

Synthesis, characterization and structure of ferrocenylketimine complexes of platinum(II)

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Abstract

The reactions of ferrocenylketimines $[(\eta^5\text{-C}_5\text{H}_4\text{CMe=NAr})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ (Ar = a variety of substituted phenyls) with *cis*-Pt(DMSO)₂Cl₂ in refluxing toluene have led to the formation of both the five-membered cycloplatinated derivatives $[\sigma\text{-Pt}\{(\eta^5\text{-C}_5\text{H}_3\text{CMe=NAr})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{DMSO})\text{Cl}]$ in the presence of sodium acetate and the coordinated compounds $[\textit{trans}\text{-PtCl}_2(\text{DMSO})\{(\eta^5\text{-C}_5\text{H}_4\text{CMe=NAr})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}]$ in the absence of sodium acetate. The compounds have been characterized by elemental analysis, IR, ¹H NMR and two-dimensional NOESY spectra. The X-ray crystal structures of $[\sigma\text{-Pt}\{(\eta^5\text{-C}_5\text{H}_3\text{CMe=NPh})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{DMSO})\text{Cl}]$ and $[\textit{trans}\text{-PtCl}_2(\text{DMSO})\{(\eta^5\text{-C}_5\text{H}_4\text{CMe=NPh})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}]$ have been determined. © 1997 Elsevier Science S.A.

Keywords: Ferrocene; Platinum; Cyclometallation; Crystal structure

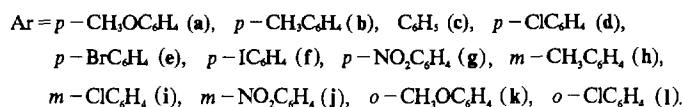
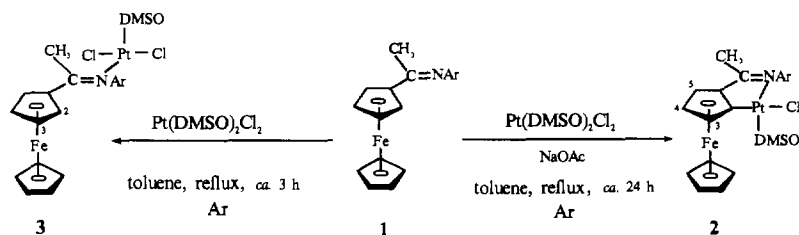
1. Introduction

The activation of C–H bond by using transition metal is a quite interesting area in organometallic chemistry. There have already appeared a lot of reports on intramolecular cyclometallation of palladium and platinum complexes [1]. Such an activation approach has been used successfully in organic synthesis [2]. Although cyclopalladated compounds have already been studied rather thoroughly, there are now only a few classical examples of cycloplatinated complexes with nitrogen donor ligands [3–5]. As for direct cycloplatinat-

ion or cyclopalladation, it has been assumed that there is an initial coordination of the metal with the donor atom, which is to be followed by ring closure with the aliphatic or aromatic carbon atom and a loss of H⁺. However, there have been few examples in relation to isolation of the stable intermediate before ring closure [4,5].

This paper is intended as a report on the synthesis of the cycloplatinated compounds $[\sigma\text{-Pt}\{(\eta^5\text{-C}_5\text{H}_3\text{CMe=NAr})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\text{DMSO})\text{Cl}]$ **2** and of the coordinated compounds $[\textit{trans}\text{-PtCl}_2(\text{DMSO})\{(\eta^5\text{-C}_5\text{H}_4\text{CMe=NAr})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}]$ **3** through a reaction involving ferrocenylketimines **1** and *cis*-Pt(DMSO)₂Cl₂ under the conditions indicated below and on characterization of these compounds.

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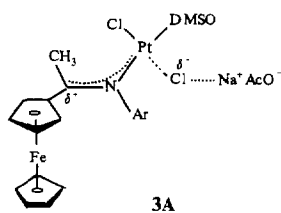
2. Results and discussion

2.1. Cycloplatination reaction

Recently we have reported on a convenient method for the preparation of cyclopalladated ferrocenylketimines by using Li₂PdCl₄ [6]. However, it has been proved to be unsuccessful in preparing cycloplatinated ferrocenylketimines by the reaction of ferrocenylketimines **1** with K₂PtCl₄ under the same condition. On the other hand, *cis*-Pt(DMSO)₂Cl₂ underwent a facile cyclometallation with **1** to give the corresponding cycloplatinated ferrocenylketimines **2**.

In the presence of NaOAc, a reaction of **1** with *cis*-Pt(DMSO)₂Cl₂ yielded cycloplatinated ferrocenylketimines **2** in refluxing toluene for about 24 h. Some experiments have indicated that a mixture of **2** and **3** was obtained simultaneously when the reaction time was shortened to 6.5–7 h, and they were separated by column chromatography because compounds **3** exhibit higher *R_f* values than those of compounds **2**. In the absence of NaOAc, a reaction of **1** with *cis*-Pt(DMSO)₂Cl₂ yielded only trans complexes **3**. Some experiments have indicated that the trans complexes **3** can be converted into the corresponding cycloplatinated products **2** when they are refluxed with NaOAc in toluene.

It is obvious that complexes **3** should be converted into the final products **2** in the presence of NaOAc. A possible mechanism for the conversion from **3** to **2** may involve a formation of transition state (**3A**). With charge transfer from the C=N double bond to the N–Pt bond, the rotation of the N moiety around the C–N bond axis could occur and result in the formation of the final products **2**.



All the new compounds are air-stable crystals and are characterized by elemental analysis, IR and ¹H NMR spectra.

2.2. Spectral properties of **2** and **3**

The IR spectra of **2** and **3** display absorption bands at 1000 and 1100 cm⁻¹ which are indicative of an unsubstituted cyclopentadienyl ring [7]. The C=N absorption of **2** and **3** has been shifted to lower values in comparison with the corresponding frequencies of **1**, indicating that nitrogen has been coordinated with platinum through its lone pair. The C=N absorption of **3** is about 30 cm⁻¹ higher than that of the corresponding compounds **2**.

With metal–dialkyl sulfoxide complexes, the shift of the S=O stretching frequency of DMSO to lower values when bonded to oxygen and to higher values when bonded to sulfur is well established [8]. The ν_{S=O} values of **2** and **3**, which are all in the range 1124–1145 cm⁻¹, are consistent with an S-bonded DMSO configuration.

The ¹H NMR spectra of compounds **2** are completely consistent with a 1,2-disubstituted structure for the compounds. In addition, it has been found in their ¹H NMR spectra that half of the CH₂Cl₂ per molecule is contained in compound **2j**. For example, the ¹H NMR spectrum of **2a** exhibited the expected AMX system of multiplets for the three different protons on the substituted Cp ring with one triplet at δ 4.64 integrating for the proton 4, and two doublets at δ 4.55 and δ 5.27 for protons 3 and 5 respectively. The singlet at δ 4.31 is for the five protons of the unsubstituted Cp ring, a singlet at δ 2.08 for protons of the C-methyl, a singlet at δ 3.85 for the protons of the methoxyl group. Two doublets at δ 6.89 and δ 6.94 which exhibited the typical AB system are for the two protons on the N-phenyl ring, a broad singlet at δ 6.98 for the other two protons which may have the same chemical shift. The appearance of ¹⁹⁵Pt–H satellites on the SME resonances of **2a**, **2c**, **2j** and **2k** is consistent with S-bonded DMSO.

It is noteworthy that the ¹H NMR spectra of compound **2** indicated that the free rotation of the N-phenyl

ring was blocked. For example, there are four doublets for the four protons on the N-phenyl ring bearing para-substituent, and the spectra of **2h–2l** which have meta- or ortho-substituent on the N-phenyl ring indicated that each compound existed as a mixture of two isomers (Fig. 1). This may be attributed to the steric hindrance between ortho-hydrogen or ortho-substituent and chlorine bonded to platinum. However, it is difficult to define exactly the structure of these isomers, because all attempts to separate them were unsuccessful.

The ^1H NMR spectra of compound **3** are consistent with the monosubstituted structure for the complexes with 2D-NOESY (Fig. 2) being measured for **3c**. It has been confirmed that the upfield broad singlet at δ 3.78

corresponds to protons 2, owing to the appearance of the negative cross-peak representing the nuclear Overhauser effect (NOE) between protons 2 and the protons of the C-methyl at δ 3.28. Accordingly the downfield broad singlet at δ 4.35 represents the resonance of protons 3, because of the appearance of the NOE cross-peak between protons 3 and protons 2. In comparison with the starting materials **1** [9], the signals for protons 2 in compounds **3** are shifted to higher fields. This phenomenon must have been caused by the shielding of the N-phenyl ring, because there is an NOE cross-peak between protons 2 and protons of N-phenyl at δ 7.31; and it can be observed from the crystal structure of **3c** that the position of proton 2 is above the N-phenyl ring.

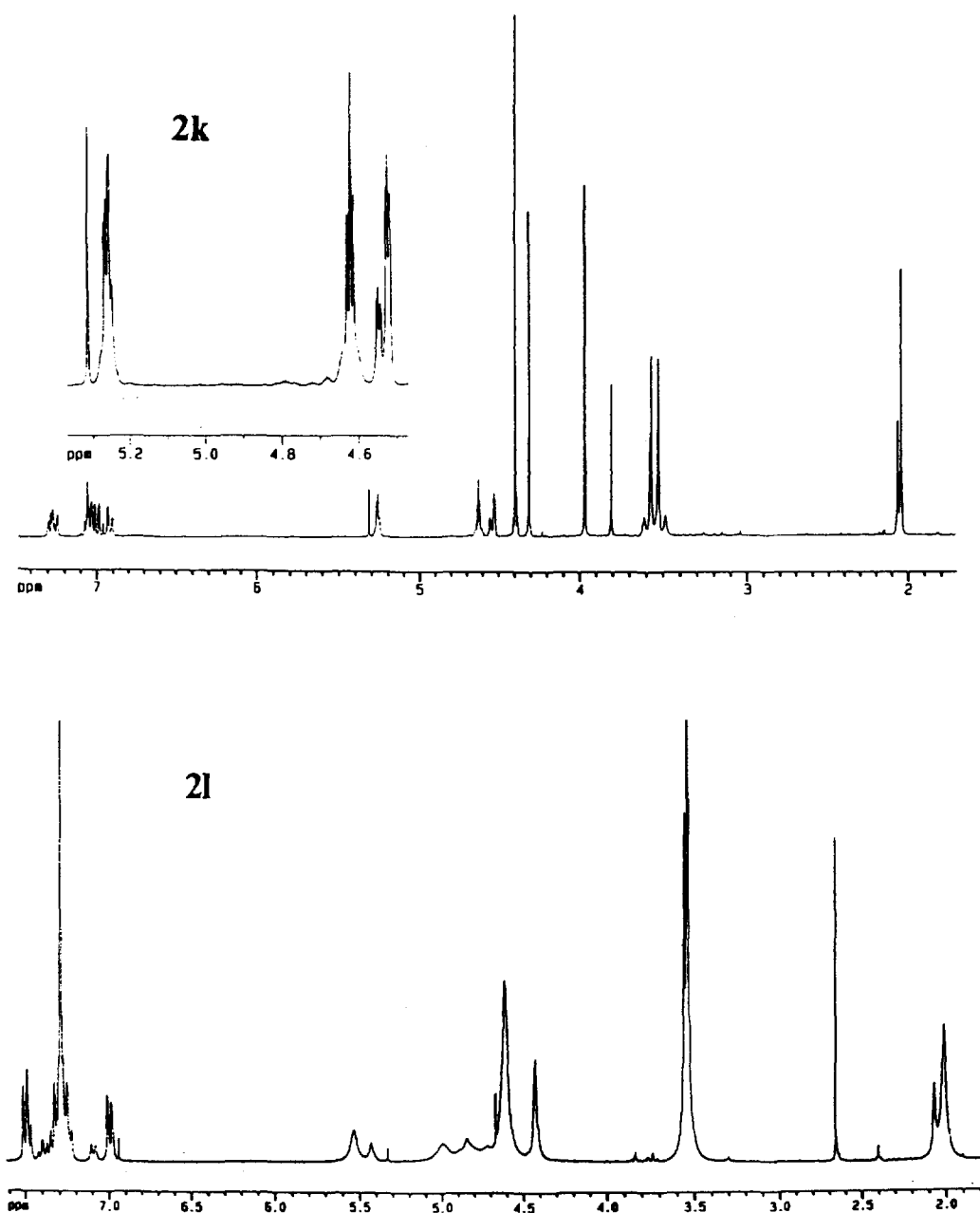


Fig. 1. ^1H NMR spectra of **2k** and **2l**.

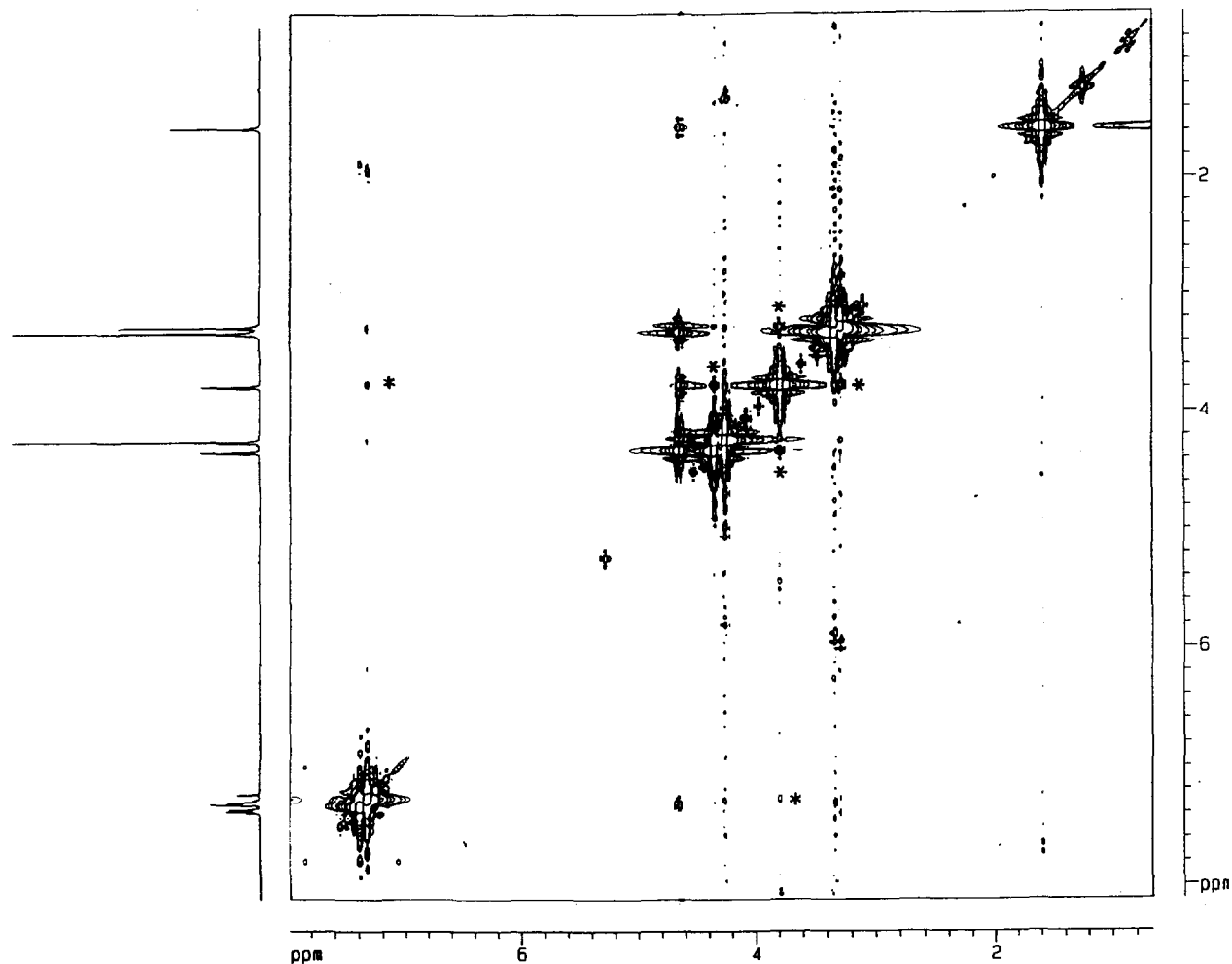


Fig. 2. 2D-NOESY spectra of **3c** (* indicates NOE peaks).

The singlet at δ 4.25 is for the five protons of the unsubstituted Cp ring, whereas a singlet at δ 3.33 is for the six protons of two methyl groups of DMSO. The downfield shift of the resonance of protons on C-methyl might be attributed to the influence of the deshielding effect of the substituted Cp ring. This can be supported by the X-ray structure in Fig. 3.

The ^1H NMR spectra of **3k** and **3l** indicated that both compounds exist as a mixture of several isomers; but all the attempts to separate them by column chromatography and fractional recrystallization have been unsuccessful. Therefore, it is difficult to assign the ^1H NMR spectrum of each isomer and define the structures. So no definite report can be given here except for their elemental analysis data and IR spectra.

2.3. X-ray crystal structures of compounds **2c** and **3c**

The structure of **3c** is shown in Fig. 3; atomic coordinates are listed in Table 1, and selected bond lengths and angles are in Table 2. The coordination sphere of platinum is square planar with two mutually trans chloride ions, an S-bound DMSO, and the N-bound

ferrocenylimine ligand. Deviations of Pt, Cl(1), Cl(2), S, N from the mean plane are -0.0007 , 0.0649 , 0.0436 , -0.0052 , -0.1010 . The angles between adjacent atoms in the coordination sphere of platinum lie in the range

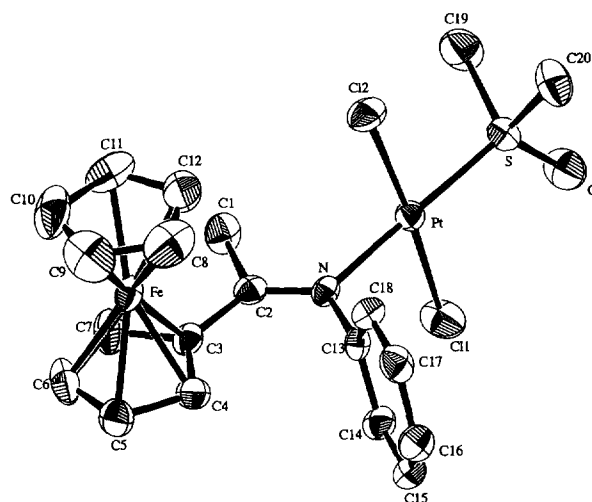


Fig. 3. Molecular structure of **3c**.

Table 1
Atomic coordinates and equivalent isotropic thermal parameters for **3c**

Atom	x	y	z	B_{eq}
Pt	0.20172(2)	-0.18740(1)	0.18820(2)	2.054(5)
Fe	0.56851(10)	-0.31525(6)	-0.1591(1)	2.44(2)
Cl(1)	0.1035(2)	-0.3203(1)	0.2368(2)	4.02(4)
Cl(2)	0.3176(2)	-0.0604(1)	0.1402(2)	3.34(3)
S	0.1165(2)	-0.07841(10)	0.3421(2)	2.59(3)
O	0.0069(6)	-0.1155(3)	0.3948(6)	3.9(1)
N	0.2716(5)	-0.2858(3)	0.0348(5)	1.92(9)
C(1)	0.5376(8)	-0.2707(4)	0.2486(7)	3.2(1)
C(2)	0.4141(7)	-0.3110(3)	0.0724(7)	2.2(1)
C(3)	0.4685(7)	-0.3750(4)	-0.0420(7)	2.3(1)
C(4)	0.3846(7)	-0.4169(4)	-0.2205(7)	2.8(1)
C(5)	0.4982(9)	-0.4642(4)	-0.2695(9)	3.6(2)
C(6)	0.6449(8)	-0.4519(5)	-0.1322(10)	3.7(2)
C(7)	0.6300(8)	-0.3967(4)	0.0100(8)	3.2(1)
C(8)	0.485(1)	-0.2168(6)	-0.298(1)	5.4(2)
C(9)	0.619(1)	-0.2541(6)	-0.313(1)	5.3(2)
C(10)	0.7482(10)	-0.2305(6)	-0.154(1)	5.2(2)
C(11)	0.697(1)	-0.1793(5)	-0.043(1)	5.0(2)
C(12)	0.5318(10)	-0.1696(5)	-0.132(1)	4.7(2)
C(13)	0.1446(6)	-0.3200(4)	-0.1309(6)	2.0(1)
C(14)	0.0518(7)	-0.4105(4)	-0.1791(7)	2.5(1)
C(15)	-0.0673(7)	-0.4421(4)	-0.3407(8)	2.9(1)
C(16)	-0.0950(7)	-0.3848(4)	-0.4523(7)	2.9(1)
C(17)	-0.0065(7)	-0.2949(4)	-0.4035(7)	2.9(1)
C(18)	0.1115(7)	-0.2612(4)	-0.2420(7)	2.5(1)
C(19)	0.2831(9)	-0.0074(5)	0.5198(9)	4.6(2)
C(20)	0.0303(9)	-0.0164(5)	0.2453(9)	3.8(2)

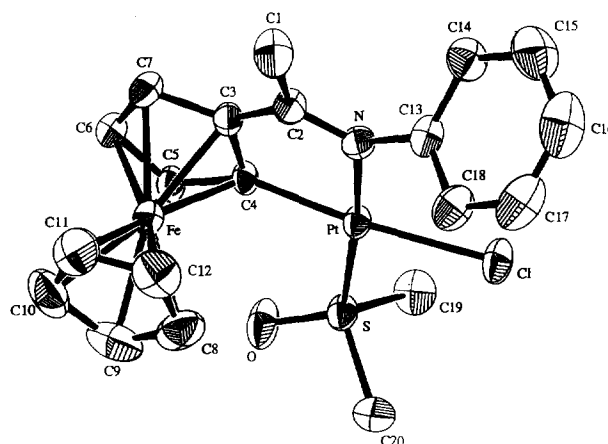


Fig. 4. Molecular structure of **2c**.

88.2–92.9°. The angles Cl(1)–Pt–Cl(2), and N–Pt–S are 175.45° and 176.9° respectively. The extent of these deviations is slightly less than those found for [*trans*-PtCl₂(DMSO){(η^5 -C₅H₄CH₂NMe₂)Fe(η^5 -C₅H₅)}] [4].

Table 2
Selected bond lengths (Å) and bond angles (deg) for **3c**

Bond lengths					
Pt–Cl(1)	2.297(2)	Fe–C(7)	2.023(6)	S–C(20)	1.762(7)
Pt–Cl(2)	2.312(1)	Fe–C(8)	2.017(7)	N–C(2)	1.293(7)
Pt–S	2.218(2)	Fe–C(9)	2.028(7)	N–C(13)	1.438(7)
Pt–N	2.049(4)	Fe–C(10)	2.046(7)	C(1)–C(2)	1.498(8)
Fe–C(3)	2.016(5)	Fe–C(11)	2.039(7)	C(2)–C(3)	1.480(8)
Fe–C(4)	2.033(6)	Fe–C(12)	2.033(7)	C(3)–C(4)	1.450(8)
Fe–C(5)	2.059(6)	S–O	1.458(4)	C(3)–C(7)	1.429(9)
Fe–C(6)	2.061(6)	S–C(19)	1.774(7)	C(13)–C(14)	1.404(7)
Bond angles					
Cl(1)–Pt–Cl(2)	175.45(6)	Pt–N–C(2)		126.2(4)	
Cl(1)–Pt–S	92.90(6)	Pt–N–C(13)		112.0(3)	
Cl(1)–Pt–N	88.3(1)	C(2)–N–C(13)		121.6(4)	
Cl(2)–Pt–S	90.74(6)	N–C(2)–C(1)		117.1(5)	
Cl(2)–Pt–N	88.2(1)	N–C(2)–C(3)		126.5(5)	
S–Pt–N	176.9(1)	C(1)–C(2)–C(3)		116.4(5)	
Pt–S–O	118.0(2)	C(2)–C(3)–C(4)		130.0(5)	
Pt–S–C(19)	109.1(3)	C(2)–C(3)–C(7)		122.5(5)	
Pt–S–C(20)	111.4(2)	C(4)–C(3)–C(7)		107.1(5)	
O–S–C(19)	109.2(4)	N–C(13)–C(14)		120.5(5)	
O–S–C(20)	107.8(3)	N–C(13)–C(18)		119.3(4)	
C(19)–S–C(20)	99.6(4)	C(14)–C(13)–C(18)		120.1(5)	

Pt–Cl, Pt–N and Pt–S bond lengths are well within the range of values obtained in similar complexes of platinum [10]. The Pt–N bond (2.049(4) Å) is less than the ferrocenylamine complexes of platinum [4]. The N-phenyl ring is almost perpendicular to the substituted Cp ring, interangles being 90.94° and 91.75° for the substituted and unsubstituted Cp rings, which account for the shielding effect of the N-phenyl ring in the ¹H NMR study. The angle between the coordination plane and unsubstituted Cp ring is 96.50°.

The structure of **2c** is shown in Fig. 4; atomic coordinates are listed in Table 3, and selected bond lengths and angles are in Table 4. The platinum atom has the square-planar coordination with a tetrahedral distortion. The following displacements are observed from the least-squares plane of the coordination sphere for **2c**: Pt, 0.0000; Cl, -0.0086; N, 0.1766; S, 0.0117; C(4), -0.1035. The angles between adjacent atoms in the coordination sphere of platinum lie in the range 80.2–95.8°, and the angles 173.3° for N–Pt–S, 174.1° for C(4)–Pt–Cl, which show larger distortion than in **3c** because of the formation of a σ -Pt–C bond ortho to the imine functionality on the cyclopentadienyl ring. The metallocycles are approximately planar; the largest deviation from the mean plane determined by the five atoms is at most 0.0441 Å for C(2). The angle between the plane N–Pt–C(4) of the metallocycle and the plane of Cl–Pt–S is 6.88°. The decrease of the angle Pt–C(4)–C(3) and of the angle C(4)–C(3)–C(2) from the normal value (126°) to 112.3° and 116.7° respectively, is mainly due to the strong interaction between the platinum and the nitrogen. The substituted Cp ring is approximately coplanar with the plane of C=N bond by a dihedral angle of 173.04°, indicating the better conjugation between the Cp ring and the C=N bond. The Pt–Cl length (2.389(1) Å) is larger than those in **3c** (Pt–Cl(1), 2.297(2) Å; Pt–Cl(2), 2.312(1) Å). This attests to the significant trans influence of the σ -Pt–C functionality.

Table 3
Atomic coordinates and equivalent isotropic thermal parameters for **2c**

Atom	x	y	z	B_{eq}
Pt	0.21282(2)	0.09763(1)	-0.23184(1)	2.006(5)
Fe	0.52242(7)	-0.03811(5)	-0.17793(5)	2.51(2)
Cl	0.0021(1)	0.1217(1)	-0.30793(9)	3.15(3)
S	0.0992(1)	0.0592(1)	-0.11948(9)	2.44(3)
O	0.1723(4)	0.0307(4)	-0.0409(3)	4.1(1)
N	0.3345(4)	0.1185(3)	-0.3363(3)	2.6(1)
C(1)	0.5712(6)	0.1126(5)	-0.3862(4)	4.0(2)
C(2)	0.4640(5)	0.1113(4)	-0.3212(4)	2.4(1)
C(3)	0.5035(5)	0.1020(4)	-0.2350(4)	2.3(1)
C(4)	0.3952(5)	0.0890(3)	-0.1761(3)	2.1(1)
C(5)	0.4610(5)	0.0728(4)	-0.0961(4)	2.4(1)
C(6)	0.6053(5)	0.0768(4)	-0.1049(4)	2.9(1)
C(7)	0.6322(6)	0.0942(4)	-0.1906(4)	3.1(1)
C(8)	0.4052(7)	-0.1602(5)	-0.2149(6)	4.8(2)
C(9)	0.4528(8)	-0.1732(5)	-0.1310(5)	5.0(2)
C(10)	0.5954(8)	-0.1752(5)	-0.1308(5)	4.8(2)
C(11)	0.6344(7)	-0.1614(5)	-0.2152(5)	4.5(2)
C(12)	0.5188(8)	-0.1521(5)	-0.2669(5)	4.5(2)
C(13)	0.2803(5)	0.1272(4)	-0.4210(3)	2.6(1)
C(14)	0.3019(6)	0.2146(5)	-0.4671(4)	3.5(1)
C(15)	0.2479(8)	0.2241(6)	-0.5483(5)	5.1(2)
C(16)	0.1703(8)	0.1453(7)	-0.5819(4)	5.4(2)
C(17)	0.1506(7)	0.0551(6)	-0.5373(5)	4.7(2)
C(18)	0.2051(6)	0.0459(5)	-0.4562(4)	3.8(1)
C(19)	-0.0178(6)	0.1591(5)	-0.0933(4)	3.6(1)
C(20)	-0.0140(6)	-0.0445(4)	-0.1448(4)	3.7(1)

The geometry of the ferrocenyl fragments in both **2c** and **3c** is very similar to that which is observed in ferrocene itself.

Table 4
Selected bond lengths (Å) and bond angles (deg) for **2c**

Bond lengths					
Pt–Cl	2.389(1)	Fe–C(7)	2.037(5)	S–C(20)	1.782(6)
Pt–S	2.195(1)	Fe–C(8)	2.033(6)	N–C(2)	1.294(7)
Pt–N	2.095(5)	Fe–C(9)	2.029(6)	N–C(13)	1.438(7)
Pt–C(4)	1.980(5)	Fe–C(10)	2.047(6)	C(1)–C(2)	1.500(8)
Fe–C(3)	2.033(5)	Fe–C(11)	2.037(6)	C(2)–C(3)	1.418(8)
Fe–C(4)	2.068(5)	Fe–C(12)	2.043(6)	C(3)–C(4)	1.451(8)
Fe–C(5)	2.042(5)	S–O	1.469(4)	C(3)–C(7)	1.434(8)
Fe–C(6)	2.041(6)	S–C(19)	1.789(6)	C(13)–C(14)	1.368(8)
Bond angles					
Cl–Pt–S	89.16(5)	Pt–N–C(2)	115.4(4)		
Cl–Pt–N	95.2(1)	Pt–N–C(13)	123.2(3)		
Cl–Pt–C(4)	174.1(1)	C(2)–N–C(13)	121.0(5)		
S–Pt–N	173.3(1)	N–C(2)–C(1)	125.6(5)		
S–Pt–C(4)	95.8(2)	N–C(2)–C(3)	115.1(5)		
N–Pt–C(4)	80.2(2)	C(1)–C(2)–C(3)	119.3(5)		
Pt–S–O	120.0(2)	C(2)–C(3)–C(4)	116.7(5)		
Pt–S–C(19)	112.0(2)	C(2)–C(3)–C(7)	133.9(5)		
Pt–S–C(20)	108.5(2)	C(4)–C(3)–C(7)	109.2(5)		
O–S–C(19)	106.6(3)	N–C(13)–C(14)	120.5(5)		
O–S–C(20)	106.8(3)	N–C(13)–C(18)	119.6(5)		
C(19)–S–C(20)	101.1(3)	C(14)–C(13)–C(18)	119.9(6)		
Pt–C(4)–Fe	125.4(2)	Pt–C(4)–C(5)	142.0(4)		
Pt–C(4)–C(3)	112.3(4)	C(3)–C(4)–C(5)	105.7(5)		

3. Experimental details

3.1. Materials and instruments

Melting points were determined on a WC-1 microscopic apparatus and are uncorrected. Elemental analyses were determined with a Carlo Erba 1106 Elemental Analyzer. IR spectra were recorded on a Perkin–Elmer FT-IR 1730 spectrophotometer. ^1H NMR spectra were recorded on Bruker DRX 300 and DPX 400 spectrometers, using CDCl_3 as a solvent and TMS as an internal standard. The 2D-NOESY spectrum was recorded on a Bruker ARX 500 spectrometer in CDCl_3 at room temperature with a mixing time of 250 ms. Some of the platinum complexes were crystallized as solvates from methylene chloride, and their compositions were determined by elemental analyses and calibrated on the basis of ^1H NMR. Chromatographic work was carried out on a short column packed with dry silica gel under reduced pressure.

All solvents were dried according to the standard methods. The compound $\text{cis-Pt}(\text{DMSO})_2\text{Cl}_2$ and ferrocenylketimines were prepared according to the literature procedures [9,11].

3.2. Preparation of the compounds

3.2.1. General procedure for the synthesis of compounds **2**

A solution of NaOAc (0.5 mmol) in 1 ml of methanol was added to a solution of 0.25 mmol of $\text{cis-Pt}(\text{DMSO})_2\text{Cl}_2$ and an equimolecular amount of ferrocenylketimines **1** in 50 ml of toluene. The mixture was refluxed for about 24 h with stirring under Ar and followed by an evaporation of the solvent in vacuo. The product was separated by passing it through a short silica gel column with CH_2Cl_2 as eluent. After the evaporation of the solvent, the residue was recrystallized from CH_2Cl_2 – C_6H_{14} to give **2**. The compounds prepared by this procedure were characterized as follows.

3.2.1.1. $[\sigma\text{-Pt}\{\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NC}_6\text{H}_4\text{OMe-4}\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}$ (**2a**). Orange plates. Yield 66%. M.p. > 198 °C (dec.). Anal. Found: C, 39.07; H, 3.74; N, 2.27. $\text{C}_{21}\text{H}_{24}\text{ClFeNO}_2\text{PtS}$. Calc.: C, 39.35; H, 3.77; N, 2.19%. IR (KBr pellet): 1553, 1505, 1481, 1413, 1245, 1126, 1105, 1025, 859, 820 cm^{-1} . ^1H NMR: δ 2.08(s, 3H, CH_3), 3.53(t, 3H, SCH_3 , $J_{\text{Pt-H}} = 26$ Hz), 3.58(t, 3H, SCH_3 , $J_{\text{Pt-H}} = 23$ Hz), 3.85(s, 3H, OCH_3), 4.31(s, 5H, C_5H_5), 4.55(d, 1H, H-3, $J = 1.7$ Hz), 4.64(t, 1H, H-4, $J = 2.3$ Hz), 5.27(d, 1H, H-5, $J = 1.9$ Hz), 6.87(d, 1H, Ar-H, $J = 8.6$ Hz), 6.92(d, 1H, Ar-H, $J = 8.6$ Hz), 6.98(bs, 2H, Ar-H) ppm.

3.2.1.2. $[\sigma\text{-Pt}(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NC}_6\text{H}_4\text{Me-4})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}$ (**2b**). Red plates. Yield 62%. M.p. $> 215^\circ\text{C}$ (dec.). Anal. Found: C, 40.21; H, 3.83; N, 2.28. $\text{C}_{21}\text{H}_{24}\text{ClFeNOPtS}$. Calc.: C, 40.36, H, 3.87, N, 2.24%. IR (KBr pellet): 1557, 1510, 1486, 1410, 1126, 1105, 1025, 1003, 859, 816 cm^{-1} . $^1\text{H NMR}$: δ 2.05(s, 3H, CH_3), 2.40(s, 3H, Ar- CH_3), 3.53(bs, 3H, SCH_3), 3.56(bs, 3H, SCH_3), 4.38(s, 5H, C_5H_5), 4.62(bs, 1H, H-3), 4.75(bs, 1H, H-4), 5.35(bs, 1H, H-5), 6.84(d, 1H, Ar-H, $J = 7.8\text{ Hz}$), 6.91(d, 1H, Ar-H, $J = 7.8\text{ Hz}$), 7.20(d, 1H, Ar-H, $J = 8.1\text{ Hz}$), 7.25(d, 1H, Ar-H, $J = 8.1\text{ Hz}$) ppm.

3.2.1.3. $[\sigma\text{-Pt}(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NC}_6\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}$ (**2c**). Red rods. Yield 57%. M.p. $> 200^\circ\text{C}$ (dec.). Anal. Found: C, 39.29; H, 3.66; N, 2.34. $\text{C}_{20}\text{H}_{22}\text{ClFeNOPtS}$. Calc.: C, 39.32; H, 3.63; N, 2.29%. IR (KBr pellet): 1555, 1480, 1409, 1126, 1104, 1020, 1000, 814, 719, 694 cm^{-1} . $^1\text{H NMR}$: δ 2.08(s, 3H, CH_3), 3.53(t, 3H, SCH_3 , $J_{\text{Pt-H}} = 25\text{ Hz}$), 3.58(t, 3H, SCH_3 , $J_{\text{Pt-H}} = 23\text{ Hz}$), 4.33(s, 5H, C_5H_5), 4.57(bs, 1H, H-3), 4.66(bs, 1H, H-4), 5.29(d, 1H, H-5, $J = 2.1\text{ Hz}$), 6.95(d, 1H, Ar-H, $J = 7.9\text{ Hz}$), 7.06(d, 1H, Ar-H, $J = 7.9\text{ Hz}$), 7.29(m, 1H, Ar-H), 7.43(m, 2H, Ar-H) ppm.

3.2.1.4. $[\sigma\text{-Pt}(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NC}_6\text{H}_4\text{Cl-4})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}$ (**2d**). Orange rods. Yield 48%. M.p. $> 225^\circ\text{C}$ (dec.). Anal. Found: C, 36.96; H, 3.25; N, 2.41. $\text{C}_{20}\text{H}_{21}\text{Cl}_2\text{FeNOPtS}$. Calc.: C, 37.22; H, 3.28; N, 2.17%. IR (KBr pellet): 1548, 1477, 1411, 1129, 1106, 1024, 1011, 859, 820 cm^{-1} . $^1\text{H NMR}$: δ 2.05(s, 3H, CH_3), 3.53(s, 3H, SCH_3), 3.54(bs, 3H, SCH_3), 4.41(s, 5H, C_5H_5), 4.69(bs, 1H, H-3), 4.84(bs, 1H, H-4), 5.42(bs, 1H, H-5), 6.90(d, 1H, Ar-H, $J = 8.4\text{ Hz}$), 6.94(d, 1H, Ar-H, $J = 8.7\text{ Hz}$), 7.37(d, 1H, Ar-H, $J = 8.4\text{ Hz}$), 7.41(d, 1H, Ar-H, $J = 8.7\text{ Hz}$) ppm.

3.2.1.5. $[\sigma\text{-Pt}(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NC}_6\text{H}_4\text{Br-4})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}$ (**2e**). Yellow-brown rods. Yield 48%. M.p. $> 223^\circ\text{C}$ (dec.). Anal. Found: C, 34.65; H, 3.02; N, 2.10. $\text{C}_{20}\text{H}_{21}\text{BrClFeNOPtS}$. Calc.: C, 34.82; H, 3.07; N, 2.03%. IR (KBr pellet): 1548, 1475, 1411, 1129, 1106, 1024, 1008, 858, 820 cm^{-1} . $^1\text{H NMR}$: δ 2.06 (s, 3H, CH_3), 3.53(bs, 3H, SCH_3), 3.54(bs, 3H, SCH_3), 4.37(s, 5H, C_5H_5), 4.64(bs, 1H, H-3), 4.78(bs, 1H, H-4), 5.37(bs, 1H, H-5), 6.84(d, 1H, Ar-H, $J = 8.3\text{ Hz}$), 6.91(d, 1H, Ar-H, $J = 8.1\text{ Hz}$), 7.20(d, 1H, Ar-H, $J = 8.3\text{ Hz}$), 7.25(d, 1H, Ar-H, $J = 8.3\text{ Hz}$) ppm.

3.2.1.6. $[\sigma\text{-Pt}(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NC}_6\text{H}_4\text{I-4})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}$ (**2f**). Orange plates. Yield 45%. M.p. $> 185^\circ\text{C}$ (dec.). Anal. Found: C, 33.08; H, 2.90; N, 2.15. $\text{C}_{20}\text{H}_{21}\text{ClFeINOtS}$. Calc.: C, 32.60; H, 2.87; N, 1.90%. IR (KBr pellet): 1547, 1474, 1412, 1129, 1106,

1024, 1006, 858, 818 cm^{-1} . $^1\text{H NMR}$: δ 2.06(s, 3H, CH_3), 3.53(s, 3H, SCH_3), 3.54(s, 3H, SCH_3), 4.36(s, 5H, C_5H_5), 4.62(bs, 1H, H-3), 4.75 (bs, 1H, H-4), 5.38(bs, 1H, H-5), 6.72(d, 1H, Ar-H, $J = 8.2\text{ Hz}$), 6.79(d, 1H, Ar-H, $J = 8.2\text{ Hz}$), 7.72(d, 1H, Ar-H, $J = 8.4\text{ Hz}$), 7.77(d, 1H, Ar-H, $J = 8.2\text{ Hz}$) ppm.

3.2.1.7. $[\sigma\text{-Pt}(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NC}_6\text{H}_4\text{NO}_2\text{-4})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}$ (**2g**). Red rods. Yield 40%. M.p. $> 200^\circ\text{C}$ (dec.). Anal. Found: C, 36.35; H, 3.20; N, 4.26. $\text{C}_{20}\text{H}_{21}\text{ClFeN}_2\text{O}_3\text{PtS}$. Calc.: C, 36.62; H, 3.23; N, 4.27%. IR (KBr pellet): 1520, 1477, 1412, 1345, 1130, 1107, 1022, 859, 818 cm^{-1} . $^1\text{H NMR}$: δ 2.09(s, 3H, CH_3), 3.54(s, 3H, SCH_3), 3.57(s, 3H, SCH_3), 4.37(s, 5H, C_5H_5), 4.65(bs, 1H, H-3), 4.80(bs, 1H, H-4), 5.40(bs, 1H, H-5), 7.12(d, 1H, Ar-H, $J = 8.7\text{ Hz}$), 7.20(d, 1H, Ar-H, $J = 8.5\text{ Hz}$), 8.30(d, 1H, Ar-H, $J = 8.6\text{ Hz}$), 8.35(d, 1H, Ar-H, $J = 8.7\text{ Hz}$) ppm.

3.2.1.8. $[\sigma\text{-Pt}(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NC}_6\text{H}_4\text{Me-3})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}$ (**2h**). Red plates. Yield 60%. M.p. $181\text{--}183^\circ\text{C}$ (dec.). Anal. Found: C, 40.18; H, 3.89; N, 2.25. $\text{C}_{21}\text{H}_{24}\text{ClFeNOPtS}$. Calc.: C, 40.36, H, 3.87, N, 2.24%. IR (KBr pellet): 1551, 1479, 1410, 1127, 1104, 1020, 1002, 861, 814, 773, 691 cm^{-1} . $^1\text{H NMR}$: δ 2.06(bs, 3H, CH_3), 2.38, 2.45(s, 3H, Ph- CH_3), 3.54(bs, 3H, SCH_3), 3.56(bs, 3H, SCH_3), 4.39, 4.41(s, 5H, C_5H_5), 4.65(bs, 1H, H-3), 4.77(bs, 1H, H-4), 5.36(bs, 1H, H-5), 6.76(bs, 1H, Ar-H), 6.82(m, 1H, Ar-H), 7.09(d, 1H, Ar-H, $J = 7.6\text{ Hz}$), 7.26–7.38(m, 1H, Ar-H) ppm. The ratio of the two isomers is 1:1.

3.2.1.9. $[\sigma\text{-Pt}(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NC}_6\text{H}_4\text{Cl-3})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}$ (**2i**). Red rods. Yield 58%. M.p. $198\text{--}200^\circ\text{C}$ (dec.). Anal. Found: C, 37.08; H, 3.28; N, 2.33. $\text{C}_{20}\text{H}_{21}\text{Cl}_2\text{FeNOPtS}$. Calc.: C, 37.22; H, 3.28; N, 2.17%. IR (KBr pellet): 1546, 1490, 1418, 1130, 1105, 1019, 1002, 890, 815, 798, 695 cm^{-1} . $^1\text{H NMR}$: δ 2.07(bs, 3H, CH_3), 3.53, 3.54(s, 3H, SCH_3), 3.55, 3.56(s, 3H, SCH_3), 4.39, 4.41(s, 5H, C_5H_5), 4.68(bs, 1H, H-3), 4.81(bs, 1H, H-4), 5.40(bs, 1H, H-5), 6.86, 6.93(d, 1H, Ar-H, $J = 7.7\text{ Hz}$), 6.97, 7.01(s, 1H, Ar-H), 7.26–7.40(m, 2H, Ar-H) ppm. The ratio of the two isomers is 1:1.

3.2.1.10. $[\sigma\text{-Pt}(\eta^5\text{-C}_5\text{H}_3\text{CMe}=\text{NC}_6\text{H}_4\text{NO}_2\text{-3})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}$ (**2j**). Red needles. Yield 66%. M.p. $172\text{--}174^\circ\text{C}$. Anal. Found: C, 35.47; H, 3.16; N, 4.04. $\text{C}_{20}\text{H}_{21}\text{ClFeN}_2\text{O}_3\text{PtS} \cdot 0.5\text{CH}_2\text{Cl}_2$. Calc.: C, 35.26; H, 3.18; N, 4.01%. IR (KBr pellet): 1531, 1486, 1413, 1351, 1124, 1106, 1024, 835, 821, 765, 692 cm^{-1} . $^1\text{H NMR}$: δ 2.07(s, 3H, CH_3), 3.53(t, 3H, SCH_3 , $J_{\text{Pt-H}} = 24\text{ Hz}$), 3.57, 3.58(bs, 3H, SCH_3), 4.35, 4.38(s, 5H, C_5H_5), 4.63(bs, 1H, H-3), 4.76(bs, 1H, H-4), 5.31(s, 1H, $0.5\text{CH}_2\text{Cl}_2$), 5.37(bs, 1H, H-5), 7.31, 7.41(d, 1H,

Ar-H, $J = 7.5$ Hz), 7.57–7.69(m, 1H, Ar-H), 7.82, 7.88(s, 1H, Ar-H), 8.17(d, 1H, Ar-H, $J = 7.0$ Hz) ppm. The ratio of the two isomers is 1:1.

3.2.1.11. $[\sigma\text{-Pt}(\eta^5\text{-C}_5\text{H}_3\text{CMe} = \text{NC}_6\text{H}_4\text{OCH}_3\text{-}2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}]$ (**2k**). Orange plates. Yield 59%. M.p. $> 210^\circ\text{C}$ (dec.). Anal. Found: C, 39.80; H, 3.88; N, 2.17. $\text{C}_{21}\text{H}_{24}\text{ClFeNO}_2\text{PtS}$. Calc.: C, 39.35; H, 3.77; N, 2.19%. IR (KBr pellet): 1562, 1478, 1411, 1257, 1125, 1106, 1021, 820, 761 cm^{-1} . ^1H NMR: δ 2.04, 2.06(s, 3H, CH_3), 3.52(bs, 3H, SCH_3 , $J_{\text{Pt-H}} = 26$ Hz), 3.57(bs, 3H, SCH_3 , $J_{\text{Pt-H}} = 19$ Hz), 3.97, 3.81(s, 3H, OCH_3), 4.39, 4.31(s, 5H, C_5H_5), 4.52, 4.55(d, 1H, H-3), 4.62(m, 1H, H-4), 5.26(m, 1H, H-5), 6.93–7.05(m, 3H, Ar-H), 7.23(m, 1H, Ar-H) ppm. The ratio of the two isomers is 2.4:1.

3.2.1.12. $[\sigma\text{-Pt}(\eta^5\text{-C}_5\text{H}_3\text{CMe} = \text{NC}_6\text{H}_4\text{Cl-}2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{DMSO})\text{Cl}]$ (**2l**). Pink needles. Yield 64%. M.p. $204\text{--}206^\circ\text{C}$ (dec.). Anal. Found: C, 37.33; H, 3.31; N, 2.55. $\text{C}_{20}\text{H}_{21}\text{Cl}_2\text{FeNOPtS}$. Calc.: C, 37.22; H, 3.28; N, 2.17%. IR (KBr pellet): 1552, 1468, 1411, 1127, 1105, 1020, 815, 776 cm^{-1} . ^1H NMR: δ 2.00, 2.06(s, 3H, CH_3), 3.53, 3.54(bs, 6H, $\text{S}(\text{CH}_3)_2$), 4.60, 4.42(bs, 5H, C_5H_5), 4.84, 4.75(bs, 1H, H-3), 4.98(bs, 1H, H-4), 5.52, 5.42(bs, 1H, H-5), 6.97, 7.08(d, 1H, Ar-H, $J = 6.7$ Hz), 7.24–7.32(m, 1H, Ar-H), 7.47(m, 2H, Ar-H) ppm. The ratio of the two isomers is 2.6:1.

3.2.2. General procedure for the synthesis of compounds 3

A solution of 0.2 mmol *cis*-Pt(DMSO) $_2$ Cl $_2$ and an equimolecular amount of **1** in 40 ml of toluene was refluxed for about 3 h under Ar. The products were treated with the same procedure as that for synthesizing compounds **2**. The compounds **3** were characterized as follows.

3.2.2.1. $[\text{trans-PtCl}_2(\text{DMSO})\{(\eta^5\text{-C}_5\text{H}_4\text{CMe} = \text{NC}_6\text{H}_4\text{OMe-}4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}]$ (**3a**). Orange needles. Yield 73%. M.p. $198\text{--}200^\circ\text{C}$ (dec.). Anal. Found: C, 35.76; H, 3.62; N, 2.30. $\text{C}_{21}\text{H}_{25}\text{Cl}_2\text{FeNO}_2\text{PtS} \cdot 0.5\text{CH}_2\text{Cl}_2$. Calc.: C, 35.87; H, 3.64; N, 2.33%. IR (KBr pellet): 1587, 1505, 1446, 1249, 1144, 1107, 1023, 831 cm^{-1} . ^1H NMR: δ 3.29(s, 3H, CH_3), 3.36(s, 6H, $\text{S}(\text{CH}_3)_2$), 3.87(bs, 2H, H-2), 3.88(s, 3H, OCH_3), 4.29(s, 5H, C_5H_5), 4.39(bs, 2H, H-3), 5.31(s, 1H, $0.5\text{CH}_2\text{Cl}_2$), 6.93(d, 2H, Ar-H, $J = 8.9$ Hz), 7.26(d, 2H, Ar-H, $J = 8.9$ Hz) ppm.

3.2.2.2. $[\text{trans-PtCl}_2(\text{DMSO})\{(\eta^5\text{-C}_5\text{H}_4\text{CMe} = \text{NC}_6\text{H}_4\text{Me-}4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}]$ (**3b**). Orange plates. Yield 87%. M.p. $> 210^\circ\text{C}$ (dec.). Anal. Found: C, 38.01; H, 3.91; N, 2.44. $\text{C}_{21}\text{H}_{25}\text{Cl}_2\text{FeNOPtS}$. Calc.: C, 38.14; H, 3.81; N, 2.42%. IR (KBr pellet): 1586,

1505, 1446, 1138, 1109, 1026, 853, 821 cm^{-1} . ^1H NMR: δ 2.41 (s, 3H, Ph-CH_3), 3.30(s, 3H, CH_3), 3.36(s, 6H, $\text{S}(\text{CH}_3)_2$), 3.87(bs, 2H, H-2), 4.30(s, 5H, C_5H_5), 4.40(bs, 2H, H-3), 7.25(m, 4H, Ar-H) ppm.

3.2.2.3. $[\text{trans-PtCl}_2(\text{DMSO})\{(\eta^5\text{-C}_5\text{H}_4\text{CMe} = \text{NC}_6\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}]$ (**3c**). Red rods. Yield 80%. M.p. $> 200^\circ\text{C}$ (dec.). Anal. Found: C, 36.70; H, 3.54; N, 2.23. $\text{C}_{20}\text{H}_{23}\text{Cl}_2\text{FeNOPtS}$. Calc.: C, 37.11; H, 3.58; N, 2.16%. IR (KBr pellet): 1586, 1487, 1446, 1139, 1108, 1024, 821, 770, 699 cm^{-1} . ^1H NMR: δ 3.28(s, 3H, CH_3), 3.33(s, 6H, $\text{S}(\text{CH}_3)_2$), 3.78(bs, 2H, H-2), 4.25(s, 5H, C_5H_5), 4.35(bs, 2H, H-3), 7.31(d, 3H, Ar-H, $J = 7.3$ Hz), 7.38(t, 2H, Ar-H, $J = 7.5$ Hz) ppm.

3.2.2.4. $[\text{trans-PtCl}_2(\text{DMSO})\{(\eta^5\text{-C}_5\text{H}_4\text{CMe} = \text{NC}_6\text{H}_4\text{Cl-}4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}]$ (**3d**). Red needles. Yield 79%. M.p. $169\text{--}172^\circ\text{C}$. Anal. Found: C, 32.62; H, 3.21; N, 2.05. $\text{C}_{20}\text{H}_{22}\text{Cl}_3\text{FeNOPtS}$. Calc.: C, 32.90; H, 3.15; N, 1.83%. IR (KBr pellet): 1592, 1485, 1446, 1142, 1106, 1025, 825 cm^{-1} . ^1H NMR: δ 3.30(s, 3H, CH_3), 3.37(s, 6H, $\text{S}(\text{CH}_3)_2$), 3.89(bs, 2H, H-2), 4.30(s, 5H, C_5H_5), 4.45(bs, 2H, H-3), 7.71(d, 2H, Ar-H, $J = 8.8$ Hz), 7.40(d, 2H, Ar-H, $J = 8.8$ Hz) ppm.

3.2.2.5. $[\text{trans-PtCl}_2(\text{DMSO})\{(\eta^5\text{-C}_5\text{H}_4\text{CMe} = \text{NC}_6\text{H}_4\text{Br-}4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}]$ (**3e**). Red needles. Yield 71%. M.p. $192\text{--}194^\circ\text{C}$. Anal. Found: C, 31.32; H, 2.94; N, 1.71. $\text{C}_{20}\text{H}_{22}\text{BrCl}_2\text{FeNOPtS} \cdot \text{CH}_2\text{Cl}_2$. Calc.: C, 31.09; H, 2.98; N, 1.73%. IR (KBr pellet): 1581, 1470, 1447, 1141, 1108, 1021, 823 cm^{-1} . ^1H NMR: δ 3.29(s, 3H, CH_3), 3.36(s, 6H, $\text{S}(\text{CH}_3)_2$), 3.89(bs, 2H, H-2), 4.29(s, 5H, C_5H_5), 4.44(bs, 2H, H-3), 5.31(s, 2H, CH_2Cl_2), 7.24(d, 2H, Ar-H, $J = 8.4$ Hz), 7.54(d, 2H, Ar-H, $J = 8.4$ Hz) ppm.

3.2.2.6. $[\text{trans-PtCl}_2(\text{DMSO})\{(\eta^5\text{-C}_5\text{H}_4\text{CMe} = \text{NC}_6\text{H}_4\text{I-}4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}]$ (**3f**). Orange needles. Yield 62%. M.p. $> 200^\circ\text{C}$ (dec.). Anal. Found: C, 29.98; H, 2.74; N, 1.94. $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{FeINOtS} \cdot 0.5\text{CH}_2\text{Cl}_2$. Calc.: C, 30.18; H, 2.84; N, 1.72%. IR (KBr pellet): 1578, 1470, 1445, 1140, 1102, 1020, 1000, 820 cm^{-1} . ^1H NMR: δ 3.28(s, 3H, CH_3), 3.36(s, 6H, $\text{S}(\text{CH}_3)_2$), 3.90(bs, 2H, H-2), 4.29(s, 5H, C_5H_5), 4.45(bs, 2H, H-3), 5.31(s, 1H, $0.5\text{CH}_2\text{Cl}_2$), 7.11(d, 2H, Ar-H, $J = 8.4$ Hz), 7.74(d, 2H, Ar-H, $J = 8.0$ Hz) ppm.

3.2.2.7. $[\text{trans-PtCl}_2(\text{DMSO})\{(\eta^5\text{-C}_5\text{H}_4\text{CMe} = \text{NC}_6\text{H}_4\text{NO}_2\text{-}4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}]$ (**3g**). Red rods. Yield 71%. M.p. $> 200^\circ\text{C}$ (dec.). Anal. Found: C, 32.29; H, 2.97; N, 3.72. $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{FeN}_2\text{O}_3\text{PtS} \cdot \text{CH}_2\text{Cl}_2$. Calc.: C, 32.45; H, 3.11; N, 3.61%. IR (KBr pellet): 1578, 1520, 1488, 1447, 1343, 1143, 1107, 1025, 856, 830 cm^{-1} . ^1H NMR: δ 3.32(s, 3H, CH_3), 3.37(s, 6H, $\text{S}(\text{CH}_3)_2$), 3.89(bs, 2H, H-2), 4.32(s, 5H,

C_5H_5), 4.49(bs, 2H, H-3), 5.31(s, 2H, CH_2Cl_2), 7.54(d, 2H, Ar-H, $J = 8.4$ Hz), 8.29(d, 2H, Ar-H, $J = 8.8$ Hz) ppm.

3.2.2.8. [*trans*-PtCl₂(DMSO)](η^5 -C₅H₄CMe=NC₆H₄CH₃-3)Fe(η^5 -C₅H₅)] (3h). Red rods. Yield 65%. M.p. 183.5–185°C. Anal. Found: C, 38.24; H, 3.95; N, 2.11. C₂₁H₂₅Cl₂FeNOPtS. Calc.: C, 38.14; H, 3.81; N, 2.12%. IR (KBr pellet): 1587, 1482, 1448, 1142, 1071, 1023, 910, 825, 775, 699 cm⁻¹. ¹H NMR: δ 2.39(s, 3H, Ar-CH₃), 3.30(s, 3H, CH₃), 3.36(s, 6H, S(CH₃)₂), 3.83(bs, 2H, H-2), 4.28(s, 5H, C₅H₅), 4.38(bs, 2H, H-3), 7.15(bs, 3H, Ar-H), 7.28(bs, 1H, Ar-H) ppm.

3.2.2.9. [*trans*-PtCl₂(DMSO)](η^5 -C₅H₄CMe=NC₆H₄Cl-3)Fe(η^5 -C₅H₅)] (3i). Red plates. Yield 62%. M.p. 164.5–165.5°C. Anal. Found: C, 34.97; H, 3.09; N, 2.07. C₂₀H₂₂Cl₃FeNOPtS. Calc.: C, 35.23; H, 3.25; N, 2.06%. IR (KBr pellet): 1588, 1483, 1447, 1143, 1106, 1013, 897, 825, 734, 693 cm⁻¹. ¹H NMR: δ 3.30(s, 3H, CH₃), 3.37(s, 6H, S(CH₃)₂), 3.75, 3.97(bs, 2H, H-2), 4.31(s, 5H, C₅H₅), 4.44(bs, 2H, H-3), 7.22(m, 1H, Ar-H), 7.24(bs, 1H, Ar-H), 7.33(m, 1H, Ar-H), 7.40(bs, 1H, Ar-H) ppm.

3.2.2.10. [*trans*-PtCl₂(DMSO)](η^5 -C₅H₄CMe=NC₆H₄NO₂-3)Fe(η^5 -C₅H₅)] (3j). Orange needles. Yield 68%. M.p. 128–130°C. Anal. Found: C, 34.31; H, 3.25; N, 3.84. C₂₀H₂₂Cl₂FeN₂O₃PtS. Calc.: C, 34.70; H, 3.20; N, 4.05%. IR (KBr pellet): 1581, 1530, 1449, 1351, 1144, 1023, 906, 832, 731, 688 cm⁻¹. ¹H NMR: δ 3.33(s, 3H, CH₃), 3.37(s, 6H, S(CH₃)₂), 3.71, 3.90(bs, 2H, H-2), 4.33(s, 5H, C₅H₅), 4.47(bs, 2H, H-3), 7.61(m, 1H, Ar-H), 7.72(d, 1H, Ar-H, $J = 8.0$ Hz), 8.21(m, 2H, Ar-H) ppm.

3.2.2.11. [*trans*-PtCl₂(DMSO)](η^5 -C₅H₄CMe=NC₆H₄OCH₃-2)Fe(η^5 -C₅H₅)] (3k). Orange needles. Yield 70%. M.p. > 200°C (dec.) Anal. Found: C, 37.17; H, 3.76; N, 1.99. C₂₁H₂₅Cl₂FeNO₂PtS. Calc.: C, 37.24; H, 3.72; N, 2.07%. IR (KBr pellet): 1582, 1493, 1458, 1256, 1138, 1111, 1022, 828, 762 cm⁻¹.

3.2.2.12. [*trans*-PtCl₂(DMSO)](η^5 -C₅H₄CMe=NC₆H₄Cl-2)Fe(η^5 -C₅H₅)] (3l). Red needles. Yield 50%. M.p. 120–122°C. Anal. Found: C, 35.30; H, 3.29; N, 2.01. C₂₀H₂₂Cl₃FeNOPtS. Calc.: C, 35.23; H, 3.25; N, 2.06%. IR (KBr pellet): 1588, 1471, 1145, 1107, 1023, 827, 768 cm⁻¹.

3.2.3. General procedure for separating compound 3 from compound 2

Preparation of these compounds was carried out by using a procedure similar to that described above for the

synthesis of compounds 2, except that the reaction time was shortened to about 7 h. The products were separated by passing them through a short silica gel column. The first orange band and the second violet band were separately collected. After the evaporation of the solvent and recrystallization from CH₂Cl₂-C₆H₁₄, compounds 3 and 2 were obtained from the first and second band respectively. The yields of 3a, 2a; 3b, 2b; 3c, 2c; 3d, 2d were 31, 14%; 15, 23%; 37, 15% and 33, 10% respectively.

3.2.4. General procedure of conversion of 3 into 2

A solution of NaOAc (0.5 mmol) in 1 ml of methanol was added to a solution of compounds 3 (0.25 mmol) in 50 ml of toluene. The mixture was refluxed for about 20 h under Ar. The products were treated with the same procedure as that for synthesizing compounds 2. The yields are 37%, 46%, 61%, 19% and 45% for 2b–2d, 2g and 2j respectively.

3.3. X-ray crystal structure determination for 2c and 3c

3.3.1. Crystal data of 2c

C₂₀H₂₂OCIFePtSN, $M_r = 610.85$, monoclinic, $P2_1/a$ (No. 14), $a = 9.844(3)$, $b = 12.937(4)$, $c = 15.904(7)$ Å, $\beta = 91.79(3)^\circ$, $V = 2024(1)$ Å³, $Z = 4$, $D_c = 2.00$ g cm⁻³, $F(000) = 1176.00$, $\lambda = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 78.34$ cm⁻¹.

3.3.2. Crystal data of 3c

C₂₀H₂₃OCl₂FePtSN, $M_r = 647.31$, triclinic, $P\bar{1}$ (No. 2), $a = 9.381(2)$, $b = 13.946(2)$, $c = 9.233(3)$ Å, $\alpha = 103.56(2)^\circ$, $\beta = 115.86(2)^\circ$, $\gamma = 89.39(2)^\circ$, $V = 1050.8(5)$ Å³, $Z = 2$, $D_c = 2.05$ g cm⁻³, $F(000) = 624.00$, $\lambda = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 76.76$ cm⁻¹.

3.3.3. Data collection

Red prismatic crystals of 2c and 3c with approximate dimensions of 0.20 × 0.20 × 0.30 mm³ were mounted on a Rigaku AFC7R diffractometer. Unit cell parameters were determined from the angular setting of 19 reflections with 2 θ angles in the range of 18.11–21.79° for 2c and from the angular setting of 21 reflections with 2 θ angles in the range of 18.18–21.15° for 3c and refined with the least squares method. Intensities were collected with graphite monochromated Mo K α radiation by using the ω -2 θ scan technique. A total of 3490 reflections for 2c and 3524 reflections for 3c were measured; 2690 reflections for 2c and 3065 reflections for 3c were considered as observed applying the condition $I > 3\sigma(I)$. Three reflections were measured after every 200 reflections as orientation and intensity control; no significant intensity decay was observed. Data were corrected for Lorentz and polarization effects and also for absorption by an empirical method using the program DIFABS [12].

3.3.4. Structure solution and refinement

The structure was solved by heavy-atom Patterson methods and expanded by using Fourier techniques. All calculations were performed by using the teXsan software package [13]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final R factors were 0.023 ($R_w = 0.031$) for **2c** and 0.025 ($R_w = 0.034$) for **3c**. For **2c** the maximum and minimum peaks on the final difference Fourier map corresponded to 0.89 and $-0.73 \text{ e}^- \text{ \AA}^{-3}$ respectively, and for **3c** they corresponded to 1.57 and $-1.1 \text{ e}^- \text{ \AA}^{-3}$ respectively.

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