. $^{195}Pt\{^1H\}$ NMR: $CDCl_3$: δ = –3831 ppm.

[Pt{(η^5-C_5H_3CH=NC_6H_4OH-2)Fe(η^5-C_5H_5)}Cl(PPh_3)] (8): This product can be obtained by using two alternative procedures [Methods (a) and (b)]. **Method (a):** Compound [Pt{(η^5-C_5H_3CH=NC_6H_4O-2)Fe(η^5-C_5H_5)}(PPh_3)] (**6**) (48 mg, 6.31×10^{-5} mol) was dissolved in $CHCl_3$ (0.5 mL), and then a 0.181 M solution of HCl in methanol (25 mL) was added. The reaction mixture was shaken for 2 min and then filtered. The filtrate was concentrated to dryness in a rotary evaporator, and the solid formed was collected and air-dried (yield: 46 mg, 92%). **Method (b):** To a suspension of **7** (37 mg, 6.04×10^{-5} mol) in benzene (10 mL), PPh_3 (16 mg, 6.10×10^{-5} mol) was added. The reaction mixture was stirred at 343 K for 1 h. After this period, the resulting solution was filtered, and the filtrate was concentrated to dryness in a rotary evaporator. The residue was dissolved in the minimum amount of CH_2Cl_2 and passed through an SiO_2 column (3.0 cm × 2.0 cm). Elution with CH_2Cl_2 released a purple band, that was collected and concentrated to dryness in a rotary evaporator to give **8** (yield: 30 mg, 62.5%). $C_{35}H_{29}ClFeNOPt\cdot2H_2O$ (802.0): calcd. C 50.46, H 3.99, N 1.68; found C 50.5, H 4.2, N 1.5. MS (MALDI-TOF$^+$): m/z = 761 [M – Cl]$^+$. IR: $\tilde{\nu}$ = 1552 [ν(>C=N–)], 3414 [ν(–OH)] cm^{-1}. ^1H NMR:[46] $CDCl_3$: δ = 3.95 (s, 5 H, C_5H_5), 3.54 (s, 1 H, 3-H), 4.36 (s, 1 H, 4-H), 4.56 (s, 1 H, 5-H), 6.98–7.03 (m, 3 H, 3′-H, 4′-H, 6′-H), 7.19 (t, ^3J = 7.0 Hz, 1 H, 5′-H), 6.23 (br. s, 1 H, OH), 8.38 (d, $^4J_{P,H}$ = 8.0, $^3J_{Pt,H}$ = 75.4 Hz, 1 H, CH=N), 7.35–7.80 (m, 15 H, aromatic protons of PPh_3) ppm; [D_3]acetonitrile: δ = 3.99 (s, 5 H, C_5H_5), 3.46 (s, 1 H, 3-H), 4.17 (s, 1 H, 4-H), 4.76 (s, 1 H, 5-H), 7.13 (d, ^3J = 8.0 Hz, 1 H, 3′-H), 7.18 (t, ^3J = 8.0 Hz, 1 H, 4′-H), 6.99 (t, ^3J = 8.0 Hz, 1 H, 5′-H), 6.96 (d, ^3J = 8.0 Hz, 1 H, 6′-H), 6.54 (br. s, 1 H, OH), 8.51 (d, $^4J_{P,H}$ = 8.4, $^3J_{Pt,H}$ = 70.4 Hz, 1 H, CH=N), 7.40–7.90 (m, 15 H, aromatic protons of PPh_3) ppm. $^{13}C\{^1H\}$ NMR:[46] $CDCl_3$: δ = 70.7 (C_5H_5), 87.0 (C-1, C-2), 77.4 (C-3), 73.0 (C-4), 67.8 (C-5), 140.2 (C-1′), 149.8 (C-2′), 119.4 (C-3′), 128.4 (C-4′), 122.0 (C-5′), 123.3 (C-6′), 177.5 (CH=N) ppm and four additional doublets centered at $\delta \approx$ 128.1, 130.8, 131.0, 134.9 ppm due to the four types of ^{13}C nuclei of the PPh_3 ligand. $^{31}P\{^1H\}$ NMR: $CDCl_3$: δ = 16.2 (s, $^1J_{Pt,P}$ = 4266 Hz) ppm. $^{195}Pt\{^1H\}$ NMR: $CDCl_3$: δ = –4206 (d, $^1J_{Pt,P}$ = 4266 Hz) ppm.

Electrochemical Studies: Electrochemical data for the compounds under study were obtained by cyclic voltammetry under nitrogen at 298 K by using HPLC-grade acetonitrile as solvent and tetrabutylammonium hexafluorophosphate {(Bu_4N)[PF_6]} (0.1 M) as supporting electrolyte and an M263A potentiostat from EG&G instruments. The measured potentials E were referenced to an $Ag/AgNO_3$ (0.1 M in acetonitrile) electrode separated from the solution by a medium-porosity fritted disk. A platinum wire auxiliary electrode was used in conjunction with a platinum disk working Tacussel EDI rotatory electrode (3.14 mm^2). Cyclic voltammograms of ferrocene were recorded before and after each sample to ensure the stability of the $Ag/AgNO_3$ electrode. Cyclic voltammograms of freshly prepared solutions (10^{-3} M) of the samples were run, and average values of the measured potentials were then referenced to ferrocene [E(Fc)] which was used as internal reference. In all the experiments, the cyclic voltammograms were registered using scan speeds varying from v = 10 mV/s to 100 mV/s. For the study of the effect induced by the acidity of the medium on the electrochemical properties of **2** and **4**–**8**, an equimolar amount of NaOH (20 μL of a 1.0 M solution) was added to the solutions containing **2**, **7** or **8** (10^{-3} M), the supporting electrolyte and acetonitrile. Then the resulting mixture was stirred at room temperature under N_2 for a few minutes, and afterwards its cyclic voltammetry was registered. Similarly, a solution of (Bu_4N)[PF_6] and compounds **4**, **5** or **6** was treated with an HCl solution (1.0 M in CH_3CN) (20 μL).

Table 3. Crystallographic data and details of the refinement for the crystal structures of the two isomeric forms of complex *trans*-[Pt(FcCH=NC_6H_4OH-2)Cl_2(dmso)] (**2b**·CH_2Cl_2 and **2c**). Standard deviation parameters are given in parentheses.

	2b·CH_2Cl_2	**2c**
Empirical formula	$C_{20}H_{23}Cl_4FeNO_2PtS$	$C_{19}H_{21}Cl_2FeNO_2PtS$
Formula mass	734.19	649.27
T/K	293(2)	293(2)
λ/Å	0.71069	0.71069
Crystal size [mm]	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	13.893(1)	13.679(4)
b/Å	11.955(1)	9.157(6)
c/Å	14.613(1)	17.082(6)
β/°	95.476(1)	102.77(2)
V/Å^3	2416.0(3)	2086.7(17)
Z	4	4
$D_{calcd.}$/g cm^{-3}	2.018	2.067
μ [mm^{-1}]	6.931	7.762
F(000)	1416	1248
θ range for data collection/°	2.58–33.14	2.44–29.99
No. of reflections collected	15071	6061
No. of unique reflections	6441 [R(int) = 0.0523]	6061 [R(int) = 0.0613]
No. of data	6441	6061
No. of parameters	275	244
Goodness of fit on F^2	1.023	0.769
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0368, wR_2 = 0.0939	R_1 = 0.0477, wR_2 = 0.0939
Final R indices (all data)	R_1 = 0.0742, wR_2 = 0.1024	R_1 = 0.2977, wR_2 = 0.1110
Largest diff. peak and hole/e Å^{-3}	0.634 and –0.798	0.816 and –0.945

Crystallography: A prismatic crystal of **2b**·CH_2Cl_2 (size in Table 3) was selected and mounted on a Mar345 diffractometer with an image plate detector. Unit-cell parameters were determined from 15901 reflections (in the range $3° < \theta < 31°$) and refined by least-squares methods. For **2c**, a crystal (size in Table 3) was selected and mounted on an Enraf-CAD4 four-circle diffractometer, and the unit cell parameters were determined from 25 automatically centered reflections (in the range $12° < \theta < 21°$). In both cases intensities were collected with graphite-monochromated Mo-K_α radiation. For **2b**·CH_2Cl_2, the number of reflections measured was 15071 (in the range $2.58° \leq \theta \leq 33.14°$), of which 6441 were non-equivalent by symmetry [R_{int}(on I) = 0.0523], and 4487 were assumed as observed by applying the condition $I > 2\sigma(I)$. For **2c**, 6061 reflections were measured (in the range $2.44° \leq \theta \leq 29.99°$), and 1729 were assumed as observed by applying the condition $I > 2\sigma(I)$. In this case, three reflections were measured every 2 h as orientation and intensity control, and no significant intensity decay was observed. Lorentz polarization and absorption corrections were applied in the two cases. The structures were solved by direct methods, using the SHELXS computer program[47] and refined by a full-matrix least-squares method with the SHELX97 computer program[48] using 6010 reflections for **2b**·CH_2Cl_2 and 6061 for **2c** (very negative intensities were not assumed). The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0629P)^2]^{-1}$ (for **2b**·CH_2Cl_2) or $[\sigma^2(I) + (0.0183P)^2]^{-1}$ (for **2c**) and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f' and f'' were obtained from the bibliography.[49] In both cases, all 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 is attached. The final R(on F) factors were 0.041 (for **2b**·CH_2Cl_2) and 0.047 (for **2c**). Further details concerning the resolution and refinement of these crystal structures are presented in Table 3. CCDC-655221 and -655222 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Graphical plots showing the variations of the UV/Vis spectra (in CH_2Cl_2) and cyclic voltammograms (in CH_3CN) of compounds **5**, **6**, **7** and **8** during the titration with HCl (for **5** and **6**) or with NaOD (for **7** and **8**) (Figures S1 and S2) and ^1H NMR spectra (400 MHz) of **1** in $CDCl_3$ at 298 K and after the addition of DCl or NaOD (in [D_4]methanol) (**B** and **C**, respectively) (Figure S3).

Acknowledgments

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[1] For a general overview on this topic, see for instance: a) Special issue devoted to "Molecular Machines": *Acc. Chem. Rev.* **2001**, *34*; b) T. Kelly (Ed.), "Molecular Machines", *Topics in Current Chemistry*, Springer, New York, USA, **2005**, vol. 262; c) A. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines – A Journey into the Nanoworld*, Wiley-VCH, Weinheim, Germany, **2003**.

[2] For recent reviews on this area, see for instance: a) S. Saha, J. F. Stoddart, *Chem. Soc. Rev.* **2007**, *36*, 77–92; b) V. Amendola, L. Fabbrizzi, F. Foti, M. Licchelli, C. Mangano, P. Pavallicini, A. Poggi, D. Sacchi, A. Taglietti, *Coord. Chem. Rev.* **2006**, *250*, 273–299; c) D. Gust, T. A. Moore, A. L. Moore, *Chem. Commun.* **2006**, 1169–1178; d) T. Bell, N. M. Herst, *Chem. Soc. Rev.* **2004**, *33*, 589–598; e) V. Balzani, P. Ceroni, B. Ferrer, *Pure Appl. Chem.* **2004**, *76*, 1887–1901.

[3] B. Feringa (Ed.), *Molecular Switches*, Wiley-VCH, Weinheim, Germany, **2001**.

[4] For recent advances on this field, see for instance: a) T. W. Hambley, *J. Chem. Soc., Dalton Trans.* **2001**, 2711–2718; b) J. Reedijk, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3611–3616; c) J. de Mier-Vinue, A. M. Montaña, V. Moreno, *Metal Compounds in Cancer Chemotherapy*, Research Signpost, Kerala, India, **2005**, chapter 3, pp. 47–150; d) C. S. Allardyce, A. Docier, C. Scolaro, P. S. Dyson, *Appl. Organomet. Chem.* **2005**, *19*, 110; e) A. S. Abu-Surrah, M. Kettunen, *Curr. Med. Chem.* **2006**, *13*, 1337–1357.

[5] a) V. G. Vaidyanathan, B. U. Nair, *Eur. J. Inorg. Chem.* **2005**, 3756–3759; b) C. M. Che, J. L. Zhang, L. R. Lin, *Chem. Commun.* **2002**, 2556–2557; c) P. K. M. Siu, D. L. Ma, C. M. Che, *Chem. Commun.* **2005**, 1025–1027.

[6] a) C. K. Koo, B. Lam, S. K. Leung, M. H. W. Lam, W. Y. Wong, *J. Am. Chem. Soc.* **2006**, *128*, 16434–16435; b) J. Müller, F. Glahé, E. Freisinger, B. Lippert, *Inorg. Chem.* **1999**, *38*, 3160–3166.

[7] a) A. Togni, T. Hayashi (Eds.), *Ferrocenes, Homogeneous Catalysis, Organic Synthesis and Materials Science*, VCH, Weinheim, Germany, **1995**; b) H. Plenio, D. Burth, *Organometallics* **1996**, *15*, 4054–4062; c) H. Plenio, A. Aberle, *Organometallics* **1997**, *16*, 5950–5957.

[8] For latest advances in this field, see for instance: a) L. Sun, S. Wang, H. Tian, *Chem. Lett.* **2007**, *36*, 250–251; b) A. Caballero, V. Lloberas, D. Curiel, A. Tárraga, A. Espinosa, R. García, J. Vidal-Gancedo, C. Rovira, K. Wurst, P. Molina, J. Veciana, *Inorg. Chem.* **2007**, *46*, 825–838; c) A. E. Radi, J. L. Acero Sánchez, E. Baldrich, C. K. O'Sullivan, *J. Am. Chem. Soc.* **2006**, *128*, 117–124; d) A. Sagi, J. Rishop, D. Shabat, *Anal. Chem.* **2006**, *78*, 1459–1461; e) U. Siemeling, D. Rother, C. Bruhm, *Chem. Commun.* **2007**, 427–4229; f) K. Heinze, S. Reinhart, *Organometallics* **2007**, *26*, 5406–5414; g) V. C. Gibson, C. K. A. Gregson, C. M. Halliway, N. J. Long, P. J. Oxford, A. T. P. White, D. J. Williams, *J. Organomet. Chem.* **2005**, *690*, 6271–6283; h) K. Kowalski, J. Zakrzewski, N. J. Long, S. Domagala, A. J. P. White, *J. Organomet. Chem.* **2006**, *691*, 3902–3908.

[9] D. R. van Staveren, N. Metzler-Nolte, *Chem. Rev.* **2004**, *104*, 5931–5986.

[10] M. Malaun, Z. R. Reeves, R. L. Paul, J. C. Jeffery, J. A. McCleverty, M. D. Ward, I. Asselberghs, K. Clays, A. Persoons, *Chem. Commun.* **2001**, 49–50.

[11] R. Martínez, I. Ratera, A. Tárraga, P. Molina, J. Veciana, *Chem. Commun.* **2006**, 3809–3811.

[12] C. López, R. Bosque, S. Pérez, A. Roig, E. Molins, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2006**, *691*, 475–484.

[13] J. H. Price, A. N. Williamson, R. F. Schramm, B. B. Wayland, *Inorg. Chem.* **1972**, *11*, 1280–1284.

[14] J. Bravo, C. Cativiela, R. Navarro, E. P. Urriolabeitia, *J. Organomet. Chem.* **2002**, *650*, 157–172.

[15] a) S. Pérez, C. López, A. Caubet, X. Solans, M. Font-Bardía, *New J. Chem.* **2003**, *27*, 975–982; b) C. López, A. Caubet, S. Pérez, X. Solans, M. Font-Bardía, *Chem. Commun.* **2004**, 540–541.

[16] P. S. Pregosin, *Coord. Chem. Rev.* **1982**, *44*, 247–291.

[17] a) X. Riera, A. Caubet, C. López, V. Moreno, X. Solans, M. Font-Bardía, *Organometallics* **2000**, *19*, 1384–1390; b) X. Riera, C. López, A. Caubet, V. Moreno, X. Solans, *Eur. J. Inorg. Chem.* **2001**, 2135–2141; c) L. Ding, Y. J. Wu, D. P. Zhou, *Polyhedron* **1998**, *17*, 1725–1728; d) A. Caubet, C. López, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2003**, *669*, 164–171.

[18] a) J. Albert, M. Gómez, J. Granell, J. Sales, X. Solans, *Organometallics* **1990**, *9*, 1405–1413; b) J. Albert, R. M. Ceder, M. Gómez, J. Granell, J. Sales, *Organometallics* **1992**, *11*, 1536–1541.

[19] R. G. Miller, R. D. Stauffer, D. R. Fahey, D. R. Parnell, *J. Am. Chem. Soc.* **1970**, *92*, 1511–1521.
[20] a) M. Crespo, *Polyhedron* **1996**, *15*, 1981–1988; b) M. Crespo, M. Font-Bardía, J. Granell, M. Martínez, X. Solans, *Dalton Trans.* **2003**, 3763–3769.
[21] T. H. Allen, *Acta Crystallogr., Sect. B Struct. Sci.* **2002**, *58*, 380–388.
[22] A. D. Ryabov, G. M. Kazankov, I. M. Panyashkina, O. V. Grozovsky, O. G. Dyachenko, V. A. Polyakov, L. G. Kuz'mina, *J. Chem. Soc., Dalton Trans.* **1997**, 4385–4392.
[23] a) A. Bondi, *J. Phys. Chem.* **1964**, *64*, 441–451; b) A. I. Kitaigorodskii, *Molecular Crystals and Molecules*, Academic Press, London, UK, **1973**.
[24] 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 cited therein; b) A. Capapé, M. Crespo, J. Granell, A. Vizcarro, J. Zafrilla, M. Font-Bardía, X. Solans, *Chem. Commun.* **2006**, 4128–4130.
[25] a) M. Albrecht, G. van Koten, *Angew. Chem. Int. Ed.* **2001**, *40*, 3750–3781; b) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759–1792.
[26] For recent advances on pallada- and platinacycles with terdentate $(C,N,S)^-$ ligands, see for instance: a) C. López, S. Pérez, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2002**, *650*, 258–267; b) S. Pérez, C. López, A. Caubet, R. Bosque, X. Solans, M. Font-Bardía, A. Roig, E. Molins, *Organometallics* **2004**, *23*, 224–236; c) 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* **2007**, *26*, 571–576.
[27] For recent advances on pallada- and platinacycles with terdentate $(C,N,N')^-$ ligands, see for instance: a) I. Favier, M. Gómez, J. Granell, M. Martínez, X. Solans, M. Font-Bardía, *Dalton Trans.* **2005**, 123–132; b) S. Pérez, C. López, A. Caubet, A. Pawełczyk, X. Solans, M. Font-Bardía, *Organometallics* **2003**, *22*, 2396–2408.
[28] For recent pallada- and platinacycles with terdentate $(C,N,O)^{q-}$ (q = 1 or 2) ligands, see for instance: a) G. Zhao, Q. G. Wang, T. C. W. Mak, *Organometallics* **1998**, *17*, 3437–3441; b) A. Fernández, D. Vázquez-García, J. J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J. M. Vila, *New J. Chem.* **2002**, *26*, 398–404; c) C. López, A. Caubet, S. Pérez, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2003**, *681*, 82–90; d) S. Pérez, C. López, A. Caubet, X. Solans, M. Font-Bardía, A. Roig, E. Molins, *Organometallics* **2006**, *25*, 596–601; e) D. Solé, S. Díaz, X. Solans, M. Font-Bardía, *Organometallics* **2006**, *25*, 1995–2001; f) S. Pérez, C. López, A. Caubet, X. Solans, M. Font-Bardía, M. Gich, E. Molins, *J. Organomet. Chem.* **2007**, *692*, 2402–2414 and references cited therein.
[29] M. Crespo, M. Font-Bardía, X. Solans, *J. Organomet. Chem.* **2006**, *691*, 1897–1906.
[30] a) A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27–110; b) C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233–350.
[31] a) I. Omae, *Applications of Organometallic Compounds*, John Wiley, Chichester, UK, **1998**; b) P. W. Jolly, G. Wilke, W. A. Hermann, B. Cornils (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, Germany, **1996**.
[32] J. Vicente, J. A. Abad, E. Martínez-Viviente, P. G. Jones, *Organometallics* **2002**, *21*, 4454–4467.
[33] C. López, R. Bosque, X. Solans, M. Font-Bardía, *New J. Chem.* **1996**, *20*, 1285–1292.
[34] C. López, R. Bosque, X. Solans, M. Font-Bardía, *New J. Chem.* **1998**, *22*, 977–982.
[35] NMR spectra of **2** and **4**–**8** in $[D_3]$acetonitrile at 298 K indicate that these compounds are stable in this solvent. However, for **5**, the presence of residual water in the solvent induces the cleavage of the σ-(Pt–O) bond. Thus, for the electrochemical studies the use of HPLC-grade acetonitrile is strongly recommended.
[36] E. R. Brown, J. R. Sandifer, *Physical Methods in Chemistry: Electrochemical Methods* (Eds.: B. W. Rossiter, J. H. Hamilton), Wiley, New York, USA, **1986**, vol. 4, chapter 4.
[37] a) N. F. Blom, E. W. Neuse, H. G. Thomas, *Trans. Met. Chem.* **1987**, *12*, 301–306; b) W. F. Little, C. N. Reilley, J. D. Johnson, A. P. Sanders, *J. Am. Chem. Soc.* **1964**, *86*, 1382–1386; c) G. L. K. Hoh, W. E. McEwen, J. Kleinberg, *J. Am. Chem. Soc.* **1961**, *83*, 3949–3953.
[38] a) E. M. McGale, R. E. Murray, C. J. McAdam, J. L. Morgan, B. H. Robinson, J. Simpson, *Inorg. Chim. Acta* **2003**, *352*, 129–135; b) X. Riera, A. Caubet, C. López, V. Moreno, *Polyhedron* **1999**, *18*, 2549–2555.
[39] a) R. Bosque, C. López, J. Sales, *Inorg. Chim. Acta* **1996**, *244*, 141–145; b) J. C. Kotz, E. E. Getty, L. Lin, *Organometallics* **1985**, *4*, 610–612; c) A. Moyano, M. Rosol, R. M. Moreno, C. López, M. A. Maestro, *Angew. Chem. Int. Ed.* **2005**, *44*, 1865–1869.
[40] For the cycle **6** → **8** → **6**,The isosbestic points appear at λ = 405 and 374 nm.
[41] K. Godula, D. Sames, *Science* **2006**, *312*, 67–72 and references cited therein.
[42] a) J. Dupont, C. S. Consorti, J. Spencer, *Chem. Rev.* **2005**, *105*, 2527–2572; b) I. Omae, *J. Organomet. Chem.* **2007**, *692*, 2608–2632 and references cited in these two articles.
[43] The success of the preparations of compounds **2**, **4**–**6** and **8** is strongly dependent on the quality of the methanol used. The presence of small amounts of water induces the formation of larger amounts of FcCHO and reduces the yields. Thus, the use of HPLC-grade MeOH is strongly recommended.
[44] D. D. Perrin, W. L. F. Amarego, *Purification of Laboratory Chemicals*, 4th ed., Butterworth-Heinemann, Oxford, UK, **1996**.
[45] The labelling of the atoms refers to those shown in Scheme 1.
[46] The labelling of the atoms refers to those shown in Scheme 2.
[47] G. M. Sheldrick, *SHELXS – A computer program for determination of crystal structures*, University of Göttingen, Germany, **1997**.
[48] G. M. Sheldrick, *SHELX97 – A computer program for determination of crystal structures*, University of Göttingen, Germany, **1997**.
[49] *International Tables of X-ray Crystallography*, Kynoch Press, Birmingham, UK, **1974**, vol. IV, pp. 99–100, 149.

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