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Synthesis, characterisation and study of the first luminescent platinum(II) compound with a [C,N,S]$^-$ terdentate ligand. X-ray crystal structure of [Pt{C_6H_4–CH=N–(C_6H_4–2-SMe)}Cl]

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Abstract

The study of the reactions of the thioimine C_6H_5–CH=N–(C_6H_4–2-SMe) with *cis*-[$PtCl_2(DMSO)_2$] or *cis*-[$PtCl_2(PhCN)_2$] is reported. The results obtained from the reactions of *cis*-[$PtCl_2(DMSO)_2$] with the Schiff base suggest that this platinum(II) complex induces the hydrolyses of the imine. In contrast to these findings, the treatment of equimolar amounts of C_6H_5–CH=N–(C_6H_4–2-SMe) and *cis*-[$PtCl_2(PhCN)_2$] under refluxing toluene lead to the cycloplatinated complex: [Pt{C_6H_4–CH=N–(C_6H_4–2-SMe)}Cl], which is luminescent in solution at 298 K. The X-ray crystal structure of this compound reveals that the ligand acts as a [C(sp^2),N,S]$^-$ ligand and has the *E* (*anti*-) conformation. The reaction of the cycloplatinated compound [Pt{C_6H_4–CH=N–(C_6H_4–2-SMe)}Cl] with PPh_3 is also reported. This process produces the cleavage of the Pt–S bond and the formation of [Pt{C_6H_4–CH=N–(C_6H_4–2-SMe)}Cl(PPh_3)] in which the ligand acts as a monoanionic (C,N)$^-$ bidentate group.

Keywords: Platinum(II); Cycloplatination; Luminiscence

1. Introduction

Platinum(II) compounds of the type [Pt(L)Cl] where L stands for a monoanionic (C,N,X)$^-$ (X = N, P, O or S) terdentate group have attracted considerable interest in recent years due to their applications in several areas [1–4]. In addition to the potential antitumoral activity of the platinum(II) compounds having (C,N,X)$^-$ ligands [2], this sort of complexes have an additional interest as precursors for the synthesis of organic or organometallic compounds [3]. For instance Johnson and Sames have recently reported the total synthesis of the antitumour agent *Rhazinilam* based on the use of a platinum(II) complex having a (C,N,N′)$^-$ terdentate group [3a]. Besides that, platinum(II) compounds with (N,N), (C,N)$^-$ or (C,N,N′)$^-$ ligands are particularly important from the point of view of their luminescent properties [4].

On the other hand, despite the wide variety of platinacycles having ‘Pt(C,N,X)Cl’ cores described so far and the potential interest of the presence of three donor atoms (C, N and X) of different hardness [5] bound to the central atom, the number of platinum(II) compounds having X = sulphur are scarce [6,7] and most of the examples reported so far arise from the activation of the σ[C(sp^2)–H] bond of azobenzene derivatives holding thioether groups [6].

As a part of a project focused on the synthesis and the study of the potential utilities of platinum(II) complexes having (N,S) or (C,N,S)$^-$ ligands, a few years ago we centred our research in the study of the reactivity of imines R–C(H)=N–R′ (where the R′ contains a thioether group as a pendant arm) towards platinum(II) [7]. Recent studies have shown that the reaction of C_6H_5–C(H)=N–(CH_2–CH_2–SEt) (**1a**) (Plate 1) with *cis*-[$PtCl_2(DMSO)_2$] leads to [Pt{C_6H_4–CH=N–(CH_2–

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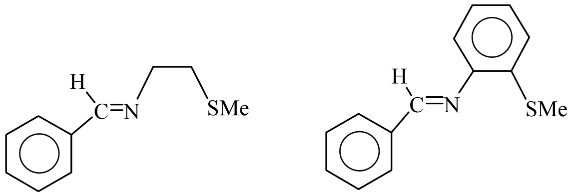


1a **1b**

Plate 1.

CH_2–SEt)}Cl] (**2a**) [7a]. In the view of these facts, we decided to elucidate whether: the replacement of the '–CH_2–CH_2–' moiety in **1a** by a less flexible moiety such as a 1,2-disubstituted phenyl ring in C_6H_5–C(H)=N–(C_6H_4-2SEt) (**1b**) (Plate 1), could be important in determining the mode of binding of this ligand to the platinum(II) or the co-planarity of all the rings around the metal which is of outstanding relevance in the view of their potential applications.

2. Results and discussion

In a first attempt to achieve the cycloplatination of ligand **1b**, we decided to use the procedure described recently for the synthesis of [Pt{C_6H_4–CH=N–(CH_2–CH_2–SEt)}Cl] (**2a**) [7a]. This method consists of the reaction of equimolar amounts of **1a** and *cis*-[$PtCl_2(DMSO)_2$] in refluxing methanol. However, when the reaction was carried out using C_6H_5–CH=N–(C_6H_4–2-SMe) (**1b**) under identical experimental conditions as described for **1a**, two different compounds could be isolated in the two cases. One of them was identified, on the basis of infrared and NMR spectroscopy, as benzaldehyde; while the characterisation data of the second component agreed with those expected for *cis*-[$PtCl_2$(H_2N–C_6H_4–2-SMe)] [8] probably resulting from the hydrolysis of the ligand. These findings are in sharp contrast with those obtained for the closely related substrate: C_6H_4–CH=N–(CH_2–CH_2–SEt) (**1a**) [7a], for which no evidences of the hydrolysis of the ligand were detected in the course of the reaction by NMR spectroscopy. Furthermore, since it has been demonstrated that ligand **1b** does not degrade in the presence of stoichiometric amounts of $Na_2[PdCl_4]$ in methanol (at room temperature or under refluxing conditions) or even in the presence of a base [9], we propose that in the reaction under study, the hydrolyses of the ligand may be promoted by the platinum(II) reagent. Recent studies focused on the reaction of diimines derived from (1*R*,2*R*)-1,2-diaminocyclohexane (L′) with *cis*-[$PtCl_2(DMSO)_2$] in refluxing 2-methoxyethanol have also lead to the formation of *cis*-[$PtCl_2$(L′)], and these results have been rationalised using a similar argument [10].

In view of this, we decided to elucidate whether the use of a different platinum(II) derivative as starting material, such as *cis*-[$PtCl_2(PhCN)_2$] and the use of non-protic solvents could prevent the hydrolysis of the ligand, and allow the stabilisation of the platinum(II) imine derivatives.

The treatment of **1b** with the stoichiometric amount of *cis*-[$PtCl_2(PhCN)_2$] in refluxing toluene produced two different platinum(II) complexes (Scheme 1).

The characterisation data of the less soluble and minor component agreed with those obtained for *cis*-[$PtCl_2$(H_2N–C_6H_4–2-SMe)] (see above), while the elemental analyses of the second compound were consistent with those expected for: [Pt{C_6H_4–CH=N–(C_6H_4–2-SMe)}Cl] (**2b**). The ^{195}Pt{^{1}H}-NMR spectrum of complex **2b** showed a singlet at ca. −3708 ppm. The position of this signal is similar to those reported for [Pt{C_6H_4–CH=N–(CH_2–CH_2–SEt)}Cl] (**2a**) [$\delta = -3716$ ppm] [7a] and [Pt{C_6H_4–CH=N–CH(CO_2Me)–CH_2–CH_2–SMe)}Cl] [$\delta = -3832$ ppm] [7b], in which the ligands also act as a $[C(sp^2),N,S]^-$ terdentate group.

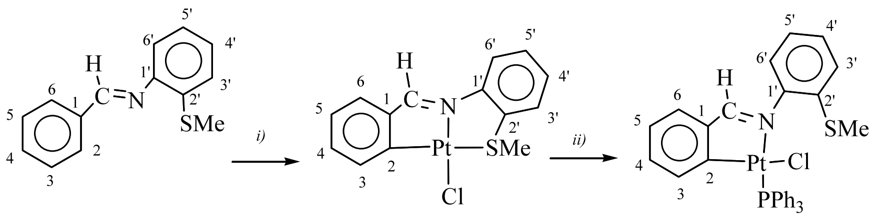
All these findings suggested that the formation of **2b** involved the activation of the $\sigma[C(sp^2)–H]$ bond, to produce a five-membered ring platinacycle. The X-ray crystal structure of this complex confirmed these results.

The molecular structure of **2b** together with the atom labelling scheme is depicted in Fig. 1. Bond lengths and a selection of bond angles are presented in Table 1. The structure consists of discrete molecules of [Pt{C_6H_4–CH=N–(C_6H_4–2-SMe)}Cl] separated by van der Waals contacts. In each of these molecules the platinum(II) is in a slightly distorted square-planar environment [11] bound to the chlorine, the sulphur, the imine nitrogen and the C(1) atom of the phenyl ring. This confirmed the conclusions reached by NMR studies which suggested a $[C(sp^2),N,S]^-$ mode of binding of the ligand.

Each molecule contains a [6,5,5,6] tetracyclic system formed by an aryl ring which shares the C(8)–C(13) bond with the chelate formed by the coordination of the two heteroatoms (N and S) to the platinum(II), a five-membered metallacycle and the other phenyl ring. The Pt–C and Pt–N bond distances are consistent with those reported for a wide variety of platinacycles having $(C,N)^-$, $(C,N,N')^-$ or $(N,C,N')^-$ ligands [12], but the Pt–S bond length in **2b** is clearly greater than the value usually found for platinum(II)–S(thioether) derivatives (ca. 2.25 Å) [13]. However, the platinum–ligand bond distances of **2b** do not differ significantly from those reported for **2a** [7a].

The angles between adjacent atoms in the coordination sphere lie in the range: 81.8(2)–96.7(2)°. The smallest values corresponding to the terdentate ligand.

The metallacycle, which is formed by the atoms: C(1), C(6), C(7), N and Pt, is nearly planar [14], contains the >C=N– functional group (*endocyclic*) and forms angles of 5.22, 4.54 and 3.13° with the attached aryl



1b **2b** **3b**

Scheme 1. (i) *Cis*-[$PtCl_2(PhCN)_2$], in refluxing toluene (**3b**). In this case compound *cis*-[$PtCl_2(H_2N{-}C_6H_4{-}2SMe)$] was also formed as a by product (see text). (ii) PPh_3 in CH_2Cl_2 in a Pt:PPh_3 molar ratio = 1.

Table 1
Bond lengths (in Å) and selected bond angles (in °) for [Pt{C_6H_4–CH=N–(C_6H_4-2-SMe)}Cl] (**2b**)

Bond lengths			
Pt–N	1.928(6)	Pt–C(1)	2.016(6)
Pt–Cl	2.292(2)	Pt–S	2.349(2)
S–C(13)	1.777(7)	S–C(14)	1.830(9)
N–C(7)	1.303(8)	N–C(8)	1.451(8)
C(1)–C(2)	1.379(9)	C(1)–C(6)	1.390(9)
C(2)–C(3)	1.410(12)	C(3)–C(4)	1.364(14)
C(4)–C(5)	1.370(11)	C(5)–C(6)	1.416(10)
C(6)–C(7)	1.461(9)	C(8)–C(9)	1.391(11)
C(8)–C(13)	1.412(10)	C(9)–C(10)	1.369(12)
C(10)–C(11)	1.377(14)	C(11)–C(12)	1.378(14)
C(12)–C(13)	1.394(10)		
Selected bond angles			
N–Pt–C(1)	81.8(2)	N–Pt–S	85.93(15)
Cl–Pt–S	95.69(8)	C(1)–Pt–Cl	96.7(2)
Pt–C(1)–C(6)	111.4(5)	C(1)–C(6)–C(7)	115.4(6)
N–C(7)–C(6)	115.2(6)	C(7)–N–Pt	115.9(4)
Pt–N–C(8)	120.2(4)	N–C(8)–C(13)	117.5(6)
C(8)–C(13)–S	119.8(5)	C(14)–S–C(13)	101.1(4)
C(13)–S–Pt	104.3(3)	C(2)–C(1)–Pt	131.1(6)

group, the five-membered chelate ring and the other phenyl ring, respectively.

The five-membered chelate ring formed by the platinum and the '–N–(C_6H_4–2-SMe)' fragment is nearly planar [15] and it forms an angle of ca. 2.73° with the phenyl ring attached to it. In this complex the two phenyl rings are planar and their main planes form an angle of 5.56°.

The separation between the Cl and the H(2) atom is (2.914 Å) slightly shorter than the sum of the van der Waals radii (Cl, 1.75 and H, 1.20 Å) [16] of these atoms, thus suggesting a Cl···H(2)···C(2) intramolecular interaction. This type of interactions has also been described for a wide variety of cyclopalladated and cycloplatinated complexes containing $(C,N)^-$ or $(C,N,N')^-$ ligands and a chloride bound to the metal atom [17].

The crystal structure also confirms that **2b** consists on a 1:1 mixture of enantiomers. This is consistent with the lack of chiral induction during the cyclometallation process.

Several authors have suggested that for cycloplatinated complexes having $(C,N,N')^-$ terdentate groups, the planarity of the terdentate group, the π-stacking of the aryl rings of the ligand and the Pt···Pt separation, are particularly important in the view of the potential photo-luminescent properties of this sort of compounds [18–20]. In complex **2b**, the atoms forming the tricyclic

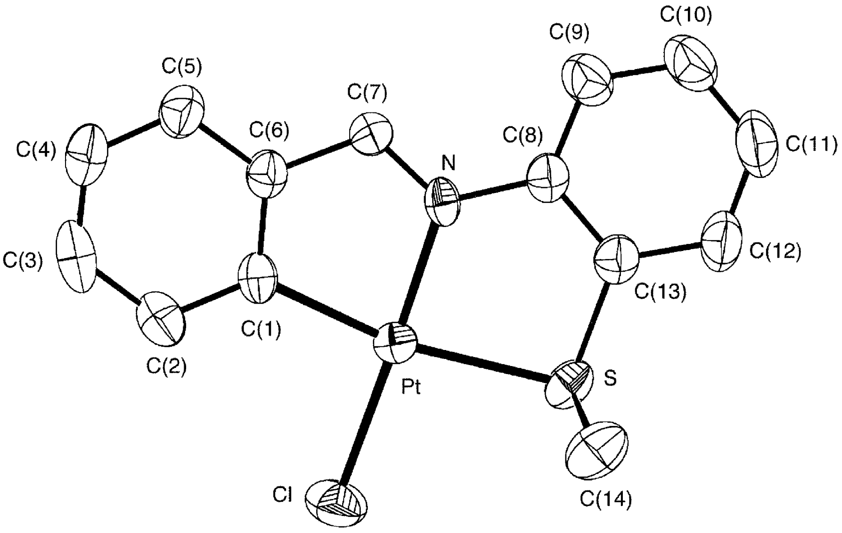


Fig. 1. View of the crystal structure of compound [Pt{C_6H_4–CH=N–(C_6H_4–2-SMe)}Cl] (**2b**) together with the atom labelling scheme.

system mentioned above are nearly coplanar [21], and in the unit cell the molecules are associated in pairs in a *head* to *tail* arrangement where the shortest interplanar separation between the $(C,N,S)^-$ ligands is 3.91 Å, which falls in the upper range expected for π-stacking systems [22]. The long intermolecular S···S distance precludes the existence of any direct interaction between these atoms. Besides that, the shortest Pt···Pt distance between neighbouring molecules is [4.216(3) Å] clearly larger than the values reported for related platinacycles holding $[C(sp^2),N,N']^-$ and $[C(sp^2),N,S]^-$ terdentate ligands for which intramolecular Pt···Pt interactions have been proposed [18–20].

In order to elucidate whether the flexibility of the moiety which links the two heteroatoms in the cycloplatinated complexes **2a** and **2b** could be important in determining the lability of the Pt–S or Pt–Cl bond, we decided to study the reaction of **2b** with PPh_3 and to compare the results with those reported for $[Pt\{C_6H_4–CH{=}N–(CH_2–CH_2–2\text{-}SMe)\}Cl]$ (**2a**).

When the stoichiometric amount of PPh_3 was added to a solution of **2b** in CH_2Cl_2 at room temperature a yellowish solution was formed. The subsequent concentration of the solution followed by the addition of *n*-hexane produced the precipitation of a yellow solid. Its elemental analyses (see Section 4.1.2) were consistent with those expected for $[Pt\{C_6H_4–CH{=}N–(C_6H_4–2\text{-}SMe)\}Cl(PPh_3)]$ (**3b**) (Scheme 1). Its $^{31}P\{^1H\}$-NMR spectrum showed a signal at $\delta = 19.34$ ppm strongly coupled with the ^{195}Pt nucleus $\{^1J(P–Pt) = 3858\ Hz\}$. Its position and multiplicity as well as the value of the coupling constant suggested the presence of one PPh_3 ligand bound to the platinum in a *trans*- arrangement to the imine nitrogen. This is the usual result of the reaction between $(C,N)^-$ cyclometallated compounds and phosphine ligands [17,23,24] due to the so-called *transphobia* effect [25]. ^{13}C-NMR spectroscopic data are presented in the Section 4 and the most relevant feature observed in the $^{13}C\{^1H\}$-NMR spectrum is the lowfield shift of the signal due to the metallated carbon, when compared with the free ligand [9]. In the ^1H-NMR spectrum of **3b**, the signal due to the imine proton appeared as a doublet at $\delta = 10.68$ ppm due to ^{31}P coupling $[^4J(H–P) = 9.0\ Hz]$ and also coupled with the ^{195}Pt nucleus $[^3J(H–Pt) = 63\ Hz]$, thus indicating the binding of the imine nitrogen to the platinum. However, the signal due to the methyl protons of the SMe group appeared as a singlet without ^{195}Pt satellites. This finding suggests that the reaction of **2b** with PPh_3 involved the cleavage of the Pt–SMe bond producing $[Pt\{C_6H_4–CH{=}N–(C_6H_4–2\text{-}SMe)\}Cl(PPh_3)]$ (**3b**). This result is similar to that reported for $[Pt\{C_6H_4–CH{=}N–(CH_2–CH_2–SEt)\}Cl]$ (**2a**), for which the addition of PPh_3 gave $[Pt\{C_6H_4–CH{=}N–(CH_2–CH_2–SEt)\}Cl(PPh_3)]$ (**3a**) under identical experimental conditions. Thus, the formation of **3a** and **3b** required not only the co-ordination of the PPh_3 ligand but also the cleavage of the Pt–S bond.

The $^{195}Pt\{^1H\}$-NMR spectrum of **3b** showed a doublet $[^1J(Pt–P) = 3858\ Hz]$ centred at $\delta = -4461$ ppm. The position of this signal is consistent with that reported for $[Pt\{C_6H_4–CH{=}N–(CH_2–CH_2–SEt)\}Cl(PPh_3)]$ (**3a**) $[\delta = -4485$ ppm, $^1J(Pt–P) = 3806\ Hz]$ [7a], in which the ligand also acts as a $[C(sp^2),N,S]^-$ terdentate group.

As mentioned above, cycloplatinated compounds having terdentate $\{[C,N,N']^-$ or $[N,C,N']^-\}$ ligands are also interesting from the point of view of their photophysical properties and in particular due to their potential luminescence, which may allow the design of new devices or materials [4,19b,19c,19d,26]. On this basis, we decided to study whether compound **2b**, which has a $(C,N,S)^-$ ligand could also exhibit luminescence. The UV–vis spectrum of **2b** in CH_2Cl_2 showed two intense bands (see Section 4) in the range 340–370 nm (also observed in the spectrum of the free ligand) assigned to intraligand transitions. At lower energies three less intense bands (in the range 400–500 nm, with extinction coefficients, ε, greater than 1000 were also observed. As can be easily seen in Fig. 2, compound **2b** exhibits emission ($\lambda_{max} = 666$ nm in CH_2Cl_2 at 298 K ($\lambda_{exc} = 469$ nm) and the excitation spectrum (also shown in Fig. 2), closely matched the corresponding absorption spectrum, even the shoulder at ca. 491 nm was observed.

In the view of these results and in order to elucidate whether the luminescence of **2b** could be induced by the presence of the 1,2-disubstituted phenyl ring which connects the two heteroatoms (N and S), we decided to carry out a ‘parallel’ study using complex $[Pt\{C_6H_4–CH{=}N–(CH_2–CH_2–SEt)\}Cl]$ (**2a**) in which the aryl ring has been replaced by a ‘$–CH_2–CH_2–$’ fragment.

The UV–vis spectrum of **2a** (Fig. 3(A)) showed four bands in the range 300–400 nm. For the bands at higher energies, the positions of their maxima [λ = 314 and 328 nm] were very similar to those of the free ligand [λ = 308

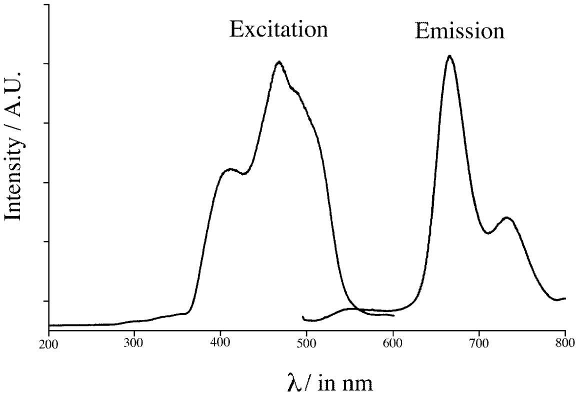


Fig. 2. Excitation and emission spectra of compound **2b** in CH_2Cl_2 at 298 K with excitation at 466 nm and emission monitored at 666 nm.

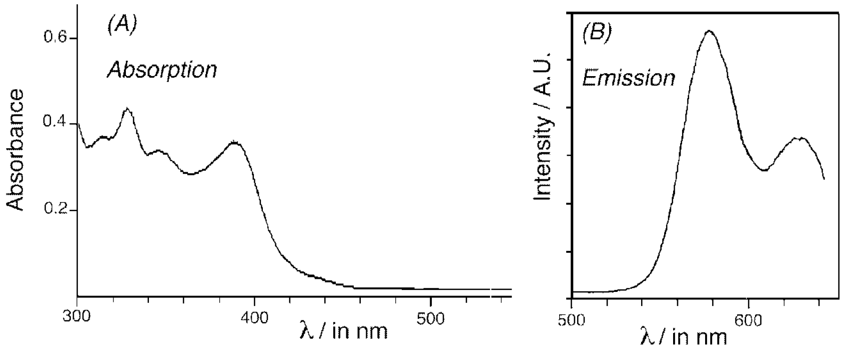


Fig. 3. (A) Absorption spectrum of compound [Pt{C_6H_4–CH=N–(CH_2–CH_2–SEt)}Cl] (**2b**) [absorption wavelengths, λ_{max} (in nm) and extinction coefficients, ε, (in dm^3 mol^{-1} cm^2) in parenthesis: 314 (3520); 328 (4188); 343 (3211) and 388 (3435)]. (B) Emission spectrum {$\lambda_{excitation} = 388$ nm and $\lambda_{emission}$ (max) = 578 nm} of **2b** in CH_2Cl_2 at 298 K.

and 325 nm]. Consequently, these absorptions can be attributed to intraligand transitions.

The position of the third band [$\lambda = 343$ nm] was nearly coincident with one of the bands observed in the UV–vis spectrum of **2b** [$\lambda = 346$ nm]; while the remaining absorption band appeared at [$\lambda = 388$ nm] higher energies than for **2a**. Excitation at this wavelength [$\lambda_{exc} = 388$ nm] gave the emission spectrum depicted in Fig. 3(B), showing a maxima [$\lambda_{max} = 578$ nm] at lower wavelengths than complex **2a** [$\lambda_{max} = 666$ nm]. This finding indicates that the replacement of a '–CH_2–CH_2–' unit between the two heteroatoms in **2a** by the 1,2-disubstituted phenyl ring (in **2b**) produces a red shift of the position of the maximum observed in the emission spectrum of compounds **2**.

3. Conclusions

The results presented in this work have allowed us to isolate and characterise two cycloplatinated complexes in which ligand **1b** acts as a monoanionic $[C(sp^2),N]^-$ bidentate ligand (in **3b**) or as a terdentate $[C(sp^2),N,S]^-$ (in **2b**). Besides that, the comparison of the results reported here and those obtained for ligand **1a**, indicate that tiny changes in the moiety bridging the two heteroatoms (a '–CH_2–CH_2–' unit in **1a** or a 1,2-disubstituted phenyl ring in **1b**) are important to modify the stability of these ligands to undergo a hydrolyses process in the presence of *cis*-[$PtCl_2(DMSO)_2$]. In contrast with these findings, the synthesis of a cycloplatinated complex derived from imine **1b** could be successfully achieved when *cis*-[$PtCl_2(PhCN)_2$] was used as starting material. The cycloplatinated complexes **2a** and **2b** exhibit similar reactivity versus PPh_3, thus suggesting that the replacement of the '–CH_2–CH_2–' fragment (in **2a**) by a more rigid 1,2-disubstituted phenyl ring (in **2b**) does not introduce significant variation in this sort of process which involves the cleavage of the Pt–S bond.

Besides that, as far as we know the new compound **2b** and complex **2a** (which was reported previously [7a]) are the first examples of a cycloplatinated complexes containing a $(C,N,S)^-$ terdentate group, which exhibit luminescence in CH_2Cl_2 at 298 K. Consequently, the results presented here provide the first step of a new field of research focused on the study of the photo-physical properties and potential applications of platinacycles similar to **2a** or **2b** formed by either the replacement of the terminal chloride ligand (by an unsaturated groups such as: $-C\equiv C-R$ moieties) or by the incorporation of substituents in the backbone of the terdentate $(C,N,S)^-$ ligand. Further work on this field is currently under study.

4. Experimental section

4.1. General comments

The ligand C_6H_5–CH=N–(C_6H_4–2-SMe) (**1b**) and complex [Pt{C_6H_4–CH=N–(CH_2–CH_2–SEt)}Cl] (**2a**) were prepared as described previously [7a,12].The platinum(II) derivatives: *cis*-[$PtCl_2(PhCN)_2$] and $K_2[PtCl_4]$ were purchased from Aldrich and used as received and *cis*-[$PtCl_2(Me_2SO)_2$] was prepared as described previously [27]. All the solvents used in this study were dried and distilled before use, except MeOH which was of HPLC grade. Elemental analyses (C, H, N and S) were carried out at the Institut de Química Bio-Organica (C.S.I.C., Barcelona). FABMS of compounds **2b** and **3b** were obtained with a VG-Quatro, Fission Instrument using 3-nitrobenzylaalcohol (NBA) as matrix. Infrared spectra were obtained with a NICOLET-Impact 400 instrument. Routine ^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded with either a Gemini-200 MHz or a Bruker-DXR-250 instrument using $CDCl_3$ as solvent and $SiMe_4$ as internal standard, except where quoted. High resolution mono-dimensional ^{1}H-NMR experiments as well as the 2D-heteronuclear (HMBC and HSQC) experiments were obtained with either a Bruker

Avance-500DMX or a Varian-VXR500 instrument using the same solvents and references as mentioned above. The ^{195}Pt{^{1}H}-NMR spectra of **3a** and **3b** were obtained with a Bruker-DXR-250 instrument and the chemical shifts given are referred to a $H_2[PtCl_6]$ solution in D_2O as external reference. The ^{31}P{^{1}H}-NMR spectrum of **3b** was obtained with a Bruker -DXR-250 instrument using $CDCl_3$ as solvent and $P(OMe)_3$ as reference [$\delta^{31}P\{P(OMe)_3\} = 140.17$ ppm]. In all cases the chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz. The assignments of the signals detected in the ^{1}H- and ^{13}C-NMR spectra were carried out with the aid of two-dimensional NMR experiments.

The UV–vis spectra of **2a** and **2b** in CH_2Cl_2 were recorded at 298 K with a SHIMADZU-160A spectrophotometer and an AMINCO-BOWMAN spectrofluorimeter was used to obtain the luminescence spectrum of 10^{-4} M solutions of **2a** and **2b** in CH_2Cl_2 at 298 K.

4.1.1. *Preparation of [Pt{C_6H_4–CH=N–(C_6H_4–2-SMe)}Cl] (**2b**)*

Cis-[$PtCl_2(PhCN)_2$] (100 mg, 2.1×10^{-4} mol) was suspended in 20 cm^3 of toluene and refluxed until complete dissolution. Then, the ligand (48 mg, 2.1×10^{-4} mol) was added and the mixture was refluxed for 3 h. The resulting solution was filtered and the brown filtrate was concentrated to ca. 5 cm^3 on a rotary evaporator. The brown solid formed was collected by filtration and air-dried. (Yield: 30 mg, 31%). Characterisation data: Anal. Calc. for: $C_{14}H_{12}NClPtS$ (Found): C, 36.81 (37.03); H, 2.64 (2.60), N, 3.07 (2.99) and S, 7.02 (6.73)%. MS (FAB$^+$): $m/z = 421$ {M–(Cl)}$^+$. IR: ν(>C=N–) = 1588 cm^{-1}. UV–vis data: λ (nm) (ε in dm^3 mol^{-1} cm^2) = 346 (7540); 363 (7846), 431 sh (1347), 466 (1971) and 492 sh (1670). ^{1}H-NMR data: 2.95 [s, 3H, –SMe, ^{3}J(Pt–H) = 20], 8.98 [s, 1H, –CH=N–, ^{3}J(Pt–H) = 131], 7.47 [d, 1H, H^3, ^{3}J(H–H) = 7.5], 7.35 [t, 1H, H^4, ^{3}J(H–H) = 7.5], 7.51 [t, 1H, H^5, ^{3}J(H–H) = 7.5], 7.67 [dd, 1H, H^6, ^{3}J(H–H) = 7.5, ^{4}J(H–H) = 1.5], 7.75 [d, 1H, H$^{3\prime}$, ^{3}J(H–H) = 7.5], 7.12 [td, 1H, H$^{4\prime}$, ^{3}J(H–H) = 7.5, ^{4}J(H–H) = 1.5], 7.46 [t, 1H, H$^{5\prime}$, ^{3}J(H–H) = 7.5] and 7.87 [dd, 1H, H$^{6\prime}$, ^{3}J(H–H) = 7.5, ^{4}J(H–H) = 1.5, ^{3}J(H–Pt) = 41]. ^{13}C{^{1}H}-NMR data: 169.2 (–CH=N–), 26.8 (–SMe), 148.5 (C^1), 130.8 (C^3), 134.0 (C^4), 131.0 (C^5), 135.1 (C^6), 155.8 (C$^{1\prime}$), 118.1 (C$^{3\prime}$), 125.1 (C$^{4\prime}$), 131.2(C$^{5\prime}$) and 132.6 (C$^{6\prime}$), the signals due to the C^2 and C$^{2\prime}$ atoms were not detected in the ^{13}C{^{1}H}-NMR spectrum. ^{195}Pt{^{1}H}-NMR data: −3708.

4.1.2. *Preparation of [Pt{C_6H_4–CH=N–(C_6H_4–2-SMe)}Cl(PPh_3)] (**3b**)*

Complex **2b** (60 mg, 1.3×10^{-4} mol) was dissolved in 10 ml of CH_2Cl_2 then the stoichiometric amount of PPh_3 (34 mg, 1.3×10^{-4} mol) was added. The reaction mixture was stirred at room temperature (r.t.) (ca. 20 °C) for ca. 10 min. The resulting yellow solution was concentrated to ca. 2 ml on a rotary evaporator, and then treated with *n*-hexane. The yellow solid formed was filtered out, washed with *n*-hexane, air-dried and then dried in vacuum for 24 h (yield: 79 mg, 83%). Characterisation data: Anal. Calc. for: $C_{32}H_{27}NClPPtS \cdot 0.5CH_2Cl_2$ (Found): C, 51.25 (51.35); H, 3.78 (3.85), N, 1.84 (2.00) and S, 4.21 (4.43)%. MS (FAB$^+$): $m/z = 652$ {M–(Cl)–(0.5CH_2Cl_2)}$^+$. IR: ν(>C=N–) = 1590 cm^{-1}. ^{1}H-NMR data (500 MHz): 10.68 [d, 1H, –CH=N–, ^{3}J(H–Pt) = 63, ^{3}J(H–Pt) = 9], 2.13 [s, 3H, –SMe], 6.40 [d, 1H, H^3, ^{3}J(H–H) = 7.3], 6.67 [t, 1H, H^4, ^{3}J(H–H) = 7.2], 7.13 [t, 1H, H^5, ^{3}J(H–H) = 7.3], 8.18 [d, 1H, H$^{3\prime}$, ^{3}J(H–H) = 7.3], 8.80 [d, 1H, H$^{6\prime}$, ^{3}J(H–H) = 7.3], 5.12 [s, 1H, CH_2Cl_2] and 6.40–7.90 [m, 20H, H$^{4\prime}$, H$^{5\prime}$ and aromatic protons of the PPh_3 ligand). ^{13}C{^{1}H}-NMR data: 177.0 (–CH=N–), 28.0 (–SMe), 152.2 [C^1, ^{3}J(C–P) = 7], 136.7 [C^2, ^{1}J(C–Pt) = 85, ^{2}J(C–P) = 5 Hz], 128.4 (C^3), 134.1 (C^4), 133.0 (C^5), 130.1 (C^6), 148.3 (C$^{1\prime}$), 134.7 (C$^{2\prime}$), 122.2 (C$^{3\prime}$), 126.5 (C$^{4\prime}$), 132.7 (C$^{6\prime}$) and four additional doublets centred at ca. 134.4, 131.6, 131.1 and 128.7 ppm due to the four types of carbon nuclei of the aromatic rings of the PPh_3 ligand. ^{31}P{^{1}H}-NMR data: 19.34 [^{1}J(P–Pt) = 3857.6 Hz]. ^{195}Pt{^{1}H}-NMR data: −4461 [^{1}J(Pt–P) = 3858].

4.2. *Crystallography*

A brown crystal of [Pt{C_6H_4–CH=N–(C_6H_4–2-SMe)}Cl] (**2b**) was selected and mounted on a ENRAF-Nonius CAD 4 four circle diffractometer. Unit cell parameter were determined from automatic centring of 25 reflections (in the range $12 < \Theta < 21°$) and refined by least-squares method. Intensities were collected with a graphite monochromatised Mo–K$_\alpha$ radiation using ω–2Θ scan-technique. The number of reflections measured in the range $2.43 \le \Theta \le 29.98°$ was 4116, of which 3912 were non-equivalent by symmetry {R_{int} (on I) = 0.043} and the number of reflections assumed as observed, applying the condition $I > 2\sigma(I)$, was 3068. Three reflections were measured every 2 h as orientation and intensity control, but no significant intensity decay was observed. Lorentz-polarisation corrections were made, but absorption corrections were not.

The structure was solved by Direct methods, using the SHELXS computer program [28] and refined by full-matrix least-squares method with the SHELX-97 computer program [29] using 3912 reflections (very negative intensities were not assumed). The function minimised was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0684P)^2 + 0.3429P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f' and f'' were obtained from the literature [30]. All hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. The final R(on F) factor was 0.041, wR(on F^2) = 0.101 and the goodness-of-fit was 1.048 for all the observed reflections. The

Table 2
Crystallographic data for [Pt{C_6H_4–CH=N–(C_6H_4–2-SMe)}Cl] (**2b**)

Formula	$C_{14}H_{12}ClNPtS$
Formula weight	456.85
T (K)	293(2)
Crystal dimensions (mm × mm × mm)	0.1 × 0.1 × 0.2
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.671(3)
b (Å)	12.579(9)
c (Å)	11.286(6)
$\alpha = \gamma$ (°)	90.0
β (°)	96.89(3)
V (Å^3)	1363.0(13)
Z	4
D_{calc} (g cm^{-3})	2.226
μ (mm^{-1})	10.623
F(000)	856
Θ Range for data collection (°)	2.43–29.98
h, k, l ranges	$-13 \leq h \leq 13$, $-1 \leq k \leq 17$, $0 \leq l \leq 15$
Number of collected reflections	4116
Number of unique reflections	3912 [$R_{int} = 0.0439$]
Number of data	3912
Number of parameters	163
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0417$, $wR_2 = 0.1015$
Final R indices (all data)	$R_1 = 0.0628$, $wR_2 = 0.1100$
Largest difference peak and hole (e A^{-3})	0.884 and −0.620

final R values as well as further details of the refinement of the structure are presented in Table 2.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre, CCDC, no. 196565. Copies of this information can be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.ac.uk or http://www.ccdc.cam.ac.uk).

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