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# X-Ray Structural Characterization of Cyclometalated Luminescent Pt(II) Complexes

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## 1. Introduction

The cyclometalated complexes represent one of the most interesting and broadly studied class of organotransition metal complexes. Although there is a strong interest in studying the mechanism of this bond-activation process, cyclometalation is a highly attractive and versatile synthetic approach for generating organometallic systems, with very important application potential (Crabtree, 2005). There are both mononuclear and dinuclear species, but also polynuclear cyclometalated complexes are known (Diez et al., 2011). Many reviews and books have been dedicated to this topic over the past years and one of the most recent can be found here (Albrecht, 2010).

The cyclometalation process consists of a transition metal-mediated activation of a C-R bond to form a metallacycle that contains a metal-carbon  $\sigma$  bond (Hill, 2002). On the other hand, cyclometalation can be regarded as a special case of oxidative addition, in which a C-R (in most cases, C-H) bond in a ligand oxidatively adds to a metal to give rise to a ring.

Although many examples are described, by far most of cyclometalation reactions occur via C-H bond activation. The reaction product is a metallacycle in which the metal is bound by a chelate C- donor ligand. It is important to note that such chelation leads to organometallic compounds with increased stability. Altogether, the cyclometalation reaction has been widely studied because it represents probably one of the mildest route for activating strong C-H and C-R bonds. The tendency of transition metal salts to undergo cyclometalation reaction, and, in particular, ortho-metalation reaction, with heteroaromatic ligands (mostly including nitrogen donors, but oxygen-, sulfur- and phosphorus-containing ligands have also been cyclometalated) to give five-membered metallocycles has been demonstrated with various metals, including, for instance, Re(I), Pt(II), Pd(II). This review will take into account only the cyclometalated Pt(II) complexes with nitrogen-containing ligands.

In comparison with Pd(II), which is by far the most used metal in cyclometalation reactions, the cycloplatination reaction is not so intensively studied and not very easy to accomplish (cycloplatination reactions which took about four weeks or required relatively forcing conditions, e.g., refluxing toluene, with poor yields, have been reported). However, it is possible to increase the yields and reduce the time of reaction by using different starting materials such as bis( $\eta^3$ -allyl)-di- $\mu$ -chlorodiplatinum(II) or  $\text{PtCl}_2(\text{DMSO})_2$ , etc, although  $\text{K}_2\text{PtCl}_4$  or  $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$  are commonly used to yield cyclometalated species. In most of the cases, the reaction products are halo-bridged dimers, that can be used further to form

mononuclear cyclometalates of the type  $[MX(C^N)L^1]$  or  $[M(C^N)L^2]$  ( $M = Pt, Pd$ ;  $C^N$  = orthometalated ligand;  $L^1$  = neutral monodentate ligand such as pyridine and phosphines;  $L^2$  = bidentate uninegative ligand such as acetylacetonate derivatives;  $X$  = halide).

The Pt(II) ions adopt a square-planar geometry, being part of the major group of exceptions to the otherwise very successful model of Kepert. They show coordinative unsaturation which can allow different interactions such as: excimer formation, chemical quenching, interactions with Lewis bases, and oxidative addition. The single-crystal X-ray diffraction is a very powerful technique for characterization of cyclometalated platinum(II) complexes and strong correlations between the structure and luminescence properties can be made as, for example, the solid-state emission is greatly influenced by the crystal packing and the presence of Pt...Pt or  $\pi\cdots\pi$  interactions is favoured by the coordinative unsaturation. This review is intended to cover the most important structural types of cyclometalated Pt(II) complexes that have been investigated by X-ray diffraction with an emphasis on their luminescence properties.

## 2. Photophysical properties of cyclometalated platinum(II) complexes

Cyclometalated Pt(II) complexes have been extensively investigated in the past years because of their interesting photophysical properties and several reviews are dealing with this topic (Evans et al., 2006; Williams et al., 2008; Balashev et al., 1997; Ma et al., 2005; Williams, 2007; McGuire Jr. et al., 2010). Although there is a particular fundamental interest in studying their intrinsic emissive states, their luminescence properties find applications in optoelectronic devices (such as OLED, Williams et al., 2008), luminescent probes for biomolecules (cell imaging, biochemistry, Siu et al., 2005) and chemical sensors (for a recent example see Li et al., 2011). Figure 1 shows a simplified schematic representation (Perrin-Jablonski diagram) of the most important processes that take place through the interaction of matter with light: photon absorption, internal conversion, fluorescence, intersystem crossing and phosphorescence (Valeur, 2001). The emission of photons that accompanies the  $S_1 \rightarrow S_0$  relaxation is called *fluorescence*. Another process visible on this diagram is the *internal conversion* that is a non-radiative transition between two electronic states of the same spin multiplicity. Also, still a non-radiative process is the *intersystem crossing* that represents a transition between two isoenergetic vibrational levels belonging to electronic states of different multiplicities. Crossing between states of different multiplicity is in principle forbidden, but spin-orbit coupling (i.e. coupling between the orbital magnetic moment and the spin magnetic moment) can be large enough to make it possible. The probability of intersystem crossing depends on the singlet and triplet states involved. If the transition  $S_0 \rightarrow S_1$  is of  $n \rightarrow \pi^*$  type, for instance, intersystem crossing is often efficient. It should also be noted that the presence of heavy atom (i.e. whose atomic number is large, as it is the case of Pt) increases spin-orbit coupling and thus favors intersystem crossing. It was found that in solution, at room temperature, non-radiative de-excitation from the triplet state,  $T_1$ , is preferred rather than the radiative de-excitation called *phosphorescence*. This happens because the transition  $T_1 \rightarrow S_0$  is forbidden (but it can be observed because of spin-orbit coupling), and the radiative rate constant is thus very low. On the contrary, at low temperatures and/or in a rigid medium, phosphorescence can be observed. The lifetime of the triplet state may, under these conditions, be long enough to observe phosphorescence on a time-scale up to seconds, even minutes or more. Fluorescence and phosphorescence are particular cases of *luminescence* (emission of light from an electronically excited species).

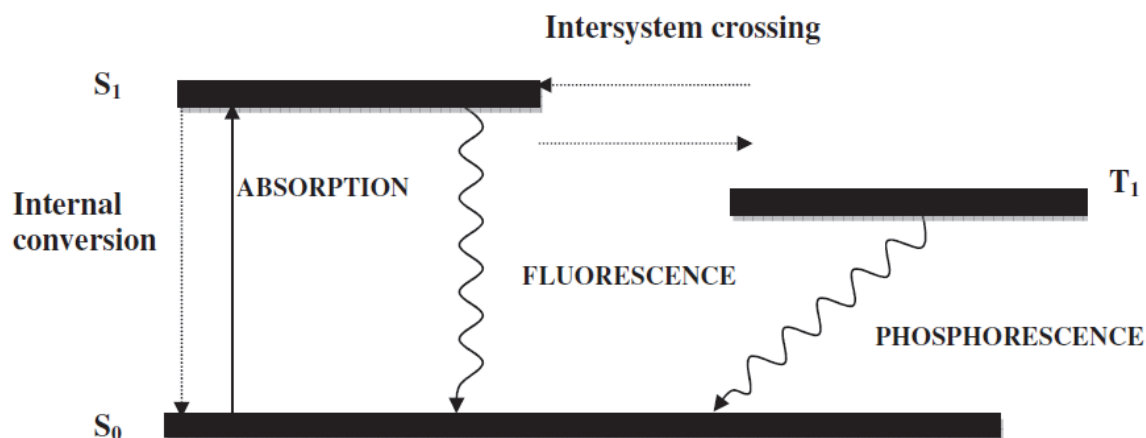
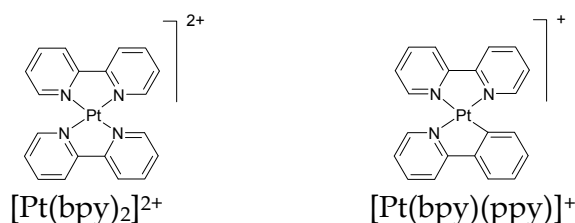


Fig. 1. Schematic representation of the radiative and non-radiative pathways

Thus, in the case of transition metal complexes, there are four types of electronic states or transitions responsible for their luminescent properties, as follows: 1)  $dd$  states (metal-centred, MC, transition). By coordination of the ligands to the metal centre, the  $d$  orbitals are split according to the symmetry of the complex. These excited  $dd$  states arise from promotion of an electron within  $d$  orbitals; 2)  $d\pi^*$  states (metal-to-ligand-charge-transfer, MLCT). These involve excitation of a metal-centred electron to a  $\pi^*$  anti-bonding orbital located on the ligand system; 3)  $\pi\pi^*$  or  $n\pi^*$  states (intraligand, IL, transition). Promotion of an electron from a  $\pi$ -bonding or non-bonding orbital to a higher energy anti-bonding orbital gives rise to these states; 4)  $\pi d$  states (ligand-to-metal-charge-transfer, LMCT). These states arise from the transfer of electronic charge from the ligand  $\pi$  system to a metal-centred orbital.



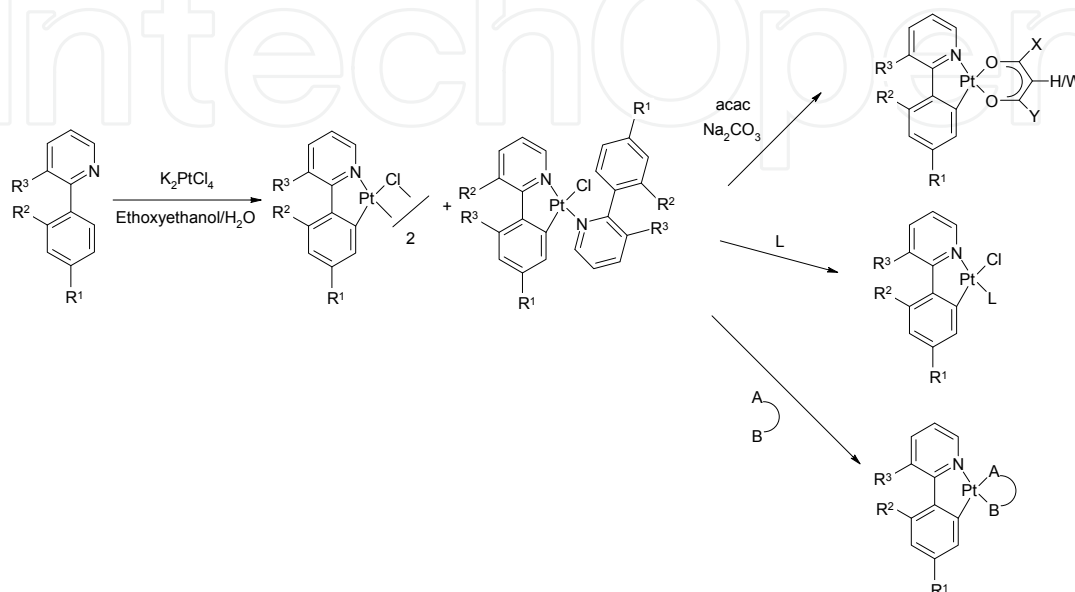
Scheme 1.

The luminescence of Pt(II) complexes is assigned to either ligand-centred (LC) or metal-to-ligand charge transfer (MLCT) states or a mixed of both. The most useful strategy to promote luminescence in platinum(II) complexes is to employ ligands with a very strong ligand field in order to raise the  $dd$  states, so that they are not easily accessible for radiationless deactivation process, and this can be achieved by using cyclometalating ligands, mostly with 2-arylpyridine or 2-thienylpyridine derivatives, resulting both homoleptic (metal complexes with identical ligands) or heteroleptic (metal complexes with different ligands) complexes. The influence of cyclometalated ligands on the photophysical properties of square-planar Pt(II) complexes is clearly seen when the Pt(II) complex with 2,2'-bipyridine (bpy) is compared to the cyclometalated Pt(II) complex with 2-phenylpyridine (ppy) (Scheme 1). While the  $[Pt(bpy)_2]^{2+}$  is almost non-emissive at room temperature, the Pt(II) cyclometalated complex  $[Pt(bpy)(ppy)]^+$  shows emission with a quantum yield nearly 0.02 at 298K (Kvam, Jongstad, 1995; Kvam et al., 1995).

### 3. X-ray structural characterization of cyclometalated Pt(II) complexes

#### 3.1 Pt(II) complexes with 2-phenylpyridine (ppy) and its derivatives as cyclometalating ligand

The homoleptic Pt(II) complex with 2-phenylpyridine was prepared by reacting  $[\text{PtCl}_2(\text{Et}_2\text{S})_2]$  with the lithiated ligand as the *cis* isomer and its crystal structure was reported in 1984 (Chassot et al., 1984).



R<sup>1</sup>=NPh<sub>2</sub>, R<sup>2</sup>=R<sup>3</sup>=H, X=Y=Me **1a**

R<sup>1</sup>=-oxadiazole-4-Ph-p-NPh<sub>2</sub>, R<sup>2</sup>=R<sup>3</sup>=H, X=Y=Me **1b**

R<sup>1</sup>=-oxadiazole-4-Ph-p-NTol<sub>2</sub>, R<sup>2</sup>=R<sup>3</sup>=H, X=Y=Me **1c**

R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H, X=Y=Ph **1d**

R<sup>1</sup>=R<sup>2</sup>=F, R<sup>3</sup>=H, X=Y=Me, W=-(CH<sub>2</sub>)<sub>2</sub>-norbornene **1e**

R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H, L=CO **2a**

R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H, L=DMSO **2b**

R<sup>1</sup>=F, R<sup>2</sup>=R<sup>3</sup>=H, L=DMSO **2c**

R<sup>1</sup>=F, R<sup>2</sup>=R<sup>3</sup>=H, L=py-2-Ph-4'-F **2d**

R<sup>1</sup>=R<sup>2</sup>=F, R<sup>3</sup>=H, L=py-2-Ph-2',4'-F<sub>2</sub> **2e**

R<sup>1</sup>=R<sup>2</sup>=F, R<sup>3</sup>=H, A<sup>^</sup>B=3,5-di-*t*Bu-catechol **3**

R<sup>1</sup>=R<sup>2</sup>=H, R<sup>3</sup>=-OHex,

A<sup>^</sup>B=5-NO<sub>2</sub>-8-quinoline **4**

R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H,

A<sup>^</sup>B=Et<sub>2</sub>NC(S)NCOPh **5a**

R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H,

A<sup>^</sup>B=MeO-4-C<sub>6</sub>H<sub>4</sub>NHC(S)NCOPh **5b**

R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H,

A<sup>^</sup>B=2-pyridyl hexafluoropropoxide **6**

R<sup>1</sup>=R<sup>2</sup>=F, R<sup>3</sup>=H, A<sup>^</sup>B=(pz)<sub>2</sub>BEt<sub>2</sub> **7**

R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H, A<sup>^</sup>B=(3,5-Me<sub>2</sub>pz)BH<sub>2</sub> **8**

R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H, A<sup>^</sup>B=dppm, PF<sub>6</sub> **9**

Scheme 2. The preparation of mononuclear cyclometalated Pt(II) complexes with 2-phenylpyridine derivatives

Generally, the heteroleptic complexes are prepared by the cyclometalation of the corresponding ligand using K<sub>2</sub>PtCl<sub>4</sub> in ethoxyethanol to give, in the first step, as a major product, the chloro-bridged dinuclear complex and, in some cases, as a minor product, the mononuclear complex having two molecules of ppy ligand. In the next step, the bridge-splitting reaction, various monodentate (L) or bidentate (A<sup>^</sup>B) ligands can be used to yield the mononuclear neutral or ionic heteroleptic complexes (see Scheme 2). By far, the most studied Pt(II) cyclometalated complexes bearing ppy ligand for their emission properties are the ones containing acetylacetonate (acac) derivatives as ancillary ligands (Brooks et al, 2002). Various other R<sup>1</sup>-R<sup>3</sup> substituents were attached on the ppy core with the aim of conferring different multifunctionalities to the resulting molecules. For instance, He et al.,

2006, reported the synthesis and structural, photophysical, electrochemical, and electroluminescent properties of a novel class of trifunctional Pt(II) cyclometalated complexes incorporating the hole-transporting triarylamine, electron-transporting oxadiazole, and electroluminescent metal components into a single molecule (**1a-c**). Other studies focused on functionalizing the acac derivatives, as it is the example reported by Cho et al., 2007, in which the norbornene-functionalized derivative of acetylacetone has been used to synthesize a series of new polymerizable norbornene-derivatized phosphorescent platinum complexes (**1e**). For these acac Pt(II) complexes, it was found that the two Pt-O bonds are different, with the Pt-O1 trans to C atom bond longer than the Pt-O2 trans to N bond due to the strong trans influence of C-ppy donor atom (Table 1).

Several crystal structures of cyclometalated Pt(II) complexes bearing monodentate neutral ligands such as DMSO or pyridine derivatives were reported (**2a-e**). Another strategy to obtain mononuclear Pt(II) species is to use bidentate mononegative ligands and various such examples were reported so far (**3 - 8**).

By using sodium salts of *N*-benzoylthiourea derivatives, a series of luminescent Pt(II) ppy complexes were prepared and investigated by single-crystal X-ray diffraction (**5a, b**) (Figure 2).

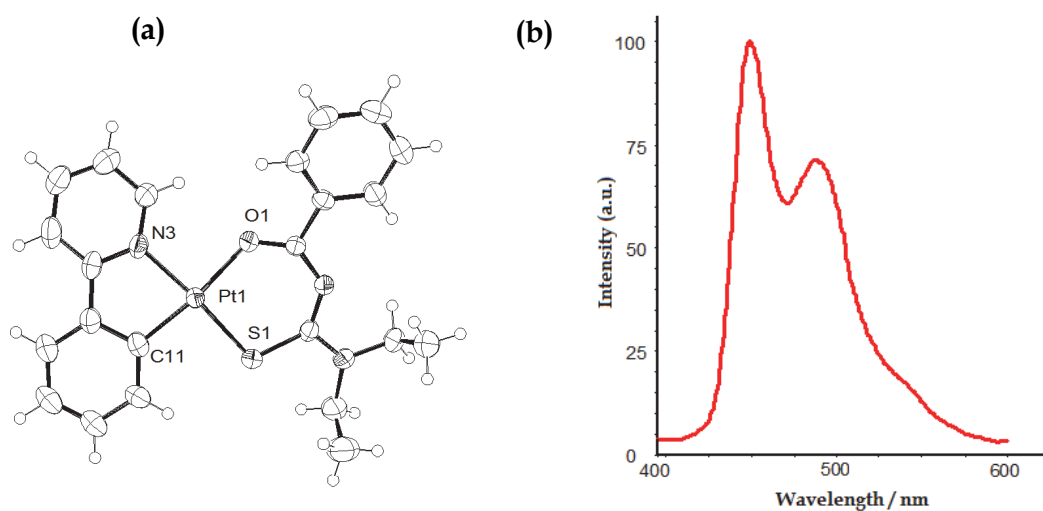


Fig. 2. ORTEP view of complex **5a** (a); the emission spectrum of **5a** recorded in  $\text{CH}_2\text{Cl}_2$  solution at room temperature (b)

An interesting feature of the structure of complex **5b** is the orientation adopted by the *p*-anisyl ring of the *N*-benzoyl thiourea ligand with a twist of  $65.1^\circ$  with respect to the core plane, leading to the formation of weak intermolecular  $\text{NH}\cdots\text{Pt}$  interactions ( $\text{H}\cdots\text{Pt}$  2.74 Å;  $\text{N}\cdots\text{H}\cdots\text{Pt}$   $156.8^\circ$ ) compared to those found in the salt  $(\text{N}^n\text{Pr}_4)_2[\text{PtCl}_4][\text{PtCl}_2(\text{NH}_2\text{Me})_2]$ . In this case, the shortest Pt-Pt distance between two neighbouring molecules is 4.18 Å.



Complex	Pt-C	Pt-N	Pt-O1	Pt-O2	Reference
1a	1.957(4)	1.995(4)	2.094(3)	2.001(3)	He et al., 2006
1b	1.921(13)	1.955(11)	2.088(9)	1.991(9)	He et al., 2006
1c	1.969(3)	1.996(3)	2.079(2)	2.002(2)	He et al., 2006
1d	1.954(5)	1.978(5)	2.082(4)	2.006(4)	Liu et al., 2009
1e	2.002(8)	2.020(9)	2.070(7)	2.058(6)	Cho et al., 2007
	Pt-C	Pt-N	Pt-Cl	Pt-L	
2a	1.981(24)	2.114(19)	2.391(11)	1.84(3)	Mdleleni et al., 1995
2b	2.001(4)	2.055(3)	2.4187(1)	2.2181(1)	Godbert et al., 2007
2c	1.998(5)	2.065(4)	2.3962(17)	2.2161(16)	Newman et al., 2007
2d	1.941(10)	2.002(7)	2.412(3)	2.023(8)	Newman et al., 2007
2e	1.987(6)	2.014(7)	2.383(2)	2.045(5)	Rausch et al., 2010
	1.983(6)	2.021(5)	2.3912(16)	2.046(5)	
	Pt-C	Pt-N	Pt-A	Pt-B	
3	1.976(10)	1.969(10)	2.123(8)	1.981(8)	Hirani et al., 2007
4	1.988(2)	1.989(2)	2.0969(18)	2.028(2)	Niedermair et al., 2008
5a	1.973(5)	2.045(5)	2.076(3)	2.2389(15)	Circu et al., 2009a
5b	1.979(6)	2.035(5)	2.075(4)	2.2447(14)	Circu et al., 2009a
6	1.992(4)	1.989(3)	2.082(3)	2.033(3)	Chang et al., 2008
7	1.981(5)	2.006(5)	2.074(4)	2.010(4)	Ma et al., 2005
8	1.997(2)	2.013(2)	2.1092(16)	2.0297(19)	Niedermair et al., 2007
9	2.038(7)	2.073(6)	2.318(2)	2.228(2)	DePriest et al., 2000

Table 1. Selected bond lengths for compounds 1 - 9

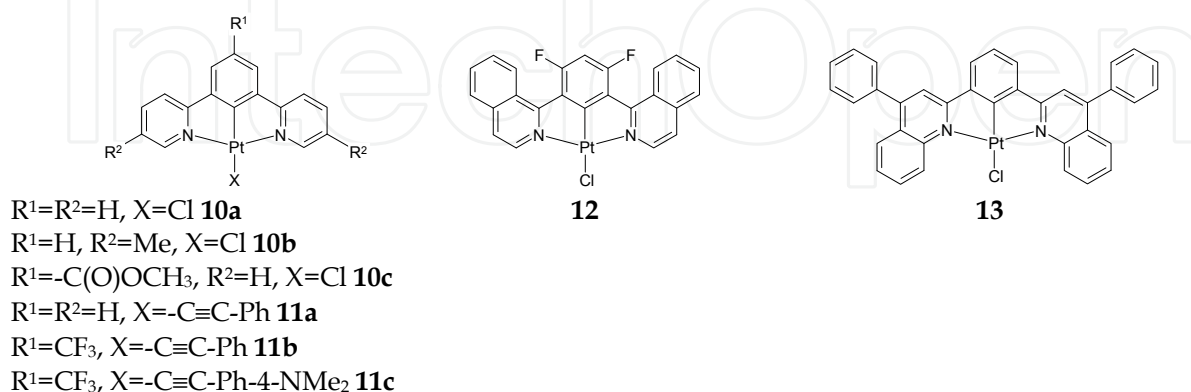
3.2 Cyclometalated Pt(II) complexes with “pincer” ligands

The cyclometalated Pt(II) complexes with terdentate “pincer” type ligands were investigated intensively, in part due to the fact that such ligands may provide additional rigidity to the molecule that could be responsible for favouring the luminescence properties. Many types of pincer ligands have been used in the preparation of both mono- or polynuclear organometallic Pt(II) complexes and they are divided according to the donor atom set involved in bond formation with the metal centre, as follows: N^C^N, C^N^N and C^C^N complexes.

3.2.1 N^C^N ligands

Several crystal structures of N^C^N Pt(II) complexes were reported and these are summarised in Scheme 3, while the selected bond lengths are included in Table 2. The chloride Pt(II) complexes (10a-c, 12, 13) can be easily obtained by orthometalation reaction of the corresponding N^C^N pincer ligand with K<sub>2</sub>PtCl<sub>4</sub> in acetic acid with high yields, while the acetylide complexes 11a-c were prepared in quantitative yields starting from the corresponding chloride precursor, with an excess of aryl acetylene in methanol in the presence of NaOH for one day at room temperature. The crystal structures of complexes 11b

and **11c** show several interesting features such as the intermolecular Pt··Pt,  $\pi\cdots\pi$  and C-H·· $\pi$ (C≡C) interactions in an orthogonal configuration. On the other hand, the crystal structure of **11a** shows the formation of dimers in a head-to-tail fashion with an interplanar distance of approximately 3.4 Å and a shortest intermetallic separation of 4.886 Å, indicating the presence of  $\pi\cdots\pi$  interaction, but not a Pt··Pt interaction. The presence of such intermetallic interactions has a marked impact upon the solid state emission properties.



Scheme 3.

Complex	Pt – C	Pt-N1	Pt-N2	Pt-X	Reference
<b>10a</b>	1.907(8)	2.033(6)	2.041(6)	2.417(2)	Cardenas et al., 1999
<b>10b</b>	1.915(3)	2.041(2)	2.027(2)	2.409(1)	Abe et al., 2007
<b>10c</b>	1.903(4)	2.036(3)	2.035(3)	2.4050(10)	Williams et al., 2003
<b>12</b>	1.918(8)	2.021(7)	2.009(7)	2.412(2)	Wang et al., 2010
<b>13</b>	1.908(3)	2.075(3)	2.060(3)	2.4343(9)	Baik et al., 2006

Table 2. A selection of bond lengths for some N<sup>^</sup>C<sup>^</sup>N Pt(II) complexes

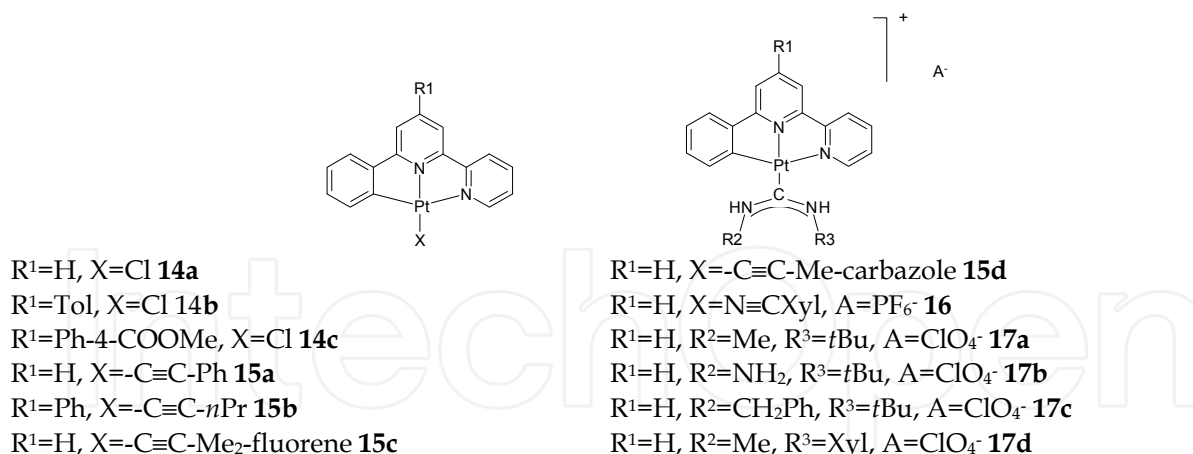
The room temperature structureless emissions at  $\lambda_{max}$  819 (**11b**) and 702 nm (**11c**), respectively, strongly red-shifted compared to solution emission ( $\lambda_{max}$  = 486 and 480, respectively), can be assigned to triplet metal-metal-to-ligand charge-transfer (<sup>3</sup>MMLCT) excited states. The photophysical properties of chloride complexes (**10a-c**) and analogous with various other  $R^1$  substituents were systematically studied by Farley et al., 2005. It is interesting to note that these N<sup>^</sup>C<sup>^</sup>N Pt(II) complexes show relatively shorter Pt-C distances than those found in C<sup>^</sup>N<sup>^</sup>N Pt(II) complexes (see comparatively Tables 2 and 3).

### 3.2.2 C<sup>^</sup>N<sup>^</sup>N ligands

The C<sup>^</sup>N<sup>^</sup>N type ligands were used in the preparation of both neutral or ionic complexes (see Scheme 4).

An important feature of these complexes is that the central Pt-N1 bond is shorter than the marginal Pt-N2 bond (Table 3) due to the *trans* influence of the strong field cyclometalated ligand. Two crystal structures of **14a** were determined (yellow and red polymorphs). The red colour of the latter polymorph was attributed to the Pt··Pt intermolecular interactions (3.366 Å).





Scheme 4.

Complex	Pt - C	Pt - N1	Pt-N2	Pt-X	Reference
<b>14a</b>	2.014(9)	1.946(6)	2.124(8)	2.316(2)	Hofmann et al., 2003
	1.995(8)	1.950(6)	2.116(6)	2.307(2)	
<b>14b</b>	1.993(3)	1.954(3)	2.109(3)	2.3657(7)	Schneider et al., 2009
<b>14c</b>	2.10(2)	2.01(2)	1.99(2)	2.323(7)	Schneider et al., 2009
	2.14(2)	2.05(3)	1.96(2)	2.306(7)	
<b>14d</b>	1.987(9)	1.943(8)	2.091(9)	2.315(3)	Qiu et al., 2009
<b>14e</b>	2.021(4)	1.868(3)	2.082(4)	2.2807(15)	Qiu et al., 2010
<b>15a</b>	1.992(5)	1.987(4)	2.123(4)	1.970(5)	Lu et al., 2004
<b>15b</b>	2.060(13)	1.986(10)	2.109(12)	1.982(16)	Shao et al., 2008
<b>15c</b>	2.068(4)	1.984(4)	2.042(4)	1.956(5)	Seneclauze et al., 2007
<b>15d</b>	1.988(9)	1.992(6)	2.119(7)	1.973(9)	Seneclauze et al., 2007
<b>16</b>	2.079(19)	2.004(25)	2.090(13)	1.839(26)	Yuen et al., 2008
<b>17a</b>	2.001(8)	1.995(6)	2.117(6)	1.997(7)	Lai et al., 1999
<b>17b</b>	2.010(5)	1.998(4)	2.109(4)	1.992(4)	Lai et al., 1999
<b>17c</b>	1.989(6)	1.999(5)	2.087(6)	1.989(6)	Lai et al., 1999
<b>17d</b>	2.033(9)	2.006(6)	2.110(8)	1.996(8)	Lai et al., 1999

Table 3. Selected bond lengths for C<sup>^</sup>N<sup>^</sup>N Pt(II) complexes **14** - **17**

The chloride ligand can be easily replaced by acetylide ligands to yield various neutral Pt(II) complexes that could be investigated by X-ray crystallography. Thus, such acetylide complexes show high efficient luminescence properties due to the combination of the strong field cyclometalated ligand with the strong field acetylide ligands and the rigidity of the terdentate ligands. Important, their emission properties could be tuned by varying either  $R^1$  substituent on the C<sup>^</sup>N<sup>^</sup>N ligand or the acetylide ligand and several studies were reported on this topic (Lu et al., 2004). A series of luminescent cyclometalated platinum(II) diamino-carbene complexes (**17a-d**) were prepared by nucleophilic attack of amines at the coordinated isocyanide ligands of  $[(C^N^N)PtC\equiv NR]^+$  ( $R = tBu$  or  $Ar$ ). Weak  $\pi\cdots\pi$  stacking interactions between the cyclometalated ligands were observed in the crystal lattice (range 3.5–3.6 Å). These complexes, **17a-d**, show structureless emissions, with  $\lambda_{max}$  ranging from

528 to 558 nm in acetonitrile at 298 K, which were assigned to  $^3\text{MLCT}$  excited states. Also, dinuclear phosphorescent  $\text{C}^{\wedge}\text{N}^{\wedge}\text{N}$  Pt(II) cyclometalated were prepared (also investigated by X-ray crystallography) by using diacetylide – carbazole bridging ligand (Seneclauze et al., 2007).

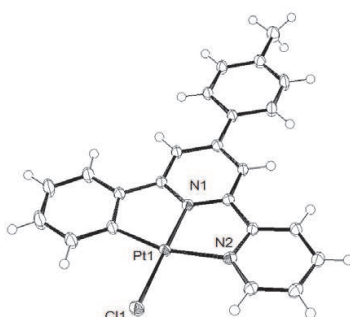
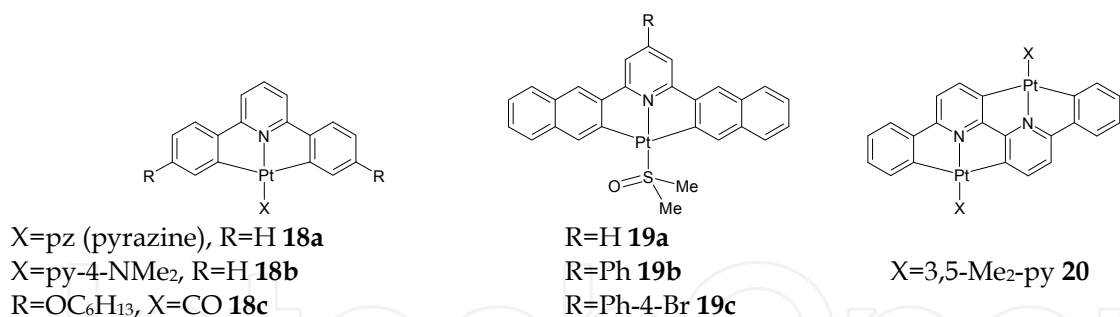


Fig. 3. ORTEP view of complex **14b**

### 3.2.3 $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$ ligands

The  $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$  cyclometalated Pt(II) complexes are synthesised by using  $\text{K}_2\text{PtCl}_4$  and the corresponding 2,6-diphenyl-pyridine derivative, in two consecutive cyclometalation reactions. In the first step, a dinuclear chloride-bridged  $\text{C}^{\wedge}\text{N}$  cyclometalated Pt(II) complex is obtained, followed by reaction with a monodentate neutral ligand to give mononuclear neutral  $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$  species. Several crystallographic studies were carried out on such systems and these are summarised in Scheme 5 and Table 4.



Scheme 5.

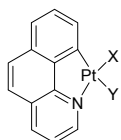
Complexes **19a-c** were prepared by reacting  $\text{K}_2\text{PtCl}_4$  with the terdentate 2,6-di-(2'-naphthyl)-pyridine ligands in glacial acetic acid, followed by heating in DMSO. Their crystal structures reveal that the molecules are paired in a head-to-tail orientation with Pt...Pt separations longer than 6.3 Å, with extensive close C-H... $\pi$  ( $d = 2.656\text{--}2.891$  Å) and  $\pi$ ... $\pi$  ( $d = 3.322\text{--}3.399$  Å) interactions. An interesting feature of such  $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$  Pt(II) complexes is that the Pt-C bonds are longer compared to the  $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$  or  $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$  Pt(II) complexes and this is due the *trans* influence of C atoms on each other. These complexes are emissive in both solid state, with the maxima in the range 600 – 650 nm (**19a-c**), and in solution at 77 K (**18a**). Additionally, several dinuclear  $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$  cyclometalated Pt(II) complexes, either by using a dicyclopentadienyl ligand (Zucca et al., 2006) or a diphosphine ligand as a bridge (dppm, diphenylphosphinomethane, Kui et al., 2006), were investigated by X-ray crystallography.

Complex	Pt-C1	Pt-C2	Pt-N	Pt-X	Reference
<b>18a</b>	2.05(1)	2.08(5)	-	1.99(7)	Kulikova et al., 2003
<b>18b</b>	2.06(1)	2.05(1)	1.98(1)	2.04(1)	Lusby et al., 2009
<b>18c</b>	2.070(6)	2.055(6)	2.007(5)	1.827(6)	Newman et al., 2001
<b>19a</b>	2.095(5)	2.074(4)	2.011(4)	2.1915(13)	Kui et al., 2006
<b>19b</b>	2.082(6)	2.058(6)	2.008(4)	2.1927(12)	Kui et al., 2006
<b>19c</b>	2.101(6)	2.070(6)	2.016(5)	2.1959(18)	Kui et al., 2006
<b>20</b>	2.054(6)	2.104(6)	1.983(5)	2.036(5)	Zucca et al., 2006

Table 4. Selected bond lengths for C<sup>N</sup>C Pt(II) compounds **18** - **20**

### 3.3 Pt(II) complexes with benzo(h)quinoline (bzq) as cyclometalating ligand

The homoleptic Pt(II) complex with benzo(h)quinoline was prepared by reacting [PtCl<sub>2</sub>(Et<sub>2</sub>S)<sub>2</sub>] with the lithiated ligand, its crystal structure being reported in 1996 (Joliet et al., 1996). It was found that the crystal structure shows an important distortion from the square planar geometry towards a two-bladed helix with average Pt-C and Pt-N distances being 1.988 and 2.151 Å, respectively.



X=Y=-C≡C-Ph, Kat=NBu<sub>4</sub><sup>+</sup> **21**

X=Y=-C≡C-Py-2, Kat=NBu<sub>4</sub><sup>+</sup> **22**

X=Y=-C≡C-Ph, Kat=Pb<sup>2+</sup> **23**

X=-C≡C-Ph, Y=PPh<sub>2</sub>(C≡CPh) **24**

X=Y=-C≡N-Xyl, A=ClO<sub>4</sub><sup>-</sup> **25a**

X=Y=-C≡N-Xyl, A=PF<sub>6</sub><sup>-</sup> **25b**

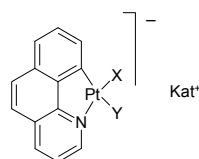
X=-C≡N-Xyl, Y=Cl **26**

X=-C≡N-*t*Bu, Y=Cl **27**

X=-C≡N-2-Np, Y=Cl, Np=Naphtyl **28**

X=PPh<sub>2</sub>, Y=Cl **29**

X=Y=2-pyridyl hexafluoropropoxide **36**



X=Y=PPh<sub>2</sub> **30**

X=Y=dppm, PF<sub>6</sub><sup>-</sup> **31a**

X=Y=dppe, A=PF<sub>6</sub><sup>-</sup> **31b**

X=Y=dppp, A=PF<sub>6</sub><sup>-</sup> **31c**

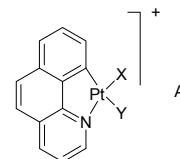
X=dppm, Y=4-Tol, Tol=tolyl **32**

X=DMSO, Y=Cl **33a**

X=4-MeO-Py, Y=Cl **33b**

X=SMe<sub>2</sub>, Y=4-Tol **34**

X=Y=[9]aneS<sub>3</sub>,  
1,4,7-trithiacyclononane, A=PF<sub>6</sub><sup>-</sup> **35**



Scheme 6. Heteroleptic cyclometalated Pt(II) complexes containing the benzo(h)quinoline ligand

Various heteroleptic cyclometalated Pt(II) complexes either ionic or neutral were synthesized starting from the binuclear  $\mu$ -chloro bridged complex, and analysed through single-crystal X-ray diffraction. They are summarised in Scheme 6 and their crystallographic data are included in Table 5.

An interesting example showing how the Pt...M interactions affect the photoluminescence properties for such complexes bearing the cyclometalated bzq together with acetylide ligands is represented by complex **23**, whose molecular structure is depicted in Figure 4, which has very short Pt<sup>II</sup>...Pb<sup>II</sup> (2.9758(5) and 2.9182(5) Å) and Pt...Pt distances (3.579 Å). For this complex, the emissive state in solid state (77 K) is attributed to a <sup>3</sup>MLM'CT [Pt(1) $\pi$ (C≡CPh)→Pt(2)/Pb(sp) $\pi^*$ (C≡CPh)] state mixed with some  $\pi\pi^*$  excimeric character.

Another interesting group of cyclometalated Pt(II) complexes bearing benzoquinolate ligand is represented by those complexes containing isocyanide ligands. They have been found to show interesting photophysical properties, including low-energy emissions in fluid solution, depending on either the counteranion, isocyanide (CNR) ligand or crystal packing. Diez et al. recently reported the X-ray crystal structures of the isocyanide benzoquinolate Pt(II) complexes  $[\text{Pt}(\text{bzq})(\text{CNR})_2]\text{X}$  ( $\text{R} = \text{Xyl}$ ,  $\text{X} = \text{ClO}_4^-$ ,  $\text{PF}_6^-$ , **25a,b**) as well as the influence of the counteranion and concentration on their luminescent properties (Diez et al., 2009a). The crystal packing of the two complexes containing the cation  $[\text{Pt}(\text{bzq})(\text{CN-Xyl})_2]^+$  and different counteranions (**25a** and **25b**) was found to show significant differences, although in both cases  $\pi\cdots\pi$  intermolecular interactions are present. The same authors (Diez et al., 2010a) reported the crystal structures and the photophysical properties of the neutral complexes  $[\text{Pt}(\text{bzq})\text{Cl}(\text{CNR})]$  ( $\text{R} = \text{Xyl}$ , **8**,  $t\text{-Bu}$  **9**, 2-Np **10**), where  $\text{Xyl} = 2,6\text{-dimethyl-phenyl}$  or  $\text{xylyl}$  and  $\text{Np} = \text{naphthyl}$ . It was found that compound **26** forms only yellow crystals in which two monomers are weakly contacting through  $\pi\cdots\pi$  (bzq) interactions. The complex **27** with tert-butyliisocyanide ligand shows solid-state pseudopolymorphic behaviour. Thus, two X-ray structures are reported: a red form, which exhibits an infinite 1-D chain network, including a molecule of chloroform as crystallizing solvent,  $[\text{27}\cdot\text{CHCl}_3]_\infty$  (**27a**), and a yellow form which consists of discrete dimers,  $[\text{27}\cdot 0.5\text{H}_2\text{O}]_2$  (**27b**). The crystal packing of these two forms is stabilised by short Pt $\cdots$ Pt distances and  $\pi\cdots\pi$  (bzq) interplanar bonding interactions. Indeed, the extended 1D-chain of **27a** exhibits equivalent Pt(II)-Pt(II) distances of 3.3547(2) Å and a nearly linear Pt $\cdots$ Pt $\cdots$ Pt angle [169.12(2)°], thus indicating some degree of Pt $\cdots$ Pt interactions along the chain.

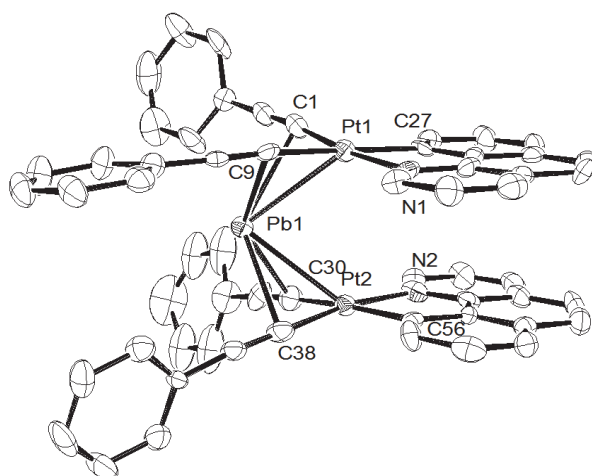


Fig. 4. ORTEP view of complex **23**

When the 2-naphthylisocyanide ligand was employed, again, two isomeric species have been isolated, a neutral yellow derivative, which crystallizes as a Pt $\cdots$ Pt dimer,  $[\text{Pt}(\text{bzq})\text{Cl}(\text{CN-2-Np})]_2$  (**28a**), and a double salt  $[\text{Pt}(\text{bzq})(\text{CN-2-Np})_2]^+[\text{Pt}(\text{bzq})\text{Cl}_2]^-$  (**28b**). Another category of ancillary ligands widely used in the preparation of cyclometalated Pt(II) benzoquinolate complexes are the phosphine ligands, both in mono and bidentate form. The simplest one is the neutral complex **29** in which the diphenylphosphine ( $\text{PPh}_2$ ) ligand is bound to the platinum center while the coordination sphere is completed with a chloride anion. It is interesting that when the  $[\text{Pt}(\text{bzq})(\mu\text{-Cl})]_2$  was reacted with  $\text{PPh}_2$  and excess of  $\text{NEt}_3$ , then a phosphide-bridge platinum dimer  $[\text{Pt}(\text{bzq})(\mu\text{-PPh}_2)]_2$  (**30**) was obtained.

Complex	Pt – C	Pt – N	Pt – X	Pt – Y	Reference
21	2.055(7)	2.065(8)	2.007(9)	1.985(11)	Fernandez et al, 2003
22	2.050(4)	2.074(4)	1.976(6)	1.992(5)	Fernandez et al., 2003
	2.047(4)	2.063(4)	1.975(6)	1.975(5)	
23	2.060(9)	2.088(7)	1.97(1)	2.02(1)	Berenguer et al., 2008
	2.06(1)	2.058(8)	1.97(1)	2.02(1)	
24	2.061(4)	2.111(4)	1.965(5)	2.316(1)	Diez et al., 2005
25a	2.034(3)	2.059(2)	1.916(2)	2.013(3)	Diez et al, 2009a
25b	2.051(2)	2.049(2)	1.956(2)	1.970(3)	Diez et al, 2009a
26	1.998(5)	2.075(4)	1.895(5)	2.393(1)	Diez et al., 2010a
27a	2.012(10)	2.049(8)	1.899(12)	2.427(3)	Diez et al., 2010a
27b	2.011(7)	2.075(6)	1.896(8)	2.398(2)	Diez et al., 2010a
28	1.972(11)	2.064(9)	1.913(14)	2.404(3)	Diez et al., 2010a
	2.011(11)	2.090(9)	1.915(1)	2.390(3)	
29	2.014(5)	2.090(4)	2.210(1)	2.387(1)	Diez et al., 2005
30	2.092(3)	2.092(4)	2.298(1)	2.298(1)	Diez et al., 2005
31a	2.09(2)	2.08(2)	2.266(5)	2.321(6)	DePriest et al., 1997
31b	2.02(2)	2.09(2)	2.235(6)	2.334(6)	DePriest et al., 1997
31c	2.100(9)	2.084(10)	2.297(3)	2.301(3)	DePriest et al., 1997
32	2.038(2)	2.139(2)	2.3095(6)	2.003(2)	Nabavizadeh et al., 2010
33a	2.006(3)	2.064(3)	2.2074(1)	2.4032(1)	Godbert et al., 2007
33b	1.981(2)	2.024(2)	2.029(2)	2.390(7)	Godbert et al., 2007
34	2.05(1)	2.141(8)	2.358(3)	2.030(9)	Nabavizadeh et al. 2010
35	2.029(9)	2.052(7)	2.334(3)	2.268(2)	Janzen et al., 2008
36	2.005(9)	2.028(6)	1.996(6)	2.041(7)	Chang et al. 2008

Table 5. Crystallographic data of the cyclometalated Pt(II) complexes containing benzoquinoline ligand

A series of cyclometalated Pt(II) complexes with several bidentate bis-diphenylphosphine ligands where the bridge length between the two phosphine units was varied (bis-diphenylphosphinomethane (dppm), bis-diphenylphosphinoethane (dppe) and bis-diphenylphosphinopropane (dppp), respectively, **31a-c**) were prepared and investigated structurally by DePriest et al., 1997. These complexes are a beautiful examples where the C and N atoms can be distinguished based on their different *trans* influence: the anionic C is a better  $\sigma$ -donor and thus, has a greater *trans* influence compared to N atom. This difference can be easily seen in the Pt-P bond lengths, with the Pt-P *trans* to C atom bond being longer than Pt-P *trans* to N atom bond. All these complexes show emission properties in solution (ethanol/methanol = 4/1, v/v) at low temperatures (77 – 180 K), assigned to ligand-centred (LC) transitions.

Several other cycloplatinated clusters containing bridged phosphine or phosphido ligands have been prepared. If the neutral binuclear phosphido complex [Pt(bzq)( $\mu$ -PPh<sub>2</sub>)]<sub>2</sub> (**30**) reacts with cis-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub> at 1:2 molar ratio, then a bent neutral triplatinum cluster [Pt<sub>3</sub>(bzq)( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] can be isolated. Its crystal structure was reported by Diez et al, 2006. The crystal structure of complex **35** reveals the two different Pt-S bonds due to

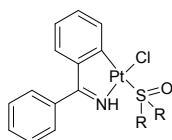


the different *trans* influence of the C and N atoms of the cyclometalated ligands, with Pt-S *trans* to C atom longer than the Pt-S *trans* to N atom.

Interestingly, complex **36** bearing chelating 2-pyridyl hexafluoropropoxide ancillary ligand shows evidence for the occurrence of  $\pi\cdots\pi$  stacking between the cyclometalated ligands, but a lack of intermolecular Pt-Pt interaction. The  $\pi\cdots\pi$  stacking was also confirmed by the observation of additional large Stokes shifted emission attributed to the aggregated counterparts in solid thin film.

### 3.4 Cyclometalated Pt(II) complexes with imine ligands

Although various cyclometalated Pt(II) species are intensively studied for their luminescent properties, surprisingly, almost no attention was given so far to the luminescent cycloplatinated imino species. It is almost very recent that these types of complexes started to be investigated for their photophysical properties as well (Scaffidi-Domianello et al., 2007).



Scheme 7. Cyclometalated Pt(II) complex with benzophenone imine ligands. R = Me, (**37a**), (Pt-C = 2.006(9)Å, Pt-N = 2.019(6)Å, Pt-S = 2.215(2)Å, Pt-Cl = 2.392(2)Å); R = (CH<sub>2</sub>)<sub>4</sub>, (**37b**), (Pt-C = 2.016(4)Å, Pt-N = 2.019(4)Å, Pt-S = 2.2063(13)Å, Pt-Cl = 2.3925(11)Å)(Scaffidi-Domianello et al., 2007)

In **37a**, the asymmetric unit contains two independent Pt complexes, while in **37b**, it includes four Pt complexes linked by the intermolecular hydrogen-bonding network between the NH group and Cl atoms (Figure 5). The Pt-X distances for only one molecule are indicated in Scheme 7. There is no significant Pt-Pt interactions in the solid state. The two Pt(II) complexes show an emission band with the maximum located at 535 nm, along with another less intense emission at 565 nm. The solution quantum yields of the complexes are rather low, with values smaller than 0.0071.

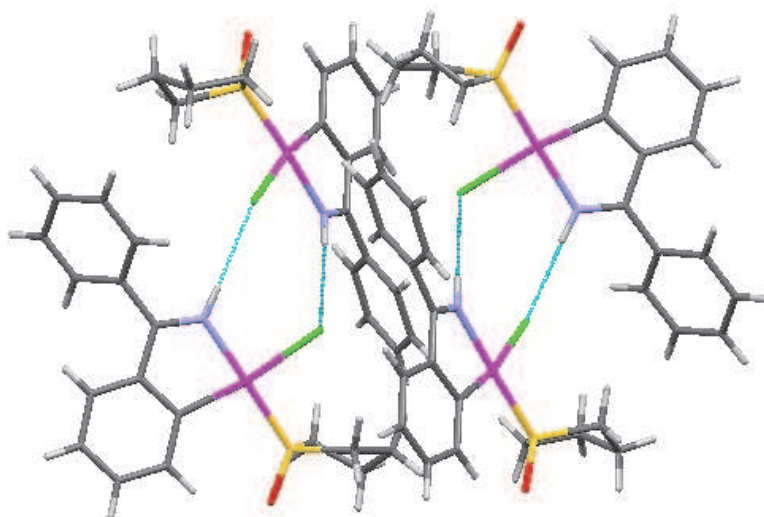


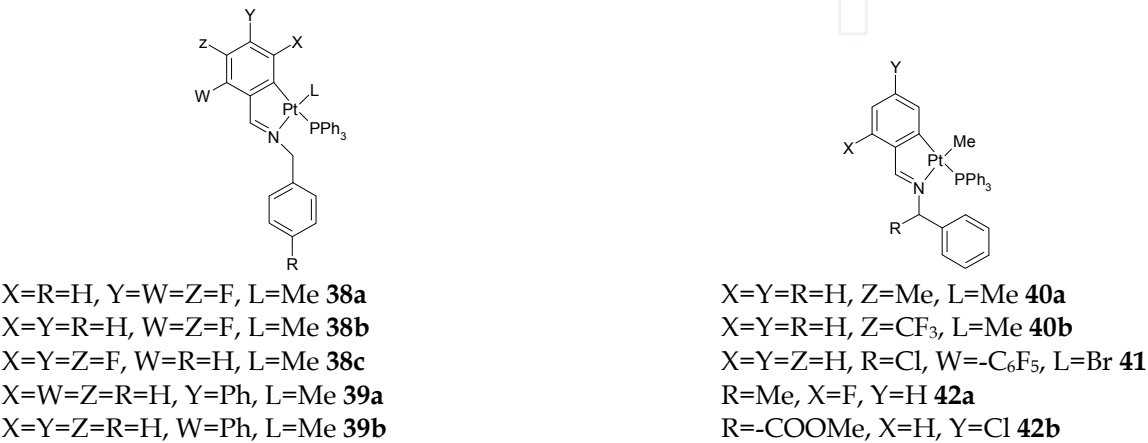
Fig. 5. The hydrogen bonding network connecting four independent molecules in the unit cell of **37b** (this figure was generated by using the Mercury 2.2 software)



The solid-state emission spectra for these complexes show emission maxima at 571 and 559 nm, respectively. These two complexes also exhibit some structure of the emission bands with high and low energy shoulders at 542 and 624 nm and at 525 and 610 nm, respectively. The excited-state emission lifetimes at 575 nm are in the range of 320-615 ns, consistent with the phosphorescence emissive mechanism.

3.4.1 Cyclometalated Pt(II) complexes with N-Benzylidenebenzylamine ligands

This class of cycloplatinated complexes was intensively investigated, but almost for mechanistic studies and not for emission properties. The most representative structural types are presented in Scheme 8.



Scheme 8. Pt(II) complexes with N-benzylidenebenzylamine ligands

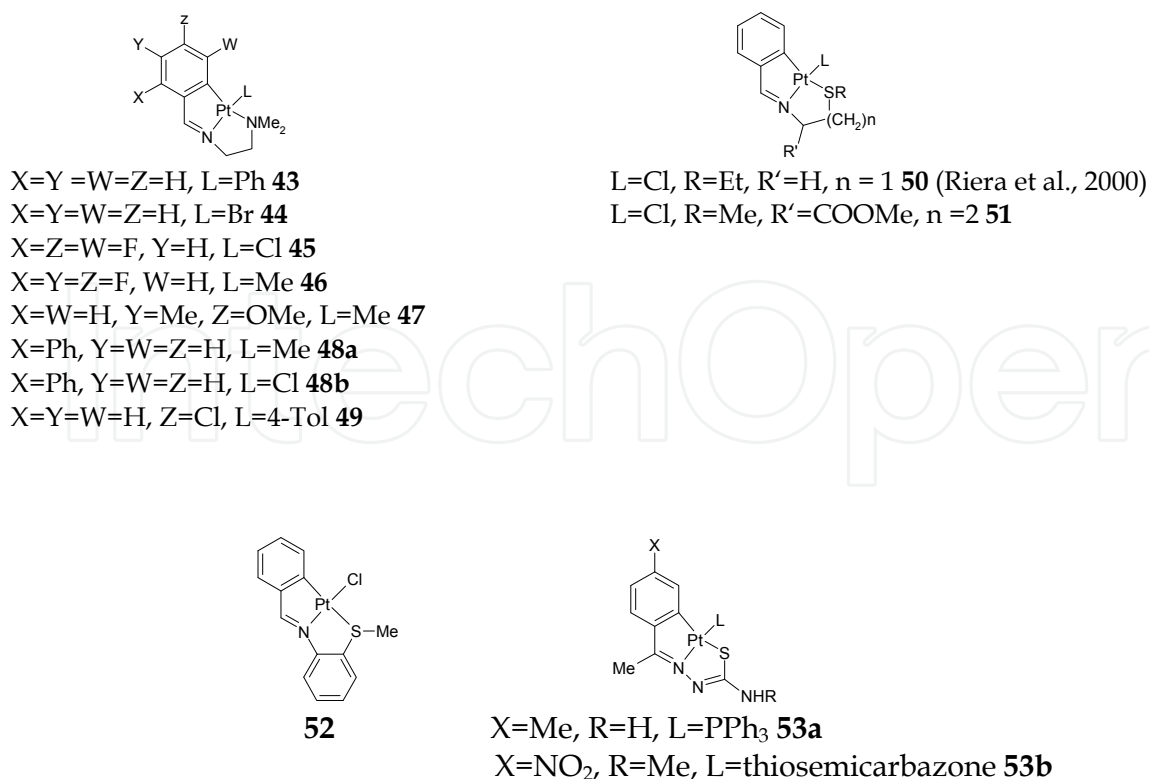
These complexes were prepared by reacting [Pt<sub>2</sub>Me<sub>4</sub>(μ-SMe<sub>2</sub>)<sub>2</sub>] with the imine ligand in the presence of sodium acetate followed by the exchange reaction with PPh<sub>3</sub> ligand. They were studied intensively from the cycloplatination reaction mechanism point of view and none of them were investigated for their potential luminescent properties. The stacked structures are well-known for platinum complexes, and they become increasingly favoured with increasing aromatic core. Despite the presence of biphenyl unit in complexes **39a,b**, no significant π...π interactions have been found for these compounds.

Complex	Pt - C	Pt - N	Pt-L	Pt - P (PPh <sub>3</sub> )	Reference
<b>38a</b>	2.026(8)	2.156(8)	2.118(9)	2.303(2)	Crespo et al., 1995
<b>38b</b>	2.051(7)	2.153(5)	2.046(8)	2.299(2)	Crespo et al., 1995
<b>38c</b>	2.064(5)	2.144(4)	2.053(6)	2.2815(12)	Crespo et al., 2002a
<b>39a</b>	2.059(4)	2.128(3)	2.062(4)	2.3022(12)	Crespo et al., 2006a
<b>39b</b>	2.056(6)	2.134(5)	2.054(8)	2.2979(17)	Crespo et al., 2006a
<b>40a</b>	2.018(5)	2.141(4)	2.028(5)	2.2717(14)	Crespo et al., 1996
<b>40b</b>	2.053(4)	2.148(3)	2.049(4)	2.2955(1)	Crespo et al., 1998a
<b>41</b>	2.072(5)	2.098(5)	2.480(2)	2.245(2)	Calvet et al., 2009
<b>42a</b>	2.057(6)	2.119(5)	2.058(7)	2.305(2)	Crespo et al., 1998b
<b>42b</b>	2.072(12)	2.131(9)	2.003(10)	2.308(3)	Rodriguez et al., 2009

Table 6. Selected bond lengths for cyclometalated Pt(II) complexes containing N-benzylidenebenzylamine

### 3.4.2 Cyclometalated Pt(II) complexes with terdentate imine ligands

The relevant Pt(II) systems bearing terdentate imine ligands are shown in Scheme 9. The cyclometalated Pt(II) complexes with thiosemicarbazone ligands were included here. The crystal structures of such complexes with terdentate imines reveal a strong *trans* influence of the carbon donor ligands. For instance, in complex **47**, the Pt-NMe<sub>2</sub> bond length of 2.162(14) Å is longer than the imine Pt-N bond length of 2.04(2) Å as a consequence of *trans* aryl group which has a high *trans* influence. On the other hand, for such complexes, the longer Pt-N bond is also consistent with the weaker ligating ability of tertiary amines for platinum. The Pt-C bond lengths are found to be in the expected range. It is interesting to note that the complex **52** represents the first luminescent platinum(II) compound with a [C<sup>N</sup>S]-terdentate ligand. The long intermolecular S...S distance precludes the existence of any direct interaction between these atoms. Also, the Pt...Pt distance between neighbouring molecules is 4.216(3) Å which is larger, for instance, than the values reported for related platinacycles having [C(sp<sup>2</sup>)<sup>N</sup>N]- and [C(sp<sup>2</sup>)<sup>N</sup>S]-terdentate ligands from the “pincer” family. The emission spectrum of this compound recorded at 298K in CH<sub>2</sub>Cl<sub>2</sub> solution shows a maximum at 578 nm when excited at 388 nm with no additional information regarding the quantum yield and lifetime provided. For the rest of complexes (**43** – **51**), no data regarding the luminescence properties were reported. Interestingly, the thiosemicarbazone ligands can be used in cycloplatination reaction to give orthometalated complexes in which the ligand acts as terdentate through the C, N and S atoms and two such examples are presented in Scheme 9 (**53a** and **53b**). **53a** was obtained by bridge-cleavage with PPh<sub>3</sub> of the first Pt(II) cyclometalated tetranuclear complexes bearing thiosemicarbazone ligands which were prepared using K<sub>2</sub>PtCl<sub>4</sub> as starting material.



Scheme 9. Pt(II) complexes with terdentate imine ligands

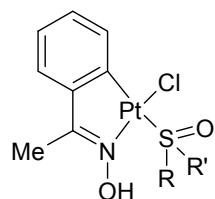
Complex	Pt – C	Pt – N	Pt – E (E=N or S)	Pt – L	References
43	1.986(6)	2.016(4)	2.139(6)	2.009(4)	Crespo et al., 2004a
44	2.008(15)	1.970(10)	2.141(12)	2.301(4)	Crespo et al., 2002c
45	1.997(10)	1.970(14)	2.135(14)	2.296(4)	Crespo et al., 2004b
46	1.996(8)	2.009(60)	2.160(7)	2.040(8)	Lopez et al., 1997
47	1.97(2)	2.04(2)	2.162(14)	2.154(13)	Vila et al., 1998
48a	1.964(3)	1.990(3)	2.138(3)	2.064(3)	Crespo et al., 2006a
48b	2.009(6)	1.967(6)	2.168(7)	2.302(2)	Crespo et al., 2006b
49	1.976(8)	2.014(5)	2.177(8)	2.026(4)	Martin et al., 2009
51	1.954(14)	1.984(11)	2.349(3)	2.308(4)	Riera et al., 2001
52	2.016(6)	1.928(6)	2.349(2)	2.292(2)	Caubet et al., 2003
53a	2.02(2)	2.03(2)	2.335(5)	2.235(5)	Vasquez-Garcia et al., 2000
53b	2.021(4)	2.006(4)	2.3296(11)	2.2832(12)	Quiroga et al., 2008

Table 7. Selected bond legths for cyclometalated Pt(II) complexes with terdentate imine ligands

On the other hand, complex **53b** was obtained by reacting the thiosemicarbazone ligand with the Pt dinuclear allyl complex [Pt(μ-Cl)(η<sup>3</sup>-C<sub>4</sub>H<sub>7</sub>)]<sub>2</sub> in refluxing acetone, when, instead of the expected tetranuclear complex, a mononuclear cyclometalated Pt(II) complex containing two thiosemicarbazone molecules was formed. One of the molecule acts as a [C<sup>^</sup>N<sup>^</sup>S]- terdentate ligand while the second one is coordinated in a monodentate fashion through the S atom, thus completing the coordination sphere of Pt(II) metal. Bis(thiosemicarbazone) ligands were used for cycloplatination reaction and the first X-ray structure of a cyclometalated Pt(II) complex with such ligands was reported by Lopez-Torres & Mendiola, 2010. No emission properties were reported for such complexes.

3.4.3 Pt(II) complexes bearing cyclometalated oxime ligands

There are several X-ray crystallographic structures reported for a series of cycloplatinated complexes with oxime ligands (see Scheme 10). They were prepared starting from [PtCl<sub>2</sub>(RR'SO)<sub>2</sub>] and the corresponding oxime ligand. Although they show an interesting structural feature, as it is the case of complex **54b** that reveals an extremely short Pt··Pt contact of 3.337 Å, these complexes were studied mostly for mechanistic and catalytic purposes and no emission properties were investigated (Ryabov et al., 1995).



R = R' = Me (Pt-C = 1.998(4) Å, Pt-N = 2.013(3) Å, Pt – S = 2.2677(11) Å, Pt – Cl = 2.4114(11) Å), (**54a**); R = Me, R' = Ph (Pt-C = 2.010(4) Å, Pt-N = 2.010(3) Å, Pt – S = 2.2192(12) Å, Pt – Cl = 2.3806(13) Å) , (**54b**) (Ryabov et al., 2002)

Scheme 10.

### 3.4.4 Bis(imine) ligands – N<sup>^</sup>C<sup>^</sup>N pincer ligands

Several crystallographic studies concerning the cycloplatinated complexes with bis(imine) ligands (where the N atom is not part of a ring) were reported (see Scheme 11). Complex **55** was prepared by reacting  $\text{LiC}\equiv\text{CSiMe}_3$  in THF with the first platinum(II) halide compounds containing the (N<sup>^</sup>C<sup>^</sup>N) isophthalaldimine ligands.

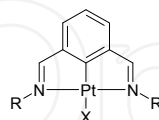
R=2,6-(iPr)<sub>2</sub>Ph, X= $\text{C}\equiv\text{CSiMe}_3$  **55**

R=2,6-(iPr)<sub>2</sub>Ph, X=CH<sub>3</sub> **56**

R=CH(CH<sub>3</sub>)Ph, X=Cl **57a**

R=<sup>t</sup>Bu, X=Cl **57b**

R=Ph, X=Cl **57c**



Scheme 11.

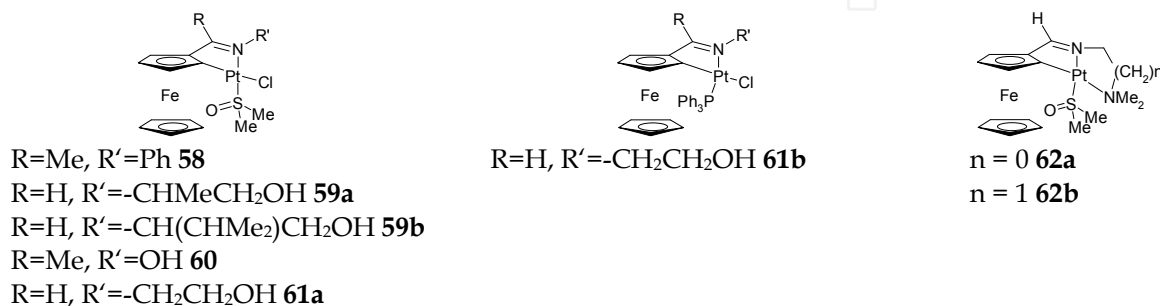
On the other hand, complex **56** represents the first X-ray crystal structure of stable trans-arylplatinum methyl complexes [PtMeN<sup>^</sup>C<sup>^</sup>N] with imine-type ligands. It is well-known that due to the strong C(sp<sup>2</sup>)-C(sp<sup>3</sup>) bond, only very few transition-metal compounds having an aryl as well as a methyl group bonded to the same metal atom are reported. The reason is that in such cases reductive elimination occurs. For complex **56** this reaction is prevented due to the trans disposition of the methyl and aryl groups and the rigid coplanarity of the chelate rings. Another representative example is complex **57a** that is the first chiral bis-aldimine (N<sup>^</sup>C<sup>^</sup>N)-pincer complexes. Unfortunately, there was no emission data reported for such complexes.

Complex	Pt-C	Pt-N1	Pt-N2	Pt-X	Reference
<b>55</b>	1.945(2)	2.043(2)	2.050(2)	2.065(3)	Hoogervorst et al., 2001
<b>56</b>	1.944(2)	2.036(2)	2.045(2)	2.156(3)	Hoogervorst et al., 2004
<b>57a</b>	1.901(7)	2.027(5)	2.049(6)	2.397(2)	Fossey et al., 2007
<b>57b</b>	1.915(6)	2.093(5)	2.097(5)	2.4192(19)	Fossey et al., 2002
<b>57c</b>	1.908(6)	2.061(5)	2.064(5)	2.3914(18)	Fossey et al., 2002

Table 8. Selected bond lengths for cyclometalated Pt(II) complexes with bis(imine) N<sup>^</sup>C<sup>^</sup>N pincer ligands

### 3.4.5 Cyclometalated Pt(II) complexes containing ferrocene based imine ligands

Several crystal structures of cyclometalated Pt(II) complexes containing imine ligands with ferrocene fragment were reported (see Scheme 12).



Scheme 12. Cycloplatinated complexes bearing ferrocene imine ligands

Complex	Pt – C	Pt – N	Pt-S	Pt-Cl	Reference
58	1.980(5)	2.095(5)	2.195(1)	2.389(1)	Wu et al., 1997
59a	2.01(3)	2.05(2)	2.214(2)	2.427(8)	Lopez et al., 2006
	2.03(3)	2.01(3)	2.197(8)	-	
59b	2.018(1)	2.090(9)	2.2182(3)	2.380(3)	Lopez et al., 2004
60	1.976(7)	2.042(6)	2.186(2)	2.395(2)	Ryabov et al., 1997
61a	2.017(7)	2.078(4)	2.198(2)	2.395(2)	Lopez et al., 2010
61b	Pt – C	Pt – N	Pt-P	Pt-Cl	Lopez et al., 2010
	2.03(1)	2.189(7)	2.243(2)	2.376(3)	
62a	Pt – C	Pt – N1	Pt-S	Pt-N2	Lopez et al., 2005
	1.993(8)	1.977(5)	2.190(4)	2.3083(16)	
62b	1.939(8)	2.020(7)	2.182(7)	2.327(2)	Perez et al., 2003

Table 9. Selected bond lengths for cyclometalated Pt(II) complexes containing imine ligands based on ferrocene fragment

Most of these complexes were prepared by reacting the imine ligand with [PtCl<sub>2</sub>(DMSO)<sub>2</sub>] in refluxing toluene for a long period of time, with or without sodium acetate as a base agent. They can react further with phosphine ligands to replace the labile DMSO ligand (61b). Several interesting structural features are presented in Table 9. It is important to note that these complexes were studied more from mechanistic, electrochemical and catalytic properties point of view and less, or not at all in most of the cases, for emissive properties.

3.5 Heteropolynuclear cycloplatinated complexes

Due to the presence of metallophilic interactions that have serious consequences on luminescence properties, the study of different heteropolynuclear cycloplatinated complexes has dramatically increased in the last years and this topic has been very recently reviewed (Diez et al., 2011). It has been shown that the cycloplatinated complexes can be useful building blocks in the design of heteropolynuclear and/or multicomponent architectures. Although several interesting heteropolymetallic cycloplatinated systems have been reported, the photoluminescence properties have been studied only in few cases.

3.6 Cyclometalated Pt(II) complexes as liquid crystals

Liquid crystals are, by far, *the most important* molecular electronic materials of the present day. They were discovered more than 100 years ago and are often thought of as the high technology materials found in high content, low power, flat-panel displays known to the whole world as LCDs, their main application (O'Neill & Kelly, 2011). Stable inorganic phosphors showing liquid crystal properties are very promising multifunctional materials because, in contrast with pure organic materials, they are not subjected to photobleaching (loss of luminescence properties upon irradiation over the time), provide anisotropic long range order and thus polarised emission that should improve display performance parameters such as brightness, contrast, energy efficiency and, in some cases, the viewing angle. Potential new materials that fulfill these requirements are the metallomesogens (liquid crystalline materials incorporating metal ions). The first option, lanthanide mesogenic complexes (lanthanidomesogens) have been proposed as potential candidates for



bright luminescent emitters (Eliseeva & Bünzli, 2010), but they have low quantum yield efficiency. Thus, by far, due to the possibility of harvesting both triplet and singlet states, as well as the emission in the red – NIR range, the late transition metallomesogens are the most promising candidates and could be employed for the preparation of highly effective phosphorescent OLEDs. In this respect, several studies have been reported recently including luminescent metallomesogens based on Pt(II), Ir(III) or Ru(II), Ag(I) or Au(I) (Binnemans, 2009). There are several studies dealing with light-emitting metallomesogens based on platinum(II) (Liao et al., 2011; Venkatesan et al., 2008; Mocanu et al., 2010) complexes, most of them containing the metal in a cyclometalating environment (Damm et al., 2006; Wang et al., 2011) with 2-arylpyridine or 2-thienylpyridine derivatives. Bruce et. al. reported phosphorescent liquid crystalline complexes of platinum(II) showing a stimulus-dependant emission (Kozhevnikov et al., 2008) as well as highly luminescent (yields higher than 0.5) Pt(II) containing metallomesogens (Santoro et al., 2009). In terms of quantum yields, these later examples were exceeded only by the recently reported Pt(II) metallomesogens bearing pyridyl pyrazole chelates that show quantum yields nearly 1, when recorded in degassed dichloromethane (Liao et al., 2011).

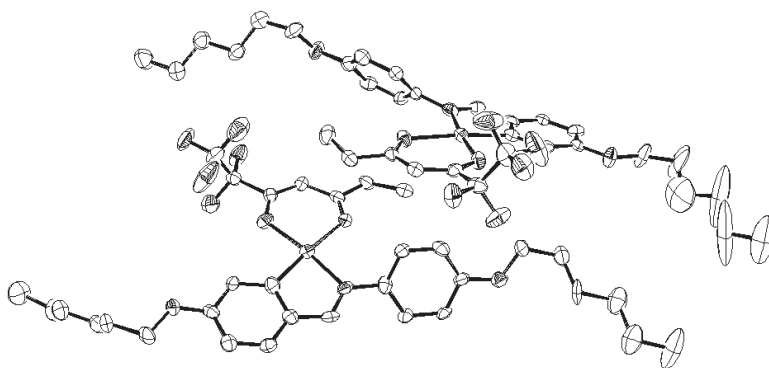


Fig. 6. Molecular structure of a mononuclear cycloplatinated metallomesogen containing an imine and an acetylacetonate ligand (**63**). The two independent molecules contained in the unit cell are shown (H atoms were omitted for clarity). (Pt-C = 1.983(10) and 1.976(11) Å, Pt-N = 1.986(8) and 2.008(7) Å, Pt-O1 = 2.101(6) and 2.080(6) Å, Pt-O2 = 1.992(7) and 2.004(6) Å (Cîrcu et al., 2007)

In most cases, luminescent Pt(II) complexes contain heterocyclic ligands, usually with one or two pyridine rings, while imine ligands were completely ignored from this point of view. Several examples of luminescent cycloplatinated (Scaffidi-Domianello et al., 2007; Pandya et al., 2010) or platinum(II) complexes with N,N-donor diimine ligands are known, though this class of ligands is widely spread in the design of Pt(II) metallomesogens (Cîrcu et al., 2009b; Buey et al., 1996; Diez, L. et al., 2002). Although several important results have been achieved in the design and the synthesis of luminescent liquid crystalline materials based on Pt(II) cyclometalated complexes, only few X-ray structural investigations have been made on such systems comprising either mononuclear (Cîrcu et al., 2007) or dinuclear species (Praefcke et al., 1994; Bilgin Eran et al., 2001). One reason could be that such molecules have long alkyl chains that make single crystals suitable for X-ray crystallography difficult to obtain. The only example of a crystal structure of a mononuclear cycloplatinated metallomesogen (**63**) is depicted in Figure 6. The Pt-C distance is similar to those found in



dinuclear chloro- or thiocyanato-bridged, orthometalated platinum compounds with Schiff bases reported by Praefcke et al., 1994, whereas the Pt–N distances are slightly smaller (2.19 and 2.064 Å in Praefcke's work), which could be assigned to the difference in trans-effect of the atoms coordinated to platinum. It is interesting to note that an *anti* configuration (the perfluoroethyl group is trans to nitrogen atom of the imine group) is adopted by the two ligands (Schiff base and acetylacetonate derivative) around platinum centre. This complex **63** shows a monotropic nematic phase on cooling at 37°C.

#### 4. Conclusion

Various cyclometalated Pt(II) complexes were structurally investigated by X-ray crystallography. The use of strong field C donor ligands provides an important route to Pt(II) complexes with interesting photophysical properties, with different applications, mainly in OLED devices. There are several classes of cyclometalated Pt(II) complexes which were not investigated so far for their emission properties, such as the cycloplatinated imino complexes, but this field continuously expands and a growing number of reports dealing with this topic are being published.

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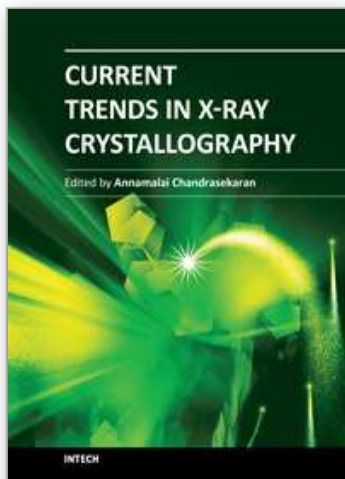


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