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Chiral Platinum(II) Compounds Containing Ferrocenyl Schiff Bases Acting as (N), (N,O)$^-$, [C(sp^2,ferrocene),N]$^-$ or [C(sp^2,ferrocene),N,O]$^{2-}$ Ligands

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A study of the reactions of the following ferrocenyl Schiff bases: (S_C)-(+)-[FcCH=NCH(R^1)CH$_2$OH] {Fc = (η^5-C$_5$H$_5$)-Fe(η^5-C$_5$H$_4$), R^1 = Me (**1a**) or CHMe$_2$ (**1b**)} with *cis*-[PtCl$_2$(dmso)$_2$] under different experimental conditions is reported. This study enabled the isolation and characterisation of the enantiomerically pure platinum(II) complexes *trans*-(S_C)-[Pt{FcCH=NCH(R^1)CH$_2$OH}Cl$_2$(dmso)] {R^1 = Me (**2a**) or CHMe$_2$ (**2b**)} and *cis*-(S_C)-[Pt{FcCH=NCH(R^1)-CH$_2$OH}Cl$_2$(dmso)] {R^1 = Me (**3a**) or CHMe$_2$ (**3b**)} as well as four isomeric forms of (S_C)-[Pt{FcCH=N–CH(R^1)-CH$_2$O}Cl(dmso)] {R^1 = Me or CHMe$_2$} (**4**–**7a**,**b**). These isomers differ in the conformation of the imine {*anti*-(*E*) (in **4** and **6**) or *syn*-(*Z*) (in **5** and **7**)} or in the relative arrangement of the nitrogen and the dmso group {*trans* (in **4** and **5**) or *cis* (in **6** and **7**)}. Imines **1** behave as a N-donor ligand in **2** and **3** and as a (N,O)$^-$ group in **4**–**7**. We also prepared the diastereomers {(S_p,S_C) and (R_p,S_C)} of the platinacycles [Pt{[(η^5-C$_5$H$_3$)CH=NCH(R^1)CH$_2$OH]Fe(η^5-C$_5$H$_5$)}Cl(dmso)] {**8** and **9**; R^1 = Me (S_p,S_C) (**8a**) and (R_p,S_C) (**9a**) or R^1 = CHMe$_2$ (S_p,S_C) (**8b**) and (R_p,S_C) (**9b**)}, [Pt{[(η^5-C$_5$H$_3$)CH=NCH(R^1)CH$_2$O]-Fe(η^5-C$_5$H$_5$)}(dmso)] {**10** and **11**; R^1 = Me (S_p,S_C) (**10a**) and (R_p,S_C) (**11a**) or R^1 = CHMe$_2$ (S_p,S_C) (**10b**) and (R_p,S_C) (**11b**)} and [Pt{[(η^5-C$_5$H$_3$)CH=NCH(R^1)CH$_2$OH]Fe(η^5-C$_5$H$_5$)}Cl-(PPh$_3$)] {**12** and **13**; R^1 = Me (S_p,S_C) (**12a**) and (R_p,S_C) (**13a**) or R^1 = CHMe$_2$ (S_p,S_C) (**12b**) and (R_p,S_C) (**13b**)}, containing a [C(sp^2,ferrocene),N]$^-$ (in **8**, **9**, **12** and **13**) or a [C(sp^2,ferrocene),N,O]$^{2-}$ (in **10** and **11**) group. The X-ray crystal structures of **1b**·H$_2$O, **3b**, **7b**·CH$_2$Cl$_2$·1/2H$_2$O and **9a** are also reported. Our study allows the elucidation of the factors affecting the preferential formation of a given platinum(II) complex.

Introduction

Palladium(II) and platinum(II) complexes containing chiral ligands attract great interest because of their potential applications in different fields.[1–11] It is well known that compounds of this kind are useful in homogeneous catalysis[3–4] and as chiral derivatising agents,[5] as reagents to determine enantio- or diastereomeric excesses of organic substrates,[6] or even due to their antitumoral activity.[1c,7] Of the examples reported, those having a bidentate [C(sp^2,aryl),N]$^-$ group are particularly relevant.[1,3,6,8–11] The utility of chiral pallada- and platinacycles in asymmetric catalytic processes[8] including asymmetric Claisen rearrangements[10] is well documented. Notably, Leung et al.[11] have recently described the first example of a platinacycle that promotes the asymmetric [4+2] Diels–Alder reaction between diphenylvinylphosphane and *N*-(diphenylphosphanyl)pyrrole.

On the other hand, palladium(II) complexes containing (N), (N,E), (C,N)$^-$ or (C,N,E)$^-$ (E = N′, S or P) ferrocenyl ligands have attracted great interest in recent years,[12–17] mainly because of their applications in homogeneous catalysis[16] or in organometallic synthesis.[17] Platinum(II) analogues are less common[18,19] but some of these also exhibit antitumoral activity against cisplatin-resistant cells.[19] Despite *a*) the wide variety of chiral ferrocene derivatives reported so far, *b*) the prochiral nature of the ferrocenyl unit in the metallation process[20] and *c*) the interest in chiral palladium(II) and platinum(II) complexes containing ferrocenyl units, only a few enantio- or diastereomerically pure palladacycles with a σ[Pd–C(sp^2,ferrocene)] bond are described,[21,22] and the platinum(II) derivatives are less common.[23] Cycloplatination of [FcCH$_2$NMe$_2$] (**I**) or [Fc-C(R^1)=NR^2] (**II**) {Fc = (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$), R^1 = H, Me or Ph, and R^2 = OH, (CH$_2$)$_3$NMe$_2$ or phenyl groups} led to the enantiomers R_p and S_p.[24] Ryabov et al.[23] have re-

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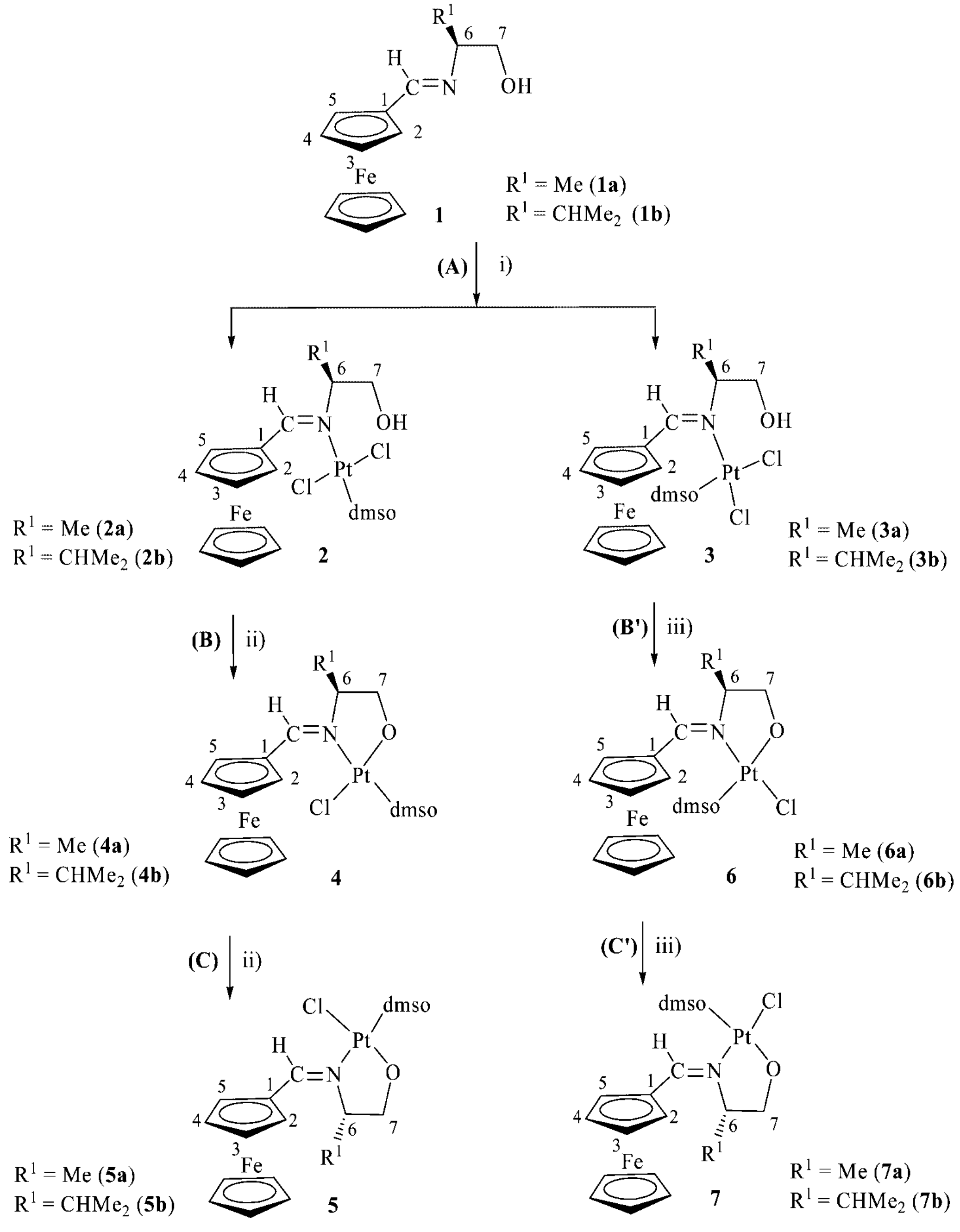
ported the synthesis of the diastereomers (R_p,S_S) and (S_p,S_S) of [Pt{[(η^5-C_5H_3)CH_2NMe_2]Fe(η^5-C_5H_5)}Cl{S(O)Me(C_6H_4-4Me)}].

In view of these facts and as a part of a project directed towards the preparation of chiral platinum(II) compounds with potentially bi- or tridentate ligands, we prepared the enantiomerically pure ferrocenyl Schiff bases: (S_C)-(+)-[FcCH=NCH(R^1)CH_2OH] (**1**) {R^1 = Me (**1a**) or $CHMe_2$ (**1b**)} (Scheme 1) and studied their reactivity with *cis*-[$PtCl_2$(dmso)$_2$]. We then *a*) evaluated the potential coordination abilities of these ligands to platinum(II), *b*) achieved a variety of enantio- and diastereomerically pure platinum(II) complexes and *c*) established the best experimental conditions required to achieve the desired chiral platinum(II) compounds. A preliminary account in this field has recently been reported.[25]



Scheme 1. *i*) Equimolar amount of *cis*-[$PtCl_2$(dmso)$_2$] in refluxing methanol for 4 h followed by SiO_2 column chromatography (see text). *ii*) Addition of NaOD (in [D$_4$]methanol) to a solution of **2** or **4** in chloroform. For molar ratios NaOD/**2** = 1 compounds **4** were the major components. The complete conversion of **2** (or **4**) into **5** requires molar ratios NaOD/**2** = 1.8. The formation of **5a** was achieved at room temperature, but that of **5b** required the reaction mixture to be warmed up at 333 K for 1.5 h (see text). *iii*) The method used was identical to that of (*ii*), but because of the small amount of compounds **3** available the intermediate species **6** were detected by NMR but they were not isolated using this procedure. A more effective method to achieve compounds **7** is presented in the text.

Results and Discussion

The Ligands

The ferrocenyl Schiff bases (S_C)-(+)-[FcCH=NCH(R^1)-CH_2OH] {R^1 = Me (**1a**) or $CHMe_2$ (**1b**)} were prepared following the procedure described for [FcCH=NR^2] with R^2 = phenyl, benzyl groups.[26] This method consists in the reaction of equimolar amounts of ferrocenecarboxaldehyde (FcCHO) and the amine under reflux using a Dean–Stark apparatus. When (S_C)-(+)-$H_2NCH(R^1)CH_2OH$ (R^1 = Me or $CHMe_2$) was used, the process yielded **1a** and **1b**, respectively. Elemental analyses of **1a** and **1b**[27] agreed with those expected for [FcCH=N–CH(Me)CH_2OH] and [FcCH=NCH($CHMe_2$)CH_2OH]·H_2O, respectively and NMR spectra suggested, according to the literature,[26] that they adopted the *anti*-(*E*) conformation in solution. The crystal structure of **1b**·H_2O (Figure 1) consists of equimolar amounts of [FcCH=NCH($CHMe_2$)-CH_2OH] and H_2O molecules. The >C=N- bond length [1.172(11) Å] is slightly shorter than the values reported for [FcC(R^3)=NR^2] (R^3 = H, Me or Ph and R^2 = phenyl, benzyl or naphthyl substituents),[26,28] the imine moiety forms an angle of 4.80(9)° with the C_5H_4 ring and the value of the torsion angle C(10)–C(11)–N–C(12) [176.6(11)°] is consistent with the *anti*-(*E*) conformation.

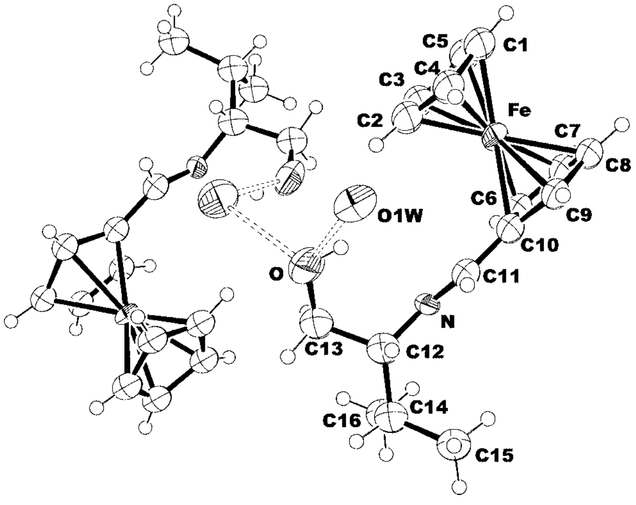


Figure 1. Molecular structure and atom labelling scheme for (S_C)-(+)-[FcCH=NCH($CHMe_2$)CH_2OH] (**1b**)·H_2O showing the H–O···H interactions. Selected bond lengths (Å) and angles (°): O–C(13) 1.523(13), N–C(11) 1.172(11), N–C(12) 1.396(9), C(10)–C(11) 1.365(9), C(12)–C(13) 1.520(9), C(12)–C(14) 1.523(12), C(14)–C(15) 1.544(10), C(14)–C(16) 1.373(13), C(6)–C(10)–C(11) 117.3(4), C(9)–C(10)–C(11) 132.7(4), C(11)–N–C(12) 134.5(12), N–C(11)–C(10) 144.4(17), N–C(12)–C(13) 113.3(6), N–C(12)–C(14) 121.2(10), C(13)–C(12)–C(14) 115.9(7), C(12)–C(13)–O 112.7(8), C(16)–C(14)–C(12) 102.3(10), C(16)–C(14)–C(15) 119.1(10), C(12)–C(14)–C(15) 110.4(8).

Bond lengths and angles of the Fc moiety agree with those reported for most ferrocene derivatives,[29] and the two pentagonal rings are planar and nearly parallel {tilt angle = 3.6(5)°}, deviating by about 7.35° from the ideal eclipsed conformation. In the crystal, the distance between the hydrogen of the O–H group of the ligand and the oxygen of the water molecule, O(1W), is 2.696(13) Å and the O–H···O bond angle is 113.98°, thus suggesting a weak O–H(10)···O(1W) intermolecular interaction.

Platinum(II) Compounds

In a first attempt to evaluate the potential coordination abilities of the ferrocenyl Schiff bases **1** to platinum(II), their reactivity with *cis*-[$PtCl_2$(dmso)$_2$] under different experimental conditions was studied. Because of the variety of products isolated, the most representative results obtained are in Table 1 and Scheme 1.

When **1a** (or **1b**) was treated with *cis*-[$PtCl_2$(dmso)$_2$] in refluxing methanol for 4 h, two compounds were isolated {Table 1, entries ***Ia*** and ***Ib*** and Scheme 1, step (A)}. One of these was identified as FcCHO. The ^{1}H NMR spectrum of the crude materials showed the typical resonances of this product. This suggests that it hydrolyses during the reaction with residual water in the solvent. Examples of a partial hydrolysis of related Schiff bases induced by the presence of palladium(II) or platinum(II) salts have been reported in the literature.[24c,30] The first portions of the second band gave [Pt{FcCH=NCH(R^1)CH_2OH}Cl_2(dmso)] {R^1 = Me (**2a**) or $CHMe_2$ (**2b**)} and the remaining ones produced orange solids containing **2a** (or **2b**) and traces of an additional isomer (**3a** and **3b**, respectively). Longer refluxing periods (6 h) did not substantially improve the molar ratios **2a**/**3a** and **2b**/**3b** (1.00:0.10 and 1.00:0.11, respectively).

Previous ^{1}H NMR spectroscopic studies of platinum(II) and palladium(II) complexes derived from imines have shown that the chemical shift of the methinic proton is indicative of the conformation of the ligand.[24b,26,30–35] If the imine is in the *syn*-(*Z*) form in the complexes, the signal of the imine proton is shifted downfield relative to the free ligand because of the paramagnetic anisotropy of the metal,[34] which is close to this proton. In contrast, for compounds where the imine is in the *anti*-(*E*) form the resonance of the methinic proton is high-field shifted. The comparison of ^{1}H NMR spectra of **2** and **3** with those of their parent ligands **1** indicated that in **2a**, **3a**, **2b** and **3b** the ligands had the *anti*-(*E*) conformation and {^{1}H-^{1}H}-NOESY spectra confirmed this result. Fractional crystallisation of the solids containing the isomeric forms enabled the isolation of small amounts of **3a** and **3b** and highly enriched (about 98%) **2a** and **2b**. Characterisation data of **2**–**3a,b**[27] agreed with the formulas presented in Scheme 1.

The crystal structure of **3b** consists of discrete molecules of [Pt{FcCH=NCH($CHMe_2$)CH_2OH}Cl_2(dmso)] separated by van der Waals contacts (Figure 2). The platinum(II) is in a slightly distorted square-planar environment bound to the imine nitrogen, the sulfur of the S(O)Me_2 ligand and two chlorines {Cl(1) and Cl(2)}. The Pt–S bond length [2.194(4) Å] agrees with the values reported for other platinum(II) complexes with dimethyl sulfoxide.[12,24,29,35] The chloro ligands are in a *cis* arrangement and the value of the torsion angle C(1)–C(11)–N(12)–C(13) [179.6(14)°] is consistent with an *anti*-(*E*) conformation. Because of the

Table 1. Summary of the experimental conditions [reagents, solvents, temperature (T) and reaction periods (t)] used in the studies of the reactivity of **1** with *cis*-[$PtCl_2(dmso)_2$], which is abbreviated as [Pt], or of some of the platinum(II) complexes together with the products isolated in these reactions.

Entry	Reagent (molar ratio)	Solvent	T [K]	t	Final products[a] (molar ratios)
Ia	**1a** and [Pt] (1:1)	MeOH	reflux	4 h	**2a** and **3a** [b]
Ib	**1b** and [Pt] (1:1)	MeOH	reflux	4 h	**2b** and **3b** (1.00:0.05)
IIa	**2a** and NaOD (1:1)	$CDCl_3$/MeOD	298	5 min	**4a**
IIb	**2b** and NaOD (1:1)	$CDCl_3$/MeOD	298	5 min	**4b**
IIIa	**2a** and NaOD (1:1.8)	$CDCl_3$/MeOD	298	5 min	**5a**
IIIb	**2b** and NaOD (1:1.8)	$CDCl_3$/MeOD	333	1.5 h	**5b**
IVa	**2a** and NaOAc (1:2)	MeOH/toluene[c]	reflux	72 h	**8a** and **9a** (1:1)
IVb	**2b** and NaOAc (1:2)	MeOH/toluene[c]	reflux	72 h	**8b** and **9b** (1:1)
Va	**1a**, [Pt] and NaOAc (1:1:2)	MeOH/toluene[c]	reflux	72 h	**8a** and **9a** (1:1)
Vb	**1b**, [Pt] and NaOAc (1:1:2)	MeOH/toluene[c]	reflux	72 h	**8b** and **9b** (1:1)
VIa	**8a** (or **8b**) and NaOD[d] (1:1)	$CHCl_3$/MeOH[d]	298		**10a** (or **10b**)
VIb	**9a** (or **9b**) and NaOD[d] (1:1)	$CHCl_3$/MeOH[d]	298		**11a** (or **11b**)

[a] In entries ***Ia,b*** and ***IV–Va,b*** small amounts of FcCHO were also isolated as a byproduct. ^{1}H NMR spectra of the crude materials obtained also showed the presence of this aldehyde, thus suggesting that the formation of FcCHO takes place during the reaction because of residual water in the solvent and that it is not a byproduct generated in the course of the work-up of the column. [b] The presence of a small amount of **3a** (about 5 mg) was detected. [c] A (1:4) mixture. [d] Saturated solution of NaOD in [D_4]methanol.

similarity between the NMR spectroscopic data[27] of **3a** and **3b** we assumed that the environment of the platinum(II) in **3a** is the same as in **3b** and consequently, in **2a** and **2b** the two Cl^- ligands would be in a *trans* arrangement.

On the other hand, the presence of the OH group in the dangling arm of **2** and **3** prompted us to study whether the addition of a base could induce the deprotonation of the OH group and the formation of enantiomerically pure platinum(II) complexes containing imines **1** acting as bidentate $(N,O)^-$ ligands. In a first attempt to achieve this aim, the reactions of **2a** (in $CDCl_3$) with NaOD dissolved in methanol (in molar ratios NaOD/**2a** varying from 0.2 to 1.8) were studied on an NMR scale {Scheme 1, steps (B) and (C)}. The results showed that, for molar ratios smaller than 0.4, **2a** and a new platinum(II) complex (**4a**) coexisted in solution. As can be easily seen in Figure 3, the proportion **2a**/**4a** decreased as the molar ratio NaOD/**2a** increased and for a NaOD/**2a** ratio of 1 (Table 1, entry ***IIa***) the major product was **4a** and only traces of **2a** and of a new byproduct (hereafter referred to as **5a**) were detected. NMR studies revealed that in **4a** the ligand adopted the *anti*-(*E*) conformation and behaved as a $(N,O)^-$ bidentate ligand. In view of the characterisation data available,[27] for **4a** we postulate the chemical formula depicted in Scheme 1. An increase of the NaOD/**2a** molar ratio (up to 1.8) reduced the relative abundance of **2a** and **4a** compared with that of **5a** and the complete conversion of **2a** into **5a** was achieved

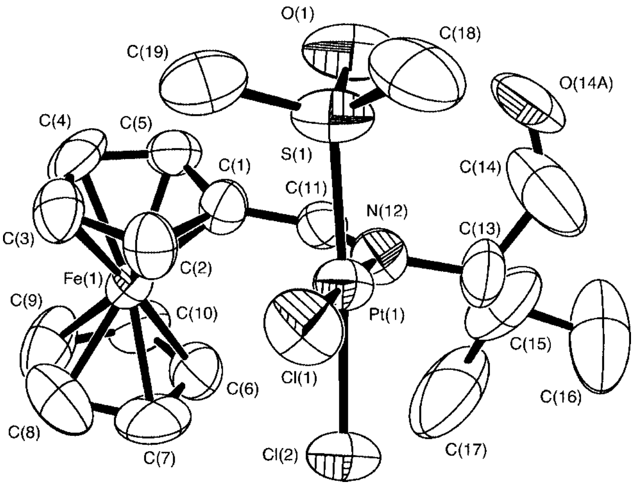


Figure 2. ORTEP plot of *cis*-(S_C)-[Pt{FcCH=NCH($CHMe_2$)-CH_2OH}Cl_2(dmso)] (**3b**). Thermal ellipsoids at 50% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–Cl(1) 2.294(4), Pt(1)–Cl(2) 2.306(4), Pt(1)–N(12) 2.041(11), Pt(1)–S(1) 2.194(4), C(1)–C(11) 1.431(18), C(11)–N(12) 1.322(16), N(12)–C(13) 1.496(19), C(13)–C(14) 1.45(3), C(14)–O(14A) 1.26(4), C(13)–C(15) 1.46(3), C(15)–C(16) 1.58(4), C(15)–C(17) 1.583(5), Cl(1)–Pt(1)–Cl(2) 89.75(16), Cl(1)–Pt(1)–S(1) 90.71(18), S(1)–Pt(1)–N(12) 91.1(4), N(12)–Pt(1)–Cl(2) 88.6(4), C(1)–C(11)–N(12) 128.9(12), C(11)–N(12)–C(13) 118.1(16), N(12)–C(13)–C(14) 114.2(19), N(12)–C(13)–C(15) 118.1(16).

using NaOD/**2a** = 1.8 {Table 1, entry ***IIIa*** and Scheme 1, step (C)}. Similar results were obtained when these experiments were performed using **2b** (Table 1, entries ***IIb***–***IIIb***),[36] showing the formation of an intermediate complex **4b**, which could be partially transformed into **5b** upon the addition of NaOD {Scheme 1, steps (B) and (C)}. The reaction **4b** → **5b** at 298 K was slower than the process **4a** → **5a**, but it could be accelerated by warming at 333 K. Characterisation data of **5**[27] were consistent with those expected for the isomeric form of [Pt{FcCH=NCH(R^1)CH$_2$O}-Cl(dmso)] {R^1 = Me (**5a**) or CHMe$_2$ (**5b**)} that contains a (N,O)$^-$ bidentate imine [in a *syn*-(*Z*) conformation] and a *trans* arrangement between the oxygen and the Cl$^-$ ligand.

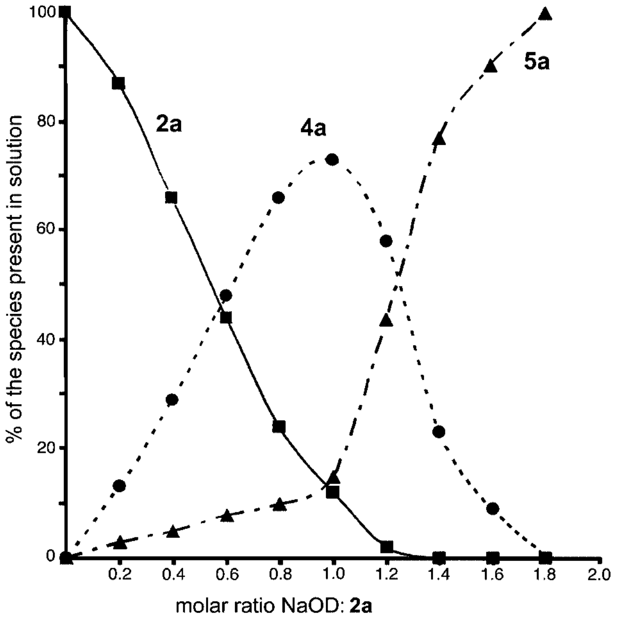


Figure 3. Graphic plot showing the dependence of the relative abundance (in %) of compounds **2a** (squares), **4a** (circles) and **5a** (triangles) on the molar ratios NaOD/**2a**.

The different ease with which **4a** and **4b** undergo the *anti*-(*E*) → *syn*-(*Z*) isomerisation of the ligand could be attributed to the different bulk of the substituents (Me or CHMe$_2$) on the stereogenic carbon.

All these findings suggest that: *a*) NaOD promotes the conversions of **2a** into **4a** and **5a** (or of **2b** into **4b** and **5b**) and *b*) these reactions proceed in two consecutive steps: the formation of the five-membered chelate ring, followed by the *anti*-(*E*) → *syn*-(*Z*) isomerisation of the imine.

In order to evaluate the potential reversibility of these reactions, the action of DCl on **5a** (or **5b**) was also studied. In all cases FcCHO was isolated as the major product and only traces of **2a** (or **2b**) could be detected by ^{1}H NMR spectroscopy. This suggests that: *a*) the hydrolysis of the coordinating ligand was promoted in acidic media and *b*) the transformations **5a** → **2a** and **5b** → **2b** were not feasible under these experimental conditions.

Similarly, the reaction of **3a** (or **3b**) with NaOD gave **7a** (or **7b**) {Scheme 1, steps (B′) and (C′)}. However, the effectiveness of this procedure is limited because of the small amounts of **3a** or **3b** available from experiments ***Ia***,***b***. In these reactions, evidence of the formation of intermediate species (**6a** and **6b**, in Scheme 1) was also detected by NMR spectroscopy.

Compounds **7** could be isolated in a higher yield using an alternative path that consists in the treatment of equimolar amounts of the corresponding ligand, *cis*-[PtCl$_2$(dmso)$_2$] and NaOAc in refluxing methanol for 72 h.[37] These reactions lead to mixtures of FcCHO and the platinum(II) complexes **2**, **3**, **5** and **7** (in molar ratios **2a**/**3a**/**5a**/**7a** = 0.51:0.40:0.02:1.00 and **2b**/**3b**/**5b**/**7b** = 0.41:0.20:0.26:1.00). Characterisation data of **7**[27] agreed with the proposed formulae and complex **7b**·CH$_2$Cl$_2$·1/2H$_2$O was also characterised by X-ray diffraction.

The crystal structure is formed by molecules of [Pt{FcCH=NCH(CHMe$_2$)CH$_2$O}Cl(dmso)] (Figure 4), CH$_2$Cl$_2$ and H$_2$O in a 1:1:0.5 molar ratio. In the heterodimetallic molecules, the platinum(II) is bound to a chloride, the sulfur of the dmso ligand, the nitrogen and the oxygen of ligand **1b** in a slightly distorted square-planar environment. Bond lengths and angles around the platinum(II) agreed with those of related compounds containing similar cores.[29] The values of the Cl(1)–Pt–O(14) bond angle [85.5(6)°] indicate a *cis* arrangement between the Cl(1) and the oxygen of the ligand and consequently the S$_{(dmso)}$ and N atoms occupy adjacent positions of the coordination plane. The metallacycle has an envelope-like conformation in which the C(13) atom deviates by about 0.667 Å (towards the Fe^{II} atom) from the mean plane. The ligand adopts the *syn*-(*Z*) form, the >C=N– group is not included in the five-membered chelate ring and the C(11)–N(12) bond length is similar to those of other platinum(II) compounds containing ferrocenyl or organic imines.[24b,24c,29,30,35]

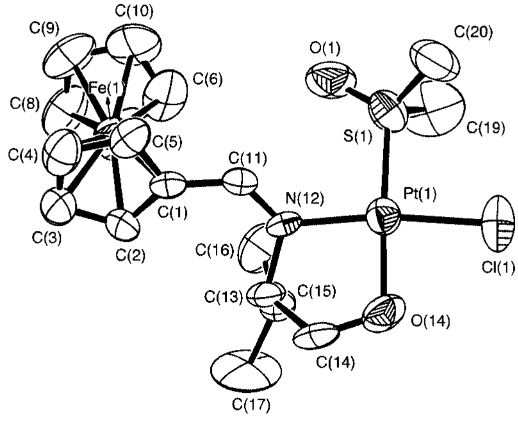


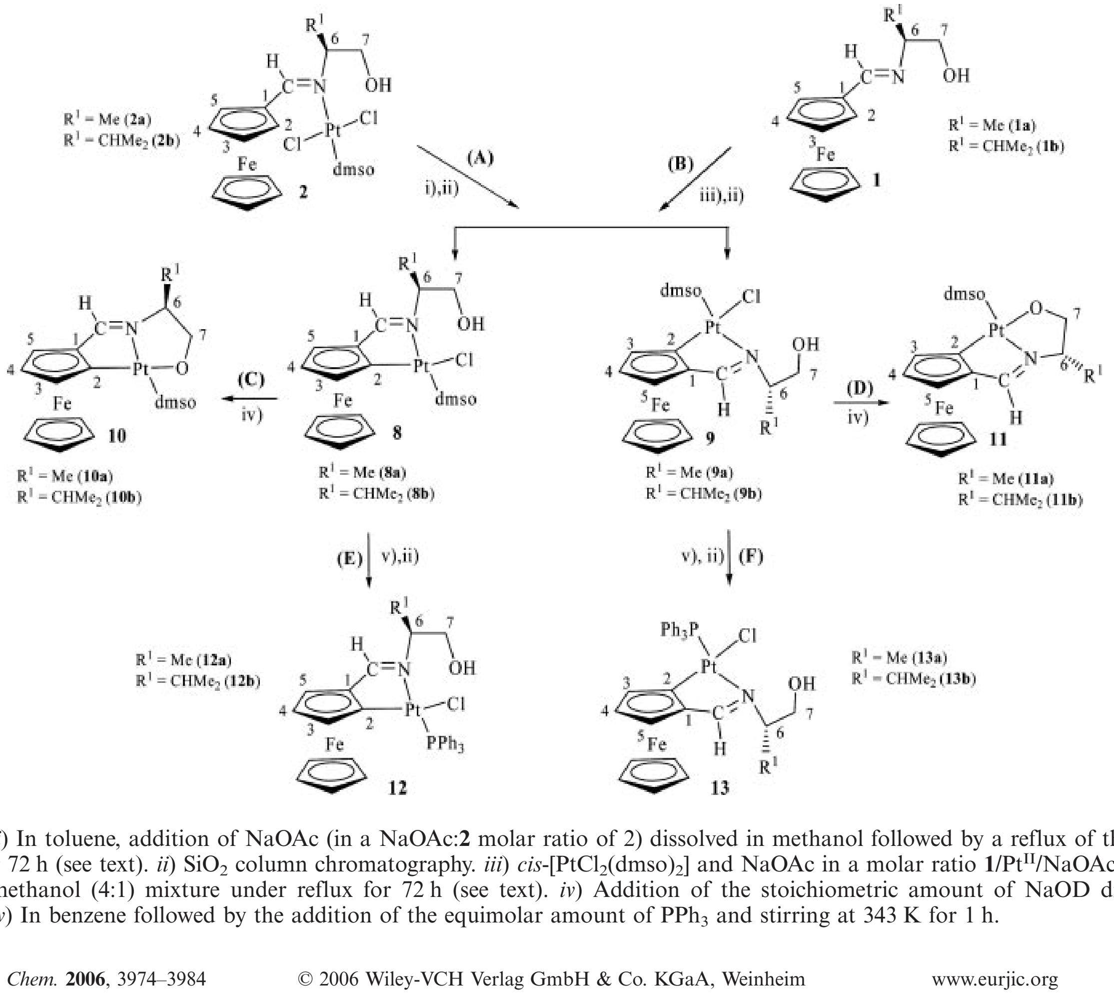
Figure 4. ORTEP plot of (S_C)-[Pt{FcCH=NCH(CHMe$_2$)-CH$_2$O}Cl(dmso)] (**7b**). Thermal ellipsoids at 50% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–Cl(1) 2.310(7), Pt(1)–S(1) 2.194(8), Pt(1)–N(12) 2.013(18), Pt(1)–O(14) 1.956(19), C(1)–C(11) 1.44(3), C(11)–N(12) 1.28(3), C(14)–O(14) 1.42(4), C(13)–C(15) 1.45(4), C(15)–C(16) 1.56(4), C(15)–C(17) 1.60(4), N(12)–Pt(1)–O(14) 96.5(5), O(14)–Pt(1)–Cl(1) 85.5(6), Cl(1)–Pt(1)–S(1) 92.4(3), S(1)–Pt(1)–N(12) 96.8(5), Pt(1)–O(14)–C(14) 109.4(15).

More interesting were the results obtained when compounds **2** were treated with sodium acetate (in a molar ratio AcO$^-$:**2** = 2) in a toluene/methanol (4:1) mixture under reflux for 72 h {Scheme 2, step (A) and Table 1, entries ***IVa*** and ***IVb***}. These reactions gave FcCHO and purple solids whose elemental analyses[27] were consistent with those expected for the platinacycles [Pt{[(η^5-C_5H_3)CH=NCH(R^1)-CH_2OH]Fe(η^5-C_5H_5)}Cl(dmso)] and their ^1H NMR spectra showed two sets of superimposed signals of identical intensity. These platinum(II) complexes arise from the activation of the σ[C(sp^2,ferrocene)–H] bond and because of the prochiral nature of the ferrocenyl moiety in process,[1a,20,21,22b,23,24] the duplicity of the signals detected in their NMR spectra could be attributed to the presence of diastereomers of [Pt{[(η^5-C_5H_3)CH=NCH(R^1)CH_2OH] Fe(η^5-C_5H_5)}Cl(dmso)] {**8** and **9**; R^1 = Me (S_p,S_C) (**8a**) and (R_p,S_C) (**9a**) or R^1 = $CHMe_2$ (S_p,S_C) (**8b**) and (R_p,S_C) (**9b**)}. Their characterisation data[27] and the crystal structures of two of these compounds (**8b** and **9a**) (see below) confirmed this result.

Compounds **8** and **9** could also be isolated when a mixture of the corresponding ligand **1**, *cis*-[$PtCl_2(dmso)_2$] and NaOAc (in a 1:1:2 molar ratio) was dissolved in a toluene/methanol (4:1) mixture and refluxed for 72 h {Scheme 2, step (B) and Table 1, entries ***Va*** and ***Vb***}. This is an alternative and more effective path to achieve compounds **8**–**9a**,**b** (with slightly higher yields and in shorter times) than that shown in entries ***IVa*** and ***IVb*** and Scheme 2, step (A).

The two diastereomers of [Pt{[(η^5-C_5H_3)CH=NCH(R^1)-CH_2OH]Fe(η^5-C_5H_5)}Cl(dmso)] {**8** and **9**; R^1 = Me (S_p,S_C) (**8a**) and (R_p,S_C) (**9a**) or R^1 = $CHMe_2$ (S_p,S_C) (**8b**) and (R_p,S_C) (**9b**)} were separated and characterised.[27] The crystal structure of **8b** was reported in a preliminary communication[25] and that of **9a** consists of two nonequivalent molecules (**I** and **II**) of [Pt{[(η^5-C_5H_3)CH=NCH(Me)CH_2OH]-Fe(η^5-C_5H_5)}Cl(dmso)] (Figure 5) separated by van der Waals contacts. In molecules **I** and **II**, the platinum(II) atom is bound to a chlorine {Cl(1) or Cl(1A)}, the sulfur {S(1) or S(1A)} of the dmso ligand, the nitrogen {N(1) or N(1A)} and the carbon atoms {C(6) (in **I**) or C(6A) (in **II**)}. This results in a slightly distorted square-planar environment. Bond lengths around the platinum(II) atom are similar to those of other platinacycles with "Pt(C,N)-$ClS_{(dmso)}$" cores.[12,18,29] The values of the bond angles Cl(1)–Pt(1)–N(1) and Cl(1A)–Pt(1A)–N(1A) {91.7(8)° and 95.2(9)°, respectively} indicate that the Cl^- and the N are in a *cis* arrangement. The platinacycles are nearly planar and the large separation between the Fe^{II} and the Pt^{II} atoms precludes the existence of any direct interaction between them.

The main difference between molecules **I** and **II** arises from the relative orientation of the pendant OH arm. The values of the torsion angles O(2)–C(14)–C(12)–C(13) and



Scheme 2. *i*) In toluene, addition of NaOAc (in a NaOAc:**2** molar ratio of 2) dissolved in methanol followed by a reflux of the reaction mixture for 72 h (see text). *ii*) SiO_2 column chromatography. *iii*) *cis*-[$PtCl_2(dmso)_2$] and NaOAc in a molar ratio **1**/Pt^{II}/NaOAc = 1:1:2 in a toluene/methanol (4:1) mixture under reflux for 72 h (see text). *iv*) Addition of the stoichiometric amount of NaOD dissolved in methanol. *v*) In benzene followed by the addition of the equimolar amount of PPh_3 and stirring at 343 K for 1 h.

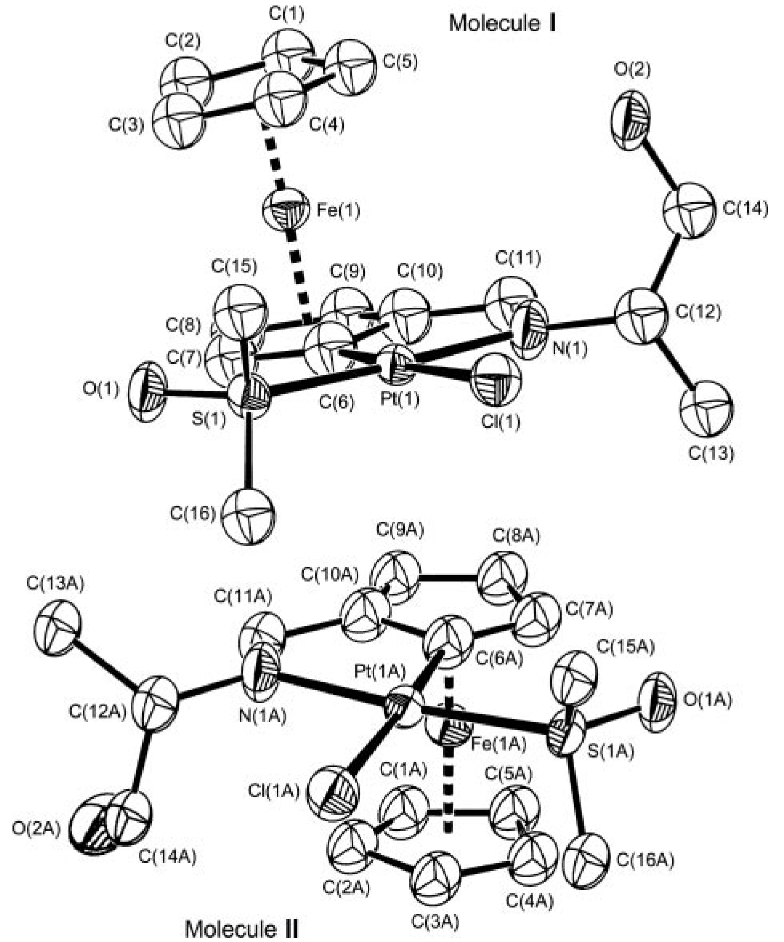


Figure 5. ORTEP plot of (R_p,S_C)-(+)-[Pt{[(η^5-C_5H_3)CH=NCH(Me)CH_2OH]Fe(η^5-C_5H_5)}Cl(dmso)] (**9a**). Thermal ellipsoids at 50% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–C(6) 2.01(3), Pt(1)–N(1) 2.05(2), Pt(1)–S(1) 2.214(2), Pt(1)–Cl(1) 2.427(8), C(10)–C(11) 1.40(4), N(1)–C(11) 1.26(3), N(1)–C(12) 1.50(2), O(2)–C(14) 1.40(3), Pt(1A)–C(6A) 2.03(3), Pt(1A)–N(1A) 2.01(3), Pt(1A)–S(1A) 2.197(8), C(10A)–C(11A) 1.46(4), N(1A)–C(11A) 1.24(4), N(1A)–C(12A) 1.51(4), O(2A)–C(14A) 1.42(3), C(6)–Pt(1)–N(1) 81.5(12), C(6)–Pt(1)–S(1) 97.8(10), N(1)–Pt(1)–Cl(1) 91.7(8), S(1)–Pt(1)–Cl(1) 89.0(3), C(6A)–Pt(1A)–N(1A) 78.6(12), C(6A)–Pt(1A)–S(1A) 95.9(9), N(1A)–Pt(1A)–Cl(1A) 95.2(9), S(1A)–Pt(1A)–Cl(1A) 90.4(3).

O(2A)–C(14A)–C(12A)–C(13A) are 174(2)° and 61(3)°; as a consequence of this arrangement the separation between the Fe^{II} and the oxygen of the OH group in **I** is greater than in **II**.

The formation of platinacycles of general formula [Pt(C,N)Cl(dmso)] {$(C,N)^-$ = cyclometallated imine (L)} from [Pt(L)Cl_2(dmso)] requires a proper orientation between the σ(C–H) bond to be activated and the platinum(II)[1a,38] and the release of one of the Cl^- ligands. The formation of a nearly equimolar ratio of **8** and **9** can be explained assuming a free rotation around the C_{ipso}–C_{imine} bond of **2a** or **2b**. A similar argument has been used for the cyclopallada- or cycloplatination of several 1,1′-ferrocenyldiimines or diamines.[39]

In order to explore the coordinating ability of the oxygen to the platinum(II) and the potential hemilability[40] of the σ(Pt–O) bond, solutions of **8a**, **8b**, **9a** or **9b** were treated separately with the equimolar amount of NaOD. In all cases, the corresponding diastereomer of [Pt{[(η^5-C_5H_3)-CH=NCH(R^1)CH_2O]Fe(η^5-C_5H_5)}(dmso)][27] {**10** and **11**; R^1 = Me (S_p,S_C) (**10a**) and (R_p,S_C) (**11a**) or R^1 = $CHMe_2$ (S_p,S_C) (**10b**) and (R_p,S_C) (**11b**)} {Scheme 2, steps (C) and (D)} was isolated. These compounds arise from the activation of the σ(O–H) bond. In their ^1H NMR spectra the signal due to the imine proton exhibited the typical satellites due to the coupling with the ^{195}Pt nucleus and appeared at higher fields than for the parent complex. Besides, the resonance of the ^{13}C nuclei of the "$>CHCH_2–$" moiety shifted downfield. These findings suggested, in keeping with the bibliography,[41] a $(C,N,O)^{2-}$ mode of binding of the ligand.

Solutions of **10** and **11** (in $CDCl_3$) changed with time and after 3 days the spectra revealed the coexistence of the pairs (**8** and **10**) or (**9** and **11**) (molar ratios **8a**/**10a** = 1.1, **9a**/**11a** = 1.0, **8b**/**10b** = 1.5 and **9b**/**11b** = 0.9). The addition of DCl to solutions of **10** (or **11**) gave **8** (or **9**) and subsequent cycles exposing **8** or **9** to acidic and basic conditions showed that the transformations **8** ↔ **10** and **9** ↔ **11** were reproducible and robust, enabling these systems to function as a simple molecular switch.[42] Therefore, the deprotonation of the OH group by the action of a base and the subsequent intramolecular replacement of the adjacent chloride moiety can be easily tuned by manipulating the acidity/basicity of the media. Examples of diastereomerically pure metallacycles exhibiting this behaviour are still unknown.

Finally, and in order to elucidate the potential utility of the platinacycles [Pt{[(η^5-C_5H_3)CH=NCH(R^1)CH_2OH]Fe(η^5-C_5H_5)}Cl(dmso)] (**8** and **9**) as precursors for the synthesis of other diastereomerically pure platinum(II) derivatives, we studied the reactions of **8**–**9a**,**b** with PPh_3. In all cases, the platinacycles [Pt{[(η^5-C_5H_3)CH=NCH(R^1)CH_2OH]Fe(η^5-C_5H_5)}Cl(PPh_3)] {**12**–**13**; R^1 = Me (S_p,S_C) (**12a**) and (R_p,S_C) (**13a**) or $CHMe_2$ (S_p,S_C) (**12b**) and (R_p,S_C) (**13b**)} {Scheme 2, steps (E) and (F)} were isolated. $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopic data[27] for **12**–**13** were consistent with those reported for other platinacycles containing a cyclometallated Schiff base,[24b,24c,43] in which the phosphane and the metallated carbon are in a *cis* arrangement, in good agreement with the *transphobia effect*.[44]

In summary, the results presented 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 ligands **1** to platinum(II). For each one of the ligands, three different pairs of enantiomerically pure complexes (**2**–**7a**,**b**) are isolated. These compounds differ in the mode of binding of the ferrocenyl ligand {N-donor group (in **2** and **3**) or a monoanionic (N,O)$^-$ group (in **4**–**7**)}, or in the relative arrangement between: *a*) the monodentate ligands bound to platinum(II) (in **2** and **3**), *b*) these groups and the two heteroatoms of the ferrocenyl Schiff base (in **4**–**7**) or *c*) the conformation of the ligand *anti*-(*E*) (in **4** and **6**) or *syn*-(*Z*) (in **5** and **7**). Moreover, these studies also enable the isolation of the diastereomerically pure platinacycles: [Pt{[(η^5-C_5H_3)CH=NCH(R^1)CH_2OH]Fe(η^5-C_5H_5)}Cl(L)] {L = dmso (**8** and **9**) or PPh_3 (**12** and **13**)} and [Pt{[(η^5-C_5H_3)CH=NCH(R^1)CH_2O]Fe(η^5-C_5H_5)}(dmso)] (in **10** and **11**) {with a [C(sp^2,ferrocene),N]$^-$ or [C(sp^2,ferrocene),N,O]$^{2-}$ ligand, respectively}. As far as we know, chiral ligands exhibiting such interesting and versatile modes of binding to transition metals and, in particular, to platinum(II) have not been described so far.

The studies undertaken also showed the outstanding reactivity of compounds **2** and their utility for the preparation of a wide variety of chiral platinum(II) complexes by: *a*) activation of the σ(O–H) to give **4** {which may be transformed into **5** by the subsequent isomerisation *anti*-(*E*) → *syn*-(*Z*) of the coordinated Schiff base, Scheme 1, steps (B) and (C)} or *b*) the cycloplatination of the ferrocenyl unit {Scheme 2, step (A)} to give the diastereomers **8** and **9**. In the presence of NaOH, **8** (or **9**) evolve to the chiral derivatives **10** (or **11**) with a [C(sp^2,ferrocene),N,O]$^{2-}$ ligand {Scheme 2, steps (C) and (D)}. Moreover, the reactivity of **2** through pathways (B) and (A) in Scheme 1 and Scheme 2, respectively, can be easily controlled by the appropriate selection of the reagent (NaOH or NaOAc) and the solvent. The use of equimolar amounts of NaOH and MeOH as solvent promotes the formation of the coordination compounds with (N,O)$^-$ bidentate ligands (**4**), while larger excesses induce the *anti*-(*E*) → *syn*-(*Z*) isomerisation of the ligands giving **5**. The replacement of NaOH by NaOAc and the decrease of the polarity of the reaction media promotes the activation of the σ[C(sp^2,ferrocene)–H] bond, giving the platinacycles **8** and **9**, which can be easily transformed into [Pt{[(η^5-C_5H_3)CH=NCH(R^1)CH_2O]Fe(η^5-C_5H_5)}(dmso)] (**10** and **11**) {with a [C(sp^2,ferrocene),N,O]$^{2-}$ ligand}. Platinacycles **8**–**13** are especially attractive as they may be used as starting materials for the synthesis of a wide variety of diastereomerically pure platinum(II) compounds, or even platinum(IV) derivatives (through oxidative addition reactions). Furthermore, the results presented have demonstrated that the interconversion between the pairs of the corresponding diastereomerically pure platinacycles (**8** and **10** or **9** and **11**) can be viewed as an acid–base controlled molecular switch.[42] These transformations modify the hapticity of the ligand and are particularly relevant in view of the potential utility of **8**–**11** in homogeneous catalysis. Moreover, the environments around the platinum(II) in **2**, **3**, **8** and **9** are similar to those of [Pt{[(η^5-C_5H_3)CH_2NMe_2]Fe(η^5-C_5H_5)}Cl(dmso)] or [Pt{$FcCH_2NMe_2$}Cl_2(dmso)],[19] which exhibit antitumoral activity, and consequently they are also interesting from this point of view.

Finally, preliminary results reveal that the procedures described here can also be extended to other imino-alcohols derived from **1** by the replacement of the ferrocenyl group by a phenyl {i.e. (S_C)-C_6H_5CH=NCH(R^1)CH_2OH with R^1 = Me or $CHMe_2$}. Thus, these studies constitute an initial step toward further research focused on the synthesis and the study of the properties and potential applications of a wide variety of novel enantio- or diastereomerically pure platinum complexes.

Experimental Section

Materials: *cis*-[$PtCl_2$(dmso)$_2$] was prepared as described.[45] Ferrocenecarboxaldehyde, (S_C)-(+)-$H_2NCH(R^1)CH_2OH$ {R^1 = Me or $CHMe_2$} and the remaining reagents were obtained from Aldrich and used as received. The methanol was HPLC grade,[46] and the remaining solvents used, except benzene, were dried and distilled before use.[47]

Instrumentation: Elemental analyses were carried out at the Serveis Cientifico-Tècnics (University of Barcelona) and Servei de Recursos Cientifics i Tècnics (University Rovira i Virgili, Tarragona). Infrared spectra were obtained with a Nicolet Impact 400 instrument using KBr discs. Proton and the two-dimensional NMR [{^1H-^1H}-(COSY) and (NOESY) and the {^1H-^{13}C}-(HSQC) and (HMBC)] experiments were run at 500 MHz with either Varian 500 or Bruker Avance 500DMX instruments. Except where quoted, the solvent used for the ^1H NMR experiments was $CDCl_3$ (99.9%) and $SiMe_4$ was the internal reference. $^{195}Pt\{^1H\}$ NMR spectra as well as $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker-250DXR instrument using $CDCl_3$ (99.9%) as solvent and referenced to $H_2[PtCl_6]$ [$\delta^{195}Pt\{H_2[PtCl_6]\}$ = 0.0 ppm] and $P(OMe)_3$ [$\delta^{31}P\{P(OMe)_3\}$ = 140.17 ppm], respectively. In all cases the chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz.

Table 2. Crystal data and details of the refinement of the crystal structures of **1b**·H_2O, **3b**, **7b**·CH_2Cl_2·1/2H_2O and **9a**.

	1b·H_2O	**3b**	**7b**·CH_2Cl_2·1/2H_2O	**9a**
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)	$P2_12_12_1$ (no.19)
a [Å]	10.749(6)	10.157(4)	10.368(3)	9.893(5)
b [Å]	6.048(8)	14.356(5)	9.259(3)	16.054(9)
c [Å]	12.411(9)	15.448(6)	14.587(3)	23.633(5)
β [°]	99.80(6)	90.0	101.74(3)	90.0
Z	2	4	2	8
T [K]	293(2)	294(2)	294(2)	293(2)
No. reflections collected	2514	6528	2563	4780
No. reflections observed	855	4520	1999	1918
R indices [$I > 2\sigma(I)$]	R_1 = 0.0426, wR_2 = 0.0902	R_1 = 0.0644, wR_2 = 0.1679	R_1 = 0.0665, wR_2 = 0.1829	R_1 = 0.0480, wR_2 = 0.0665
R indices (all data)	R_1 = 0.2394, wR_2 = 0.1393	R_1 = 0.1036, wR_2 = 0.1959	R_1 = 0.1030, wR_2 = 0.2044	R_1 = 0.2410, wR_2 = 0.0993
Max. and min. diff. density [e A^{-3}]	0.42 and –0.99	4.69 and –3.41	1.79 and –1.61	0.19 and –0.11
Flack coefficient[a]	0.10(6)	–0.008(19)	0.00(3)	–0.004(18)

[a] Data from ref.[51]

The optical rotations were determined in CH_2Cl_2 at 293 K using a Perkin–Elmer 241 MC polarimeter and the concentration used is specified in the characterisation section of each compound. Mass spectra (FAB^+) were obtained with a VG-Quattro Fisions instrument using 3-nitrobenzylalcohol (NBA) as matrix.

Crystallography: A prismatic crystal of **1b**·H_2O (orange, 0.2×0.1×0.1 mm), **3b** (orange, 0.59×0.16×0.14 mm), **7b**·CH_2Cl_2·1/2H_2O (red, 0.53×0.12×0.12 mm) or **9a** (purple, 0.2×0.1×0.1 mm) was selected and mounted on an Enraf–Nonius CAD4 diffractometer. Unit-cell parameters (Table 2) were determined from automatic centring of 25 reflections {in the ranges: 12° $< \Theta <$ 21° (for **1b**·H_2O and **9a**), 8.3° $< \Theta <$ 15.4°(for **3b**) and 8.73° $< \Theta <$ 17.9° (for **7b**·CH_2Cl_2·1/2H_2O)} and refined by the full-matrix least-squares method. For **3b**, **7b**·CH_2Cl_2·1/2H_2O and **9a** Lorentz polarisation corrections and absorption corrections were made.

The structures were solved by direct methods using the SHELXS computer program[48] and refined by the full-matrix least-squares method with the SHELX97 or SHELX93 computer programs.[49] The function minimised was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0434P)^2]^{-1}$ (for **1b**·H_2O), $[\sigma^2(I) + (0.1070P)^2 + 9.0330P]^{-1}$ (for **3b**), $[\sigma^2(I) + (0.1467P)^2]^{-1}$ (for **7b**·CH_2Cl_2·1/2H_2O) and $[\sigma^2(I) + (0.0132P)^2]^{-1}$ (for **9a**) and $P = (|F_o|^2 + 2|F_c|^2)/3$; scattering factors were taken from the literature.[50] The chirality of the structures was determined by the Flack coefficient.[51]

CCDC-299520 to -2999523 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 also the footnote on the first page of this article): Experimental procedures for the preparation of all the compounds and their characterisation data; graphical plot of the relative abundance of the species present on solution when **2b** was treated with NaOD (Figure S1).

Acknowledgments

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[1] a) J. Dupont, C. S. Consorti, J. Spencer, *Chem. Rev.* **2005**, *105*, 2527–2572; b) V. I. Sokolov, *Chirality and Optical Activity in Organometallic Compounds*, Gordon and Breach, London, UK, **1990**; c) E. Wong, C. M. Giandomenico, *Chem. Rev.* **1999**, *99*, 2451–2466; d) T. W. Hambley, *Coord. Chem. Rev.* **1997**, *166*, 181–223; e) I. Omae, *Coord. Chem. Rev.* **2004**, *248*, 995–1023.

[2] For a general overview of the latest advances on chiral palladium(II) and platinum(II) compounds, see for instance: a) G. Du, A. Ellern, L. K. Woo, *Inorg. Chem.* **2003**, *42*, 873–877; b) L. Diez, P. Espinet, J. A. Miguel, M. B. Ros, *J. Mater. Chem.* **2002**, *12*, 3694–3695; c) H. Hamaskima, D. Hotta, M. Sodeaka, *J. Am. Chem. Soc.* **2002**, *124*, 11240–11241; d) A. Ikeda, H. Udzu, Z. Zhong, S. Shinkai, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* **2001**, *123*, 3872–3877; e) V. P. Munk, C. I. Diakos, B. A. Messerle, R. R. Fenton, T. W. Hambley, *Chem. Eur. J.* **2002**, *8*, 5486–5493; f) J. Bravo, C. Cativela, J. E. Chaves, R. Navarro, E. P. Urriolabeitia, *Inorg. Chem.* **2003**, *42*, 1006–1013.

[3] a) I. Omae, *Applications of Organometallic Compounds*, John Wiley, Chichester, UK, **1998**; b) P. W. Jolly, G. Wilke, W. A. Kermann, B. Cornils (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, Germany, **1996**.

[4] For the latest applications of these compounds in homogeneous catalysis, see for instance: a) S. F. Kirsch, L. E. Overman, M. P. Watson, *J. Org. Chem.* **2004**, *69*, 8101–8104; b) K. Ito, Y. Imahayashi, T. Kuroda, S. Eno, B. Saito, T. Katsuki, *Tetrahedron Lett.* **2004**, *45*, 7277–7281; c) D. Franco, M. Gómez, F. Jiménez, G. Muller, M. Rocamora, M. A. Maestro, J. Mahía, *Organometallics* **2004**, *23*, 3197–3209; d) T. J. Brunker, J. R. Moncarz, D. J. Glueck, L. N. Zakharov, J. A. Golen, A. L. Rheingold, *Organometallics* **2004**, *23*, 2228–2230; e) P. Dotta, P. G. A. Kumar, P. S. Pregosin, A. Albinati, S. Rizzato, *Organometallics* **2004**, *23*, 2295–2304.

[5] G. Uccello-Barretta, R. Bernardini, F. Balzano, P. Salvadori, *Chirality* **2002**, *14*, 484–489.

[6] a) S. B. Wild, *Coord. Chem. Rev.* **1997**, *166*, 291–311 and references cited therein; b) G. He, K. F. Mok, P. H. Leung, *Organometallics* **1999**, *18*, 4027–4031.

[7] a) C. Sacht, M. S. Datt, S. Otto, A. Roodt, *J. Chem. Soc., Dalton Trans.* **2000**, 727–733; b) T. W. Failes, M. D. Hall, T. W. Hambley, *Dalton Trans.* **2003**, *8*, 1596–1600.

[8] a) M. Albrecht, G. van Koten, *Angew. Chem. Int. Ed.* **2001**, *40*, 3750–3781; b) J. Dupont, M. Pfeffer, J. Spencer, *Eur. J. Inorg.*

Chem. **2001**, 1917–1927; c) R. B. Bedford, *Chem. Commun.* **2003**, 1787–1796.

[9] a) C. Anderson, M. Crespo, F. D. Rochon, *J. Organomet. Chem.* **2001**, *631*, 164–174; b) R. Wünch, G. Bosl, C. Robl, W. Weigand, *J. Organomet. Chem.* **2001**, *621*, 352–358; c) C. Cativela, L. R. Falvello, J. C. Ginés, R. Navarro, E. P. Urriolabeitia, *New J. Chem.* **2001**, *25*, 334–352.

[10] a) T. K. Hollis, L. E. Overman, *Tetrahedron Lett.* **1997**, *38*, 8837–8840; b) P. X. Liu, K. F. Mok, J. J. Vittal, P. H. Leung, *Organometallics* **2000**, *19*, 3722–3729.

[11] W. C. Yeo, J. J. Vittal, L. L. Koh, G. K. Tan, P. H. Leung, *Organometallics* **2004**, *23*, 3474–3482.

[12] 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.

[13] For recent reports concerning cyclopalladated complexes with (N) or [C(sp^2,ferrocene),N]$^-$ ligands, see for instance: C. López, R. Bosque, J. Arias, E. Evangelio, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2004**, *672*, 34–42 and references cited therein.

[14] For palladacycles with tridentate [C(sp^2,ferrocene),N,E]$^-$ (E = N′ or O) ligands: a) S. Pérez, C. López, A. Caubet, A. Pawełczyk, X. Solans, M. Font-Bardía, *Organometallics* **2003**, *22*, 2396–2408; b) C. López, A. Caubet, S. Pérez, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2002**, *651*, 105–113; c) C. J. Isaac, C. Price, B. R. Horrocks, A. Houlton, M. R. J. Elsegood, W. Clegg, *J. Organomet. Chem.* **2000**, *598*, 248–253.

[15] Latest contributions on palladium and platinum(II) complexes with a [C(sp^2,ferrocene),N,S]$^-$ ligand: a) S. Pérez, C. López, A. Caubet, R. Bosque, X. Solans, M. Font-Bardía, A. Roig, E. Molins, *Organometallics* **2004**, *23*, 224–236; b) C. López, S. Pérez, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2005**, *690*, 228–243.

[16] Y. Wu, J. Hou, H. Yun, C. Cui, R. Yuan, *J. Organomet. Chem.* **2001**, *637–639*, 793–795.

[17] a) M. Pfeffer, J. P. Sutter, A. de Cian, J. Fischer, *Organometallics* **1993**, *12*, 1167–1173; b) G. Zhao, Q. G. Wang, T. C. W. Mak, *J. Organomet. Chem.* **1999**, *574*, 311–317; c) M. Benito, C. López, X. Morvan, X. Solans, M. Font-Bardía, *J. Chem. Soc., Dalton Trans.* **2000**, 4470–4478; d) R. Bosque, M. Benito, C. López, *New J. Chem.* **2001**, *25*, 827–853; e) C. López, A. Caubet, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2000**, *598*, 87–102.

[18] P. R. R. Ranatunge-Bandarage, N. W. Duffy, S. M. Johnston, B. H. Robinson, J. Simpson, *Organometallics* **1994**, *13*, 511–521 and references cited therein.

[19] R. W. Wason, K. McGrouther, P. R. R. Ranatunge-Bandarage, B. H. Robinson, J. Simpson, *Appl. Organomet. Chem.* **1999**, *13*, 163–174.

[20] A. Togni, T. Hayashi, *Ferrocenes, Homogeneous Catalysis, Organic Synthesis and Materials Science*, VCH, Weinheim, Germany, **1995**.

[21] a) G. Zhao, Q. G. Wang, T. C. W. Mak, *Tetrahedron: Asymmetry* **1998**, *9*, 2253–2257; b) M. Benito, C. López, X. Solans, M. Font-Bardía, *Tetrahedron: Asymmetry* **1998**, *9*, 4219–4238; c) C. López, R. Bosque, D. Sainz, X. Solans, M. Font-Bardía, *Organometallics* **1997**, *16*, 3261–3266.

[22] Recent contributions in this field: a) A. Moyano, M. Rosol, R. M. Moreno, C. López, M. A. Maestro, *Angew. Chem. Int. Ed.* **2005**, *44*, 1865–1869; b) C. E. Anderson, Y. Donde, C. J. Douglas, L. E. Overman, *J. Org. Chem.* **2005**, *70*, 648–657.

[23] A. D. Ryabov, I. M. Panyashkina, V. A. Polyakov, J. A. K. Howard, L. G. Kuz′mina, M. S. Datt, C. Sacht, *Organometallics* **1998**, *17*, 3615–3618.

[24] a) A. D. Ryabov, G. M. Kazankov, I. M. Panyashkina, O. G. Grozovsky, O. G. Dyachenko, V. A. Polyakov, L. G. Kuz'mina, *J. Chem. Soc., Dalton Trans.* **1997**, 4385–4391; b) Y. J. Wu, L. Ding, H. X. Wang, Y. H. Liu, H. Z. Yuan, X. A. Mao, *J. Organomet. Chem.* **1997**, *535*, 49–58; c) S. Pérez, C. López, A. Caubet, X. Solans, M. Font-Bardía, *New J. Chem.* **2003**, *27*, 975–982.

[25] C. López, A. Caubet, S. Pérez, X. Solans, M. Font-Bardía, *Chem. Commun.* **2004**, 540–541.

[26] a) C. López, J. Sales, R. Zquiak, X. Solans, *J. Chem. Soc., Dalton Trans.* **1992**, 2321–2328; b) R. Bosque, C. López, J. Sales, X. Solans, M. Font-Bardía, *J. Chem. Soc., Dalton Trans.* **1994**, 735–745.

[27] Characterisation data are provided in the Supporting Information.

[28] C. López, R. Bosque, X. Solans, M. Font-Bardía, *New J. Chem.* **1996**, *20*, 1285–1292.

[29] T. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 380–388.

[30] a) J. Bravo, C. Cativela, R. Navarro, E. P. Urriolabeitia, *J. Organomet. Chem.* **2002**, *650*, 157–172; b) A. Caubet, C. López, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2003**, *669*, 164–171.

[31] Y. J. Wu, X. L. Cui, C. X. Du, W. L. Wang, R. Y. Guo, R. F. Chen, *J. Chem. Soc., Dalton Trans.* **1998**, 3727–3730.

[32] A. Caubet, C. López, R. Bosque, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **1999**, *577*, 292–304.

[33] 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*, 1536–1536.

[34] R. G. Miller, R. D. Stauffer, D. R. Fahey, D. R. Pernell, *J. Am. Chem. Soc.* **1970**, *92*, 1511–1521.

[35] a) M. Crespo, M. Font-Bardía, J. Granell, M. Martínez, X. Solans, *Dalton Trans.* **2003**, 3763–3769; b) M. Crespo, J. Granell, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2003**, *681*, 143–149.

[36] The variations of the composition of the solutions obtained from **2b** upon the addition of NaOD [in NaOD/**2b** molar ratios varying from 0.2 to 1.8] are presented in the Supporting Material (Figure S1).

[37] Shorter reaction periods produced a considerable decrease of the relative abundance of compounds **7**. In particular, after 27 h of reflux the molar ratios **2a/3a/5a/7a** and **2b/3b/5b/7b** were 0.38:0.18:1.00:0.43 and 0.30:0.23:1.00:0.39, respectively.

[38] a) I. Omae, *Coord. Chem. Rev.* **1976**, *18*, 327–352; b) A. D. Ryabov, *Chem. Rev.* **1990**, *90*, 403–424; c) V. V. Dunina, O. A. Zalevskaya, V. M. Potatov, *Russ. Chem. Rev.* **1988**, *57*, 250–260.

[39] a) R. Bosque, C. López, X. Solans, M. Font-Bardía, *Organometallics* **1999**, *18*, 1267–1274; b) Y. J. Wu, Y. H. Liu, L. Yang, Q. X. Zhu, *Polyhedron* **1997**, *16*, 335–339; c) L. Ding, D. P. Zou, Y. J. Wu, *Polyhedron* **1998**, *17*, 2511–2516.

[40] a) A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27–110; b) C. S. Stone, D. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233–350.

[41] C. López, A. Caubet, S. Pérez, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2003**, *681*, 82–90.

[42] For a general overview on molecular devices see for instance the special issue devoted to “Molecular Machines” published in *Acc. Chem. Res.* **2001**, *34*.

[43] X. Riera, A. Caubet, C. López, V. Moreno, X. Solans, M. Font-Bardía, *Organometallics* **2000**, *19*, 1384–1390.

[44] J. Vicente, J. A. Abad, E. Martínez-Viviente, P. G. Jones, *Organometallics* **2002**, *21*, 4454–4467 and references cited therein.

[45] J. H. Price, A. N. Williamson, F. R. Schram, B. Wayland, *Inorg. Chem.* **1972**, *11*, 1280–1286.

[46] The success of the preparations of compounds **2**–**11a,b** is strongly dependent on the quality of the methanol used. The presence of small amounts of water induces the formation of large amounts of FcCHO and reduces the yields. Thus, the use of MeOH (HPLC grade) is strongly required.

[47] D. D. Perrin, W. L. F. Amarego, *Purification of Laboratory Chemicals*, 4th ed., Butterworth-Heinemann, Oxford, UK, **1996**.

[48] G. M. Sheldrick, *SHELXS. A computer program for determination of crystal structures*, University of Göttingen, Germany, **1997**.

[49] a) G. M. Sheldrick, *SHELX93. A computer program for determination of crystal structures*, University of Göttingen, Germany, **1994**; b) *SHELX97. A computer program for determination of crystal structures*, University of Göttingen, Germany, **1997**.

[50] *International Table of X-ray Crystallography*, The Kynoch Press, Birmingham, UK, **1974**, vol. IV, pp. 99–100 and 149.

[51] H. D. Flack, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *39*, 876–888.

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