

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



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

Viorel Cîrcu and Marin Micutz
*University of Bucharest,
Romania*

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 σ 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(η^3 -allyl)-di- μ -chlorodiplatinum(II) or PtCl₂(DMSO)₂, etc, although K₂PtCl₄ or [Pt₂Me₄(μ -SMe₂)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).

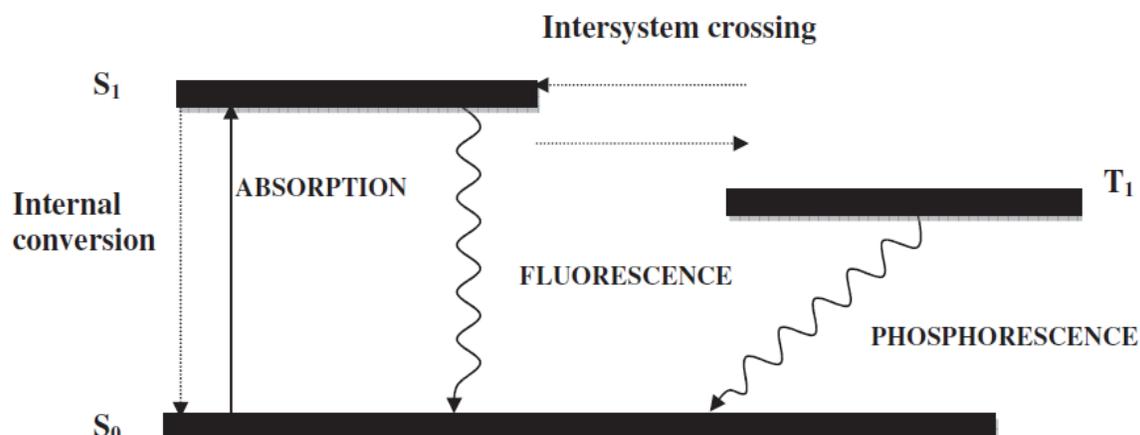
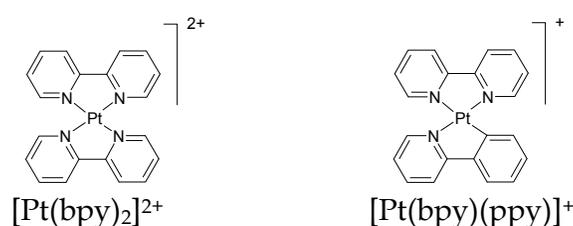


Fig. 1. Schematic representation of the radiative and non-radiative pathways

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 π^* anti-bonding orbital located on the ligand system; 3) $\pi\pi^*$ or $n\pi^*$ states (intraligand, IL, transition). Promotion of an electron from a π -bonding or non-bonding orbital to a higher energy anti-bonding orbital gives rise to these states; 4) πd states (ligand-to-metal-charge-transfer, LMCT). These states arise from the transfer of electronic charge from the ligand π system to a metal-centred orbital.



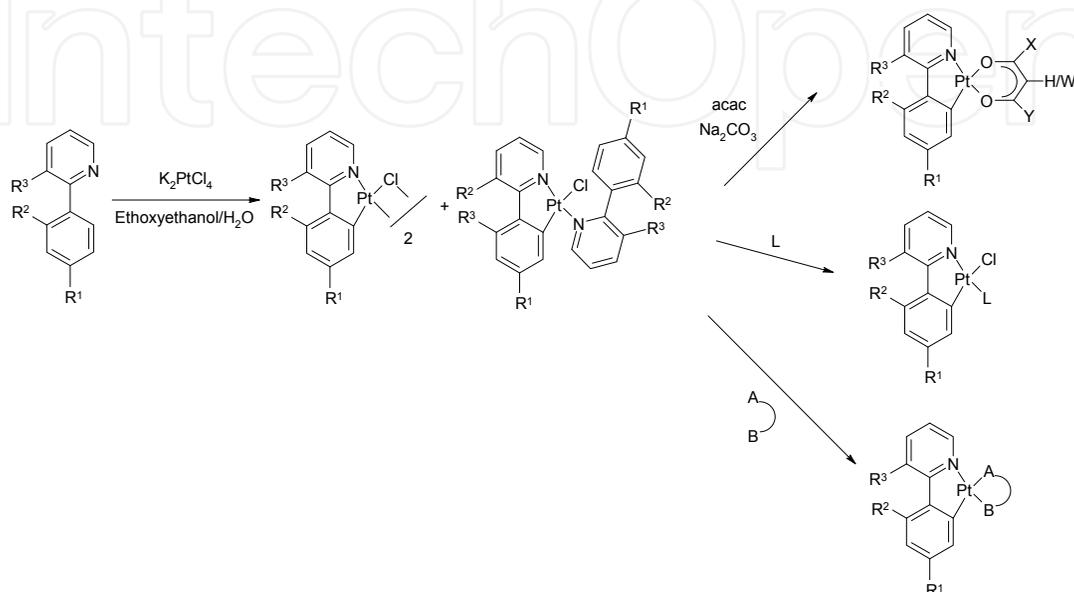
Scheme 1.

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 $[\text{Pt}(\text{bpy})_2]^{2+}$ is almost non-emissive at room temperature, the Pt(II) cyclometalated complex $[\text{Pt}(\text{bpy})(\text{ppy})]^+$ 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).



$\text{R}^1=\text{NPh}_2$, $\text{R}^2=\text{R}^3=\text{H}$, $\text{X}=\text{Y}=\text{Me}$ **1a**

$\text{R}^1=-\text{oxadiazole-4-Ph-p-NPh}_2$, $\text{R}^2=\text{R}^3=\text{H}$, $\text{X}=\text{Y}=\text{Me}$ **1b**

$\text{R}^1=-\text{oxadiazole-4-Ph-p-NTol}_2$, $\text{R}^2=\text{R}^3=\text{H}$, $\text{X}=\text{Y}=\text{Me}$ **1c**

$\text{R}^1=\text{R}^2=\text{R}^3=\text{H}$, $\text{X}=\text{Y}=\text{Ph}$ **1d**

$\text{R}^1=\text{R}^2=\text{F}$, $\text{R}^3=\text{H}$, $\text{X}=\text{Y}=\text{Me}$, $\text{W}=-(\text{CH}_2)_2\text{-norbornene}$ **1e**

$\text{R}^1=\text{R}^2=\text{R}^3=\text{H}$, $\text{L}=\text{CO}$ **2a**

$\text{R}^1=\text{R}^2=\text{R}^3=\text{H}$, $\text{L}=\text{DMSO}$ **2b**

$\text{R}^1=\text{F}$, $\text{R}^2=\text{R}^3=\text{H}$, $\text{L}=\text{DMSO}$ **2c**

$\text{R}^1=\text{F}$, $\text{R}^2=\text{R}^3=\text{H}$, $\text{L}=\text{py-2-Ph-4'-F}$ **2d**

$\text{R}^1=\text{R}^2=\text{F}$, $\text{R}^3=\text{H}$, $\text{L}=\text{py-2-Ph-2',4'-F}_2$ **2e**

$\text{R}^1=\text{R}^2=\text{F}$, $\text{R}^3=\text{H}$, $\text{A}^{\wedge}\text{B}=\text{3,5-di-}t\text{Bu-catechol}$ **3**

$\text{R}^1=\text{R}^2=\text{H}$, $\text{R}^3=-\text{OHex}$,

$\text{A}^{\wedge}\text{B}=\text{5-NO}_2\text{-8-quinoline}$ **4**

$\text{R}^1=\text{R}^2=\text{R}^3=\text{H}$,

$\text{A}^{\wedge}\text{B}=\text{Et}_2\text{NC(S)NCOPh}$ **5a**

$\text{R}^1=\text{R}^2=\text{R}^3=\text{H}$,

$\text{A}^{\wedge}\text{B}=\text{MeO-4-C}_6\text{H}_4\text{NHC(S)NCOPh}$ **5b**

$\text{R}^1=\text{R}^2=\text{R}^3=\text{H}$,

$\text{A}^{\wedge}\text{B}=\text{2-pyridyl hexafluoropropoxide}$ **6**

$\text{R}^1=\text{R}^2=\text{F}$, $\text{R}^3=\text{H}$, $\text{A}^{\wedge}\text{B}=(\text{pz})_2\text{BEt}_2$ **7**

$\text{R}^1=\text{R}^2=\text{R}^3=\text{H}$, $\text{A}^{\wedge}\text{B}=(\text{3,5-Me}_2\text{pz})\text{BH}_2$ **8**

$\text{R}^1=\text{R}^2=\text{R}^3=\text{H}$, $\text{A}^{\wedge}\text{B}=\text{dppm}$, PF_6^- **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_2PtCl_4 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[^]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 R¹-R³ 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 acetylacetonone 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).

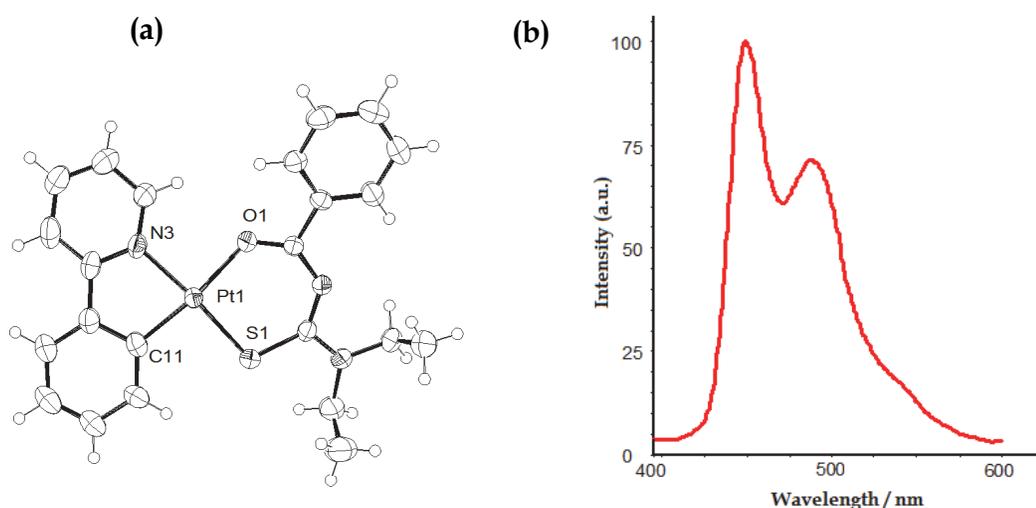


Fig. 2. ORTEP view of complex **5a** (a); the emission spectrum of **5a** recorded in CH₂Cl₂ solution at room temperature (b)

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° with respect to the core plane, leading to the formation of weak intermolecular NH...Pt interactions (H...Pt 2.74 Å; N-H...Pt 156.8°) compared to those found in the salt (NⁿPr₄)₂[PtCl₄][PtCl₂(NH₂Me)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)	Niedermaier 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)	Niedermaier 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**

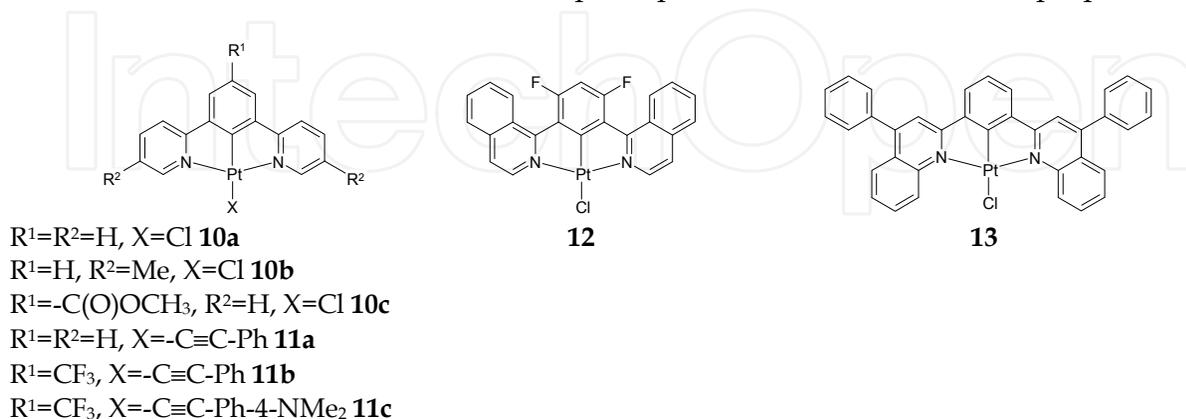
3.2 Cyclometalated Pt(II) complexes with “pincer” ligands

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 K₂PtCl₄ 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, π ·· π and C-H·· π (C \equiv 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 π ·· π 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
10a	1.907(8)	2.033(6)	2.041(6)	2.417(2)	Cardenas et al., 1999
10b	1.915(3)	2.041(2)	2.027(2)	2.409(1)	Abe et al., 2007
10c	1.903(4)	2.036(3)	2.035(3)	2.4050(10)	Williams et al., 2003
12	1.918(8)	2.021(7)	2.009(7)	2.412(2)	Wang et al., 2010
13	1.908(3)	2.075(3)	2.060(3)	2.4343(9)	Baik et al., 2006

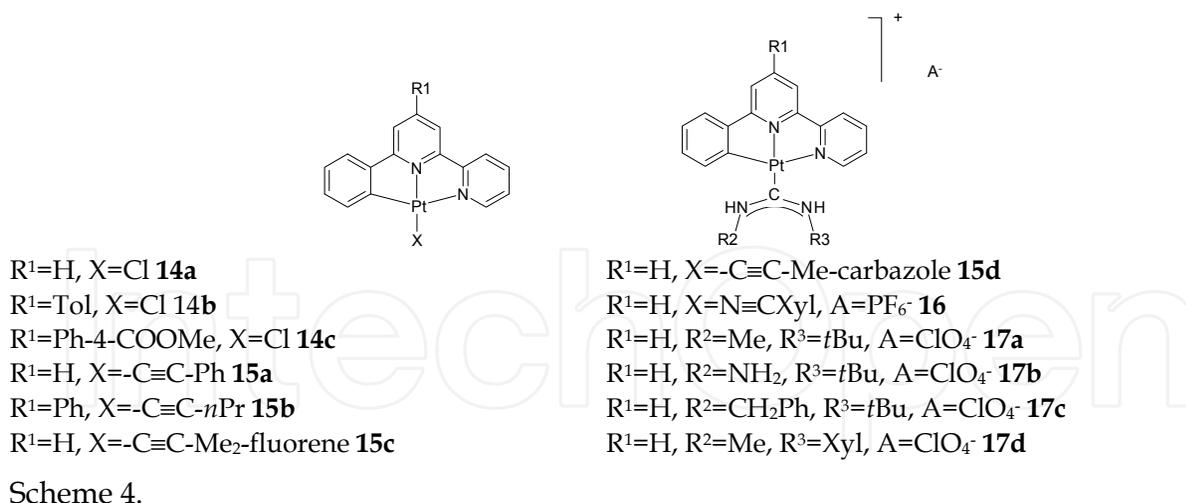
Table 2. A selection of bond lengths for some N[^]C[^]N Pt(II) complexes

The room temperature structureless emissions at λ_{max} 819 (**11b**) and 702 nm (**11c**), respectively, strongly red-shifted compared to solution emission (λ_{max} = 486 and 480, respectively), can be assigned to triplet metal-metal-to-ligand charge-transfer (³MMLCT) excited states. The photophysical properties of chloride complexes (**10a-c**) and analogous with various other R¹ substituents were systematically studied by Farley et al., 2005. It is interesting to note that these N[^]C[^]N Pt(II) complexes show relatively shorter Pt-C distances than those found in C[^]N[^]N Pt(II) complexes (see comparatively Tables 2 and 3).

3.2.2 C[^]N[^]N ligands

The C[^]N[^]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).



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

Table 3. Selected bond lengths for C[^]N[^]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 R¹ substituent on the C[^]N[^]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≡NR]⁺ (R = *t*Bu or Ar). Weak π··π 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 λ_{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).

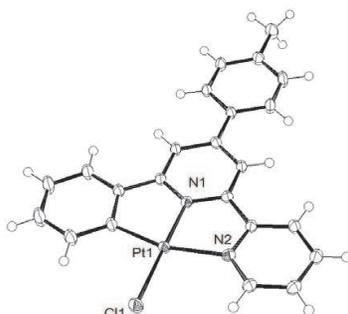
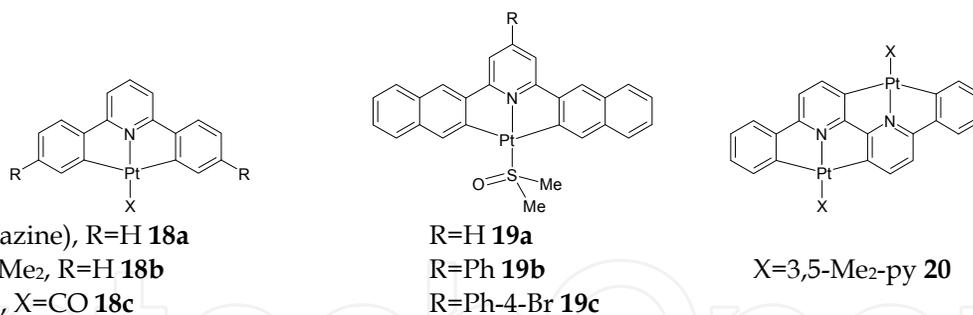


Fig. 3. ORTEP view of complex **14b**

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 K_2PtCl_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.

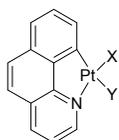
Complexes **19a-c** were prepared by reacting K_2PtCl_4 with the terdentate 2,6-di-(2'-naphthyl)-pyridine ligands in glacial acetic acid, followed by heating in DMSO. Their crystal structures reveal that the molecules are paired in a head-to-tail orientation with $\text{Pt}\cdots\text{Pt}$ separations longer than 6.3 Å, with extensive close $\text{C-H}\cdots\pi$ ($d = 2.656\text{--}2.891$ Å) and $\pi\cdots\pi$ ($d = 3.322\text{--}3.399$ 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 dicyclopentylated 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
18a	2.05(1)	2.08(5)	-	1.99(7)	Kulikova et al., 2003
18b	2.06(1)	2.05(1)	1.98(1)	2.04(1)	Lusby et al., 2009
18c	2.070(6)	2.055(6)	2.007(5)	1.827(6)	Newman et al., 2001
19a	2.095(5)	2.074(4)	2.011(4)	2.1915(13)	Kui et al., 2006
19b	2.082(6)	2.058(6)	2.008(4)	2.1927(12)	Kui et al., 2006
19c	2.101(6)	2.070(6)	2.016(5)	2.1959(18)	Kui et al., 2006
20	2.054(6)	2.104(6)	1.983(5)	2.036(5)	Zucca et al., 2006

Table 4. Selected bond lengths for C^NC Pt(II) compounds **18 - 20**

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

The homoleptic Pt(II) complex with benzo(h)quinoline was prepared by reacting [PtCl₂(Et₂S)₂] with the lithiated ligand, its crystal structure being reported in 1996 (Jolliet 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=NBu₄⁺ **21**

X=Y=-C≡C-Py-2, Kat=NBu₄⁺ **22**

X=Y=-C≡C-Ph, Kat=Pb²⁺ **23**

X=-C≡C-Ph, Y=PPh₂(C≡CPh) **24**

X=Y=-C≡N-Xyl, A=ClO₄⁻ **25a**

X=Y=-C≡N-Xyl, A=PF₆⁻ **25b**

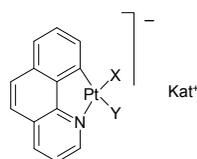
X=-C≡N-Xyl, Y=Cl **26**

X=-C≡N-tBu, Y=Cl **27**

X=-C≡N-2-Np, Y=Cl, Np=Naphtyl **28**

X=PPh₂, Y=Cl **29**

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



X=Y=PPh₂ **30**

X=Y=dppm, PF₆⁻ **31a**

X=Y=dppe, A=PF₆⁻ **31b**

X=Y=dppp, A=PF₆⁻ **31c**

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

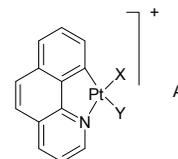
X=DMSO, Y=Cl **33a**

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

X=SMe₂, Y=4-Tol **34**

X=Y=[9]aneS₃,

1,4,7-trithiacyclononane, A=PF₆⁻ **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 μ -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 bqz together with acetylide ligands is represented by complex **23**, whose molecular structure is depicted in Figure 4, which has very short Pt^{II}...Pb^{II} (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 ³MLM'CT [Pt(1) π (C≡CPh) \rightarrow Pt(2)/Pb(sp) π^* (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 $[\text{Pt}(\text{bzq})(\text{CNR})_2]\text{X}$ ($\text{R} = \text{Xyl}$, $\text{X} = \text{ClO}_4^-$, 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 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.

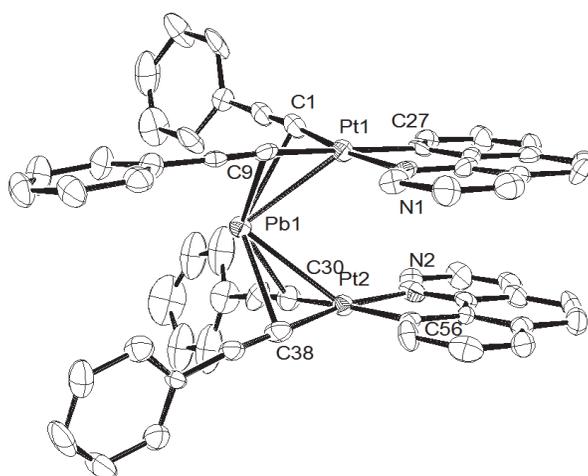


Fig. 4. ORTEP view of complex **23**

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 (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 PPh_2 and excess of 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 σ -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)(μ -PPh₂)₂] (**30**) reacts with cis-[Pt(C₆F₅)₂(thf)₂] in CH₂Cl₂ at 1:2 molar ratio, then a bent neutral triplatinum cluster [Pt₃(bzq)(μ -PPh₂)₂(C₆F₅)₃] 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 = (CH₂)₄, (**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.

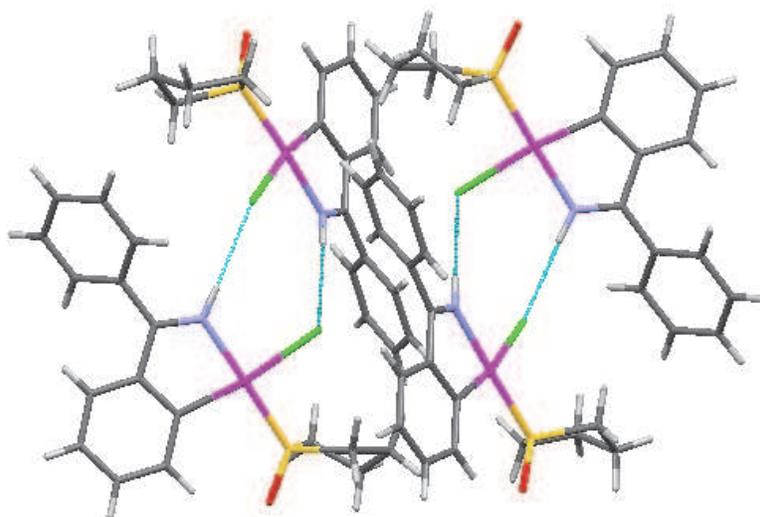
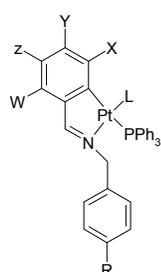


Fig. 5. The hydrogen bonding network connecting four independent molecules in the unit cell of **37b** (this figure was generated by using the Mercury 2.2 software)

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



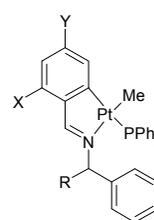
X=R=H, Y=W=Z=F, L=Me **38a**

X=Y=R=H, W=Z=F, L=Me **38b**

X=Y=Z=F, W=R=H, L=Me **38c**

X=W=Z=R=H, Y=Ph, L=Me **39a**

X=Y=Z=R=H, W=Ph, L=Me **39b**



X=Y=R=H, Z=Me, L=Me **40a**

X=Y=R=H, Z=CF₃, L=Me **40b**

X=Y=Z=H, R=Cl, W=-C₆F₅, L=Br **41**

R=Me, X=F, Y=H **42a**

R=-COOMe, X=H, Y=Cl **42b**

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

These complexes were prepared by reacting [Pt₂Me₄(μ-SMe₂)₂] with the imine ligand in the presence of sodium acetate followed by the exchange reaction with PPh₃ ligand. They were studied intensively from the cyclometalation reaction mechanism point of view and none of them were investigated for their potential luminescent properties.

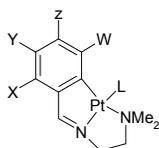
The stacked structures are well-known for platinum complexes, and they become increasingly favoured with increasing aromatic core. Despite the presence of biphenyl unit in complexes **39a,b**, no significant π···π interactions have been found for these compounds.

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

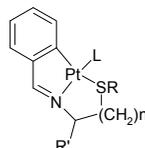
Table 6. Selected bond lengths for cyclometalated Pt(II) complexes containing N-benzylidenebenzylamine

3.4.2 Cyclometalated Pt(II) complexes with terdentate imine ligands

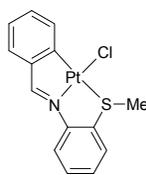
The relevant Pt(II) systems bearing terdentate imine ligands are shown in Scheme 9. The cyclometalated Pt(II) complexes with thiosemicarbazone ligands were included here. The crystal structures of such complexes with terdentate imines reveal a strong *trans* influence of the carbon donor ligands. For instance, in complex **47**, the Pt-NMe₂ 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[^]N[^]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(sp²)[^]N[^]N]- and [C(sp²)[^]N[^]S]-terdentate ligands from the “pincer” family. The emission spectrum of this compound recorded at 298K in CH₂Cl₂ 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 PPh₃ of the first Pt(II) cyclometalated tetranuclear complexes bearing thiosemicarbazone ligands which were prepared using K₂PtCl₄ as starting material.



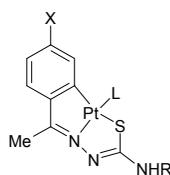
X=Y=W=Z=H, L=Ph **43**
 X=Y=W=Z=H, L=Br **44**
 X=Z=W=F, Y=H, L=Cl **45**
 X=Y=Z=F, W=H, L=Me **46**
 X=W=H, Y=Me, Z=OMe, L=Me **47**
 X=Ph, Y=W=Z=H, L=Me **48a**
 X=Ph, Y=W=Z=H, L=Cl **48b**
 X=Y=W=H, Z=Cl, L=4-Tol **49**



L=Cl, R=Et, R'=H, n = 1 **50** (Riera et al., 2000)
 L=Cl, R=Me, R'=COOMe, n = 2 **51**



52



X=Me, R=H, L=PPh₃ **53a**
 X=NO₂, R=Me, L=thiosemicarbazone **53b**

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

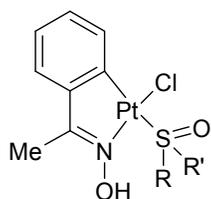
Complex	Pt - C	Pt - N	Pt - E (E=N or S)	Pt - L	References
43	1.986(6)	2.016(4)	2.139(6)	2.009(4)	Crespo et al., 2004a
44	2.008(15)	1.970(10)	2.141(12)	2.301(4)	Crespo et al., 2002c
45	1.997(10)	1.970(14)	2.135(14)	2.296(4)	Crespo et al., 2004b
46	1.996(8)	2.009(6)	2.160(7)	2.040(8)	Lopez et al., 1997
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 lengths 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 $[\text{Pt}(\mu\text{-Cl})(\eta^3\text{-C}_4\text{H}_7)]_2$ 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 $[\text{C}^{\wedge}\text{N}^{\wedge}\text{S}]$ -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 $[\text{PtCl}_2(\text{RR}'\text{SO})_2]$ 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[^]C[^]N pincer ligands

Several crystallographic studies concerning the cyclometalated 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[^]C[^]N) isophthalaldimine ligands.

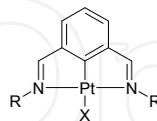
R=2,6-(^{*i*}Pr)₂Ph, X= $\text{C}\equiv\text{CSiMe}_3$ **55**

R=2,6-(^{*i*}Pr)₂Ph, X=CH₃ **56**

R=CH(CH₃)Ph, X=Cl **57a**

R=^{*t*}Bu, X=Cl **57b**

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



Scheme 11.

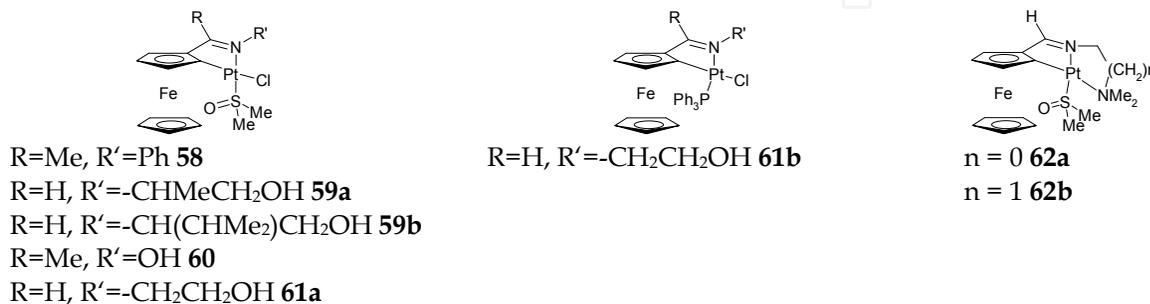
On the other hand, complex **56** represents the first X-ray crystal structure of stable trans-arylplatinum methyl complexes [PtMeN[^]C[^]N] with imine-type ligands. It is well-known that due to the strong C(sp²)-C(sp³) bond, only very few transition-metal compounds having an aryl as well as a methyl 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[^]C[^]N)-pincer complexes. Unfortunately, there was no emission data reported for such complexes.

Complex	Pt-C	Pt-N1	Pt-N2	Pt-X	Reference
55	1.945(2)	2.043(2)	2.050(2)	2.065(3)	Hoogervorst et al., 2001
56	1.944(2)	2.036(2)	2.045(2)	2.156(3)	Hoogervorst et al., 2004
57a	1.901(7)	2.027(5)	2.049(6)	2.397(2)	Fossey et al., 2007
57b	1.915(6)	2.093(5)	2.097(5)	2.4192(19)	Fossey et al., 2002
57c	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[^]C[^]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
	Pt - C	Pt - N	Pt-P	Pt-Cl	
61b	2.03(1)	2.189(7)	2.243(2)	2.376(3)	Lopez et al., 2010
	Pt - C	Pt - N1	Pt-S	Pt-N2	
62a	1.993(8)	1.977(5)	2.190(4)	2.3083(16)	Lopez et al., 2005
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 $[\text{PtCl}_2(\text{DMSO})_2]$ 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).

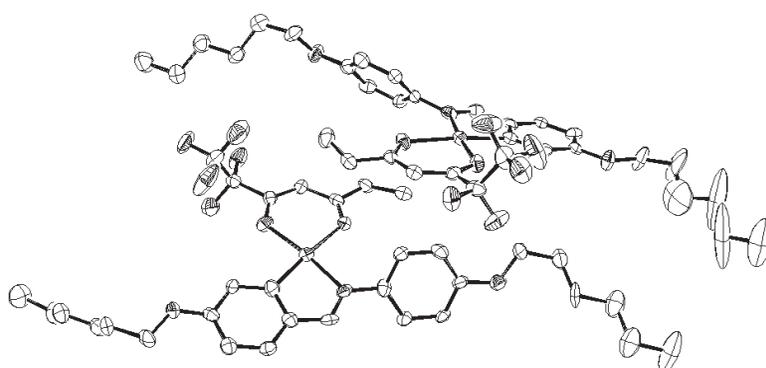


Fig. 6. Molecular structure of a mononuclear cycloplatinated metallomesogen containing an imine and an acetylacetonate ligand (**63**). The two independent molecules contained in the unit cell are shown (H atoms were omitted for clarity). (Pt-C = 1.983(10) and 1.976(11) Å, Pt-N = 1.986(8) and 2.008(7)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

5. Acknowledgment

The authors acknowledge the financial support from CNCSIS -UEFISCSU, project number PNII ID_954/2007. The molecular structures were generated by using ORTEP-3 for Windows (L. J. Farrugia, University of Glasgow, UK).

6. References

- Abe, T.; Shinozaki, K.; Ikeda, N. & Suzuki, T. (2007). [2,6-Bis(5-methyl-2-pyridyl)phenyl- κ^3N,C^1,N']chloridoplatinum(II). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 63, M456 – M458
- Albrecht, M. (2010). Cyclometalation using d-block transition metals: fundamental aspects and recent trends. *Chem. Rev.*, 110, 576 – 623
- Baik, C.; Han, W.-S.; Kang, Y.; Kang, S. O. & Ko, J. (2006). Synthesis and photophysical properties of luminescent platinum(II) complexes with terdentate polypyridine ligands: [Pt(bpqb)X] and [Pt(tbbpppy)X](PF₆) (bpqb-H=1,3-bis(4'-phenyl-2'-quinolinyl) benzene; tbbpppy =4-tert-butyl-1,3-bis(4'-phenyl-2'-quinolinyl) pyridine; X=Cl, C≡CC₆H₅, C≡CC₆H₄NMe₂, C≡CC₆H₄NO₂). *J. Organomet. Chem.*, 691, 5900 – 5910
- Balashov, K. P.; Puzyk, M. V.; Kotlyar, V. S. & Kulikova, M. V. (1997). Photophysics, photochemistry and electrochemistry of mixed-ligand platinum(II) complexes with 2-phenylpyridine and 2-(2'-thienyl)pyridine as cyclometalating ligands. *Coord. Chem. Rev.*, 159, 109 – 120
- Berenguer, J. R.; Diez, A.; Fernandez, J.; Fornies, J.; Garcia, A.; Gil, B.; Lalinde, E. & Moreno, M. T. (2008). [Pt]₂Pb Trinuclear systems: impact of the anionic platinum fragment on the lead environment and photoluminescence. *Inorg. Chem.*, 47, 7703 – 7716
- Bilgin Eran, B.; Singer, D.; Pickardt, J. & Praefcke, K. (2001). Thiocyanato-bridged platinum heterocycles: structure and properties of disc-like metallomesogens. *J. Organomet. Chem.*, 620, 249 – 255

- Binnemans, K. (2009). Luminescence of metallomesogens in the liquid crystal state. *J. Mater. Chem.*, 19, 448 - 453
- Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R. & Thompson, M. E. (2002). Synthesis and characterization of phosphorescent cyclometalated platinum complexes. *Inorg. Chem.*, 41, 3055 - 3066
- Buey, J.; Diez, L.; Espinet, P.; Kitzlerow, H.-S. & Miguel, J. A. (1996). Platinum orthometalated liquid crystals compared with their palladium analogues. First optical storage effect in an organometallic liquid crystal. *Chem. Mater.*, 8, 2375 - 2381
- Cardenas, D. J. & Echavarren, A. M.; de Arellano, M. C. R. (1999). Divergent behavior of palladium(II) and platinum(II) in the metalation of 1,3-di(2-pyridyl)benzene. *Organometallics*, 18, 3337 - 3341
- Caubet, A.; Lopez, C.; Solans, X. & Font-Bardia, M. (2003). Synthesis, characterisation and study of the first luminescent platinum(II) compound with a [C,N,S]- terdentate ligand. X-ray crystal structure of [Pt{C₆H₄-CH=N-(C₆H₄-2-SMe)}Cl]. *J. Organomet. Chem.*, 669, 164-171
- Chang, S.-Y.; Cheng, Y.-M.; Chi, Y.; Lin, Y.-C.; Jiang, C.-M.; Lee, G.-H. & Chou, P.-T. (2008). Emissive Pt(II) complexes bearing both cyclometalated ligand and 2-pyridyl hexafluoropropoxide ancillary chelate. *Dalton Trans.*, 6901 - 6911
- Chassot, L.; Mueller, R. & von Zelewsky, A. (1984). cis-Bis(2-phenylpyridine)platinum(II) (CBPPP): a simple molecular platinum compound. *Inorg. Chem.*, 23, 4249 - 4253
- Cho, J.-Y.; Domercq, B.; Barlow, S.; Saponitsky, K. Yu.; Li, J.; Timofeeva, T. V.; Jones, S. C.; Hayden, L. E.; Kimyonok, A.; South, C. R.; Weck, M.; Kippelen, B. & Marder, S. R. (2007). Synthesis and characterization of polymerizable phosphorescent platinum(II) complexes for solution-processible organic light-emitting diodes. *Organometallics*, 26, 4816 - 4829
- Cîrcu, V.; Horton, P. N.; Hursthouse, M. B. & Bruce, D. W. (2007). Mesomorphism of ortho-metallated imine complexes of the β-diketonatoplatinum(II) fragment. Crystal and molecular structure of three platinum imine complexes. *Liq. Cryst.*, 34, 1463 - 1472
- Cîrcu, V.; Ilie, M.; Ilis, M.; Dumitrascu, F.; Neagoe, I. & Pasculescu, S. (2009). Luminescent cyclometalated platinum(II) complexes with N-benzoyl thiourea derivatives as ancillary ligands. *Polyhedron*, 28, 3739 - 3746
- Cîrcu, V.; Manaila-Maximean, D.; Rosu, C.; Iliş, M.; Molard, Y. & Dumitraşcu, F. (2009). Mesomorphic behaviour and TSDC measurements of ortho-metallated palladium(II) and platinum(II) complexes with S,O-donor co-ligands. *Liq. Cryst.*, 36, 123 - 132
- Crabtree, R. H. (2005). *The organometallic chemistry of the transition metals* (4th Edition), Wiley Interscience, New Jersey
- Crespo, M.; Solans, X. & Font-Bardia, M. (1995). Cyclometalated Platinum(II) Compounds with Fluorinated Iminic Ligands: Synthesis and Reactivity Tuning. Crystal Structures of the Compounds [PtMe(RCH=NCH₂C₆H₅)(PPh₃)] (R = 2,3,4-C₆HF₃ and 2,3-C₆H₂F₂). *Organometallics*, 14, 355 - 364
- Crespo, M.; Solans, X. & Font-Bardia, M. (1996). Steric and electronic effects on the regioselective formation of platinum(II) metallacycles: crystal structure of [PtMe(3-MeC₆H₃CH=NCH₂C₆H₅)(PPh₃)]. *J. Organomet. Chem.*, 509, 29 - 36

- Crespo, M.; Solans, X. & Font-Bardia, M. (1998). Cyclometallated platinum compounds with N-benzylidenebenzylamines bearing trifluoromethyl groups. Crystal structure of [PtMe{3-(CF₃)C₆H₃CH=NCH₂Ph}(PPh₃)]. *Polyhedron*, 17, 1651 - 1658
- Crespo, M.; Solans, X. & Font-Bardia, M. (1998). Cyclometallated platinum compounds with chiral imines. Crystal structure of [PtMe(2-FC₅H₂CH=N-(S)-CHMePh)(PPh₃)]. *Polyhedron*, 17, 3927 - 3934
- Crespo, M.; Font-Bardia, M. & Solans, X. (2002). Formation and cleavage of platinacycles containing a fluorinated imine. Crystal structure of [PtMe(3,4,5-C₆HF₃CH=NCH₂C₆H₅)PPh₃]. *Polyhedron*, 21, 105 - 114
- Crespo, M.; Granell, J.; Solans, X. & Font-Bardia, M. (2002). Preparation of metallacycles with anionic terdentate [C,N,N'] ligands by intramolecular oxidative addition of C-X (X = Br, Cl) bonds to [Pt(dba)₂]. An unexpected effect of chloro substituents. *Organometallics*, 21, 5140 - 5143
- Crespo, M.; Font-Bardia, M. & Solans, X. (2004). Compound [PtPh₂(SMe₂)₂] as a versatile metalating agent in the preparation of new types of [C,N,N'] cyclometalated platinum compounds. *Organometallics*, 23, 1708 - 1713
- Crespo, M.; Granell, J.; Font-Bardia, M. & Solans, X. (2004). Intramolecular oxidative addition of C-F and C-H bonds to [Pt(dba)₂]. Crystal structure of [PtCl{Me₂NCH₂CH₂NCH(2,4,5-C₆HF₃)}]. *J. Organomet. Chem.*, 689, 3088 - 3092
- Crespo, M.; Font-Bardia, M. & Solans, X. (2006). Synthesis, reactivity and crystal structures of platinum (II) and platinum (IV) cyclometallated compounds derived from 2- and 4-biphenylimines. *J. Organomet. Chem.*, 691, 444 - 454
- Crespo, M.; Font-Bardia, M. & Solans, X. (2006). A comparative study of metallating agents in the synthesis of [C,N,N']-cycloplatinated compounds derived from biphenylimines. *J. Organomet. Chem.*, 691, 1897 - 1906
- Damm, C.; Israel, G.; Hegmann, T. & Tschierske, C. (2006). Luminescence and photoconductivity in mononuclear ortho-platinated metallomesogens. *J. Mater. Chem.*, 16, 1808 - 1816
- DePriest, J.; Zheng, G. Y.; Woods, C.; Rillema, D. P.; Mikirova, N. A. & Zandler, M. E. (1997). Structure, physical and photophysical properties of platinum(II) complexes containing 7,8-benzoquinoline and various bis (diphenylphosphine) ligands. *Inorg. Chim. Acta*, 264, 287 - 296
- DePriest, J.; Zheng, G. Y.; Goswami, N.; Eichhorn, D. M.; Woods, C. & Rillema, D. P. (2000). Structure, physical, and photophysical properties of platinum(II) complexes containing bidentate aromatic and bis(diphenylphosphino)methane as ligands. *Inorg. Chem.*, 39, 1955 - 1963
- Diez, A.; Fornies, J.; Garcia, A.; Lalinde, E. & Moreno, M. T. (2005). Synthesis, structural characterization, and photophysical properties of palladium and platinum(II) complexes containing 7,8-benzoquinolinolate and various phosphine ligands. *Inorg. Chem.*, 44, 2443 - 2453
- Diez, A.; Fornies, J.; Garcia, A.; Lalinde, E. & Moreno, M. T. (2006). Formation and characterization of a benzoquinolate triplatinum cluster containing a μ_3 -PPh₂ bridging system and two Pt-Pt bonds. *Inorg. Chem. Commun.*, 9, 255 - 258
- Diez, A.; Fornies, J.; Fuertes, S.; Larraz, C.; Lalinde, E.; Lopez, J. A.; Martin, A.; Moreno, M. T. & Sicilia, V. (2009). Synthesis and luminescence of cyclometalated compounds with nitrile and isocyanide ligands. *Organometallics*, 28, 1705 - 1718

- Diez, A.; Fornies, J.; Larraz, C.; Lalinde, E. & Lopez, A. J. (2010). Structural and luminescence studies on π - π and Pt-Pt interactions in mixed chloro-isocyanide cyclometalated platinum(II) complexes. *Inorg. Chem.*, 49, 3239 - 3251
- Diez, A.; Lalinde, E. & Moreno, M. T. (2011). Heteropolynuclear cycloplatinated complexes: Structural and photophysical properties. *Coord. Chem. Rev.*, in press, doi:10.1016/j.ccr.2010.12.024
- Diez, L.; Espinet, P.; Miguel, J. A. & Ros, M. B. (2002). Ferroelectric liquid crystal behavior in platinum orthometalated complexes. *J. Mater. Chem.*, 12, 3694 - 3698
- Eliseeva, S. V. & Bünzli, J. C. G. (2010). Lanthanide luminescence for functional materials and bio-sciences. *Chem. Soc. Rev.*, 39, 189-227
- Evans, R. C.; Douglas, P. & Winscom, C. J. (2006). Coordination complexes exhibiting room-temperature phosphorescence: Evaluation of their suitability as triplet emitters in organic light emitting diodes. *Coord. Chem. Rev.*, 250, 2093 - 2126
- Farley, S.J.; Rochester D. L.; Thompson, A. L.; Howard, J. A. K. & Williams, J. A. G. (2005). Controlling emission energy, self-quenching, and excimer formation in highly luminescent N²-coordinated platinum(II) complexes. *Inorg. Chem.*, 44, 9690 - 9703
- Fernandez, S.; Fornies, J.; Belen, G.; Gomez, J. & Lalinde, E. (2003). Synthesis, structural characterisation and photophysics of anionic cyclometalated bis(alkynyl) (benzo[h]quinolate) platinate(II) species. *Dalton Trans*, 822 - 830
- Fossey, J. S. & Richards, J. C. (2002). A direct route to platinum NCN-pincer complexes derived from 1,3-bis(imino)benzenes and an investigation into their activity as catalysts for carbon-carbon bond formation. *Organometallics*, 21, 5259 - 5264
- Fossey, J. S.; Russell, M. L.; Malik, K. M. A. & Richards, C. J. (2007). Synthesis and crystal structures of the first C₂-symmetric bis-aldimine NCN-pincer complexes of platinum and palladium. *J. Organomet. Chem.*, 692, 4843 - 4848
- Godbert, N.; Pugliese, T.; Aiello, I.; Bellusci, A.; Crispini, A. & Ghedini, M. (2007). Efficient, ultrafast, microwave-assisted syntheses of cycloplatinated complexes. *Eur. J. Inorg. Chem.*, 5105 - 5111
- He, Z.; Wong, W.-Y.; Yu, X.; Kwok, H.-S. & Lin, Z. (2006). Phosphorescent platinum(II) complexes derived from multifunctional chromophores: synthesis, structures, photophysics, and electroluminescence. *Inorg. Chem.*, 45, 10922 - 10937
- Hill, A. F. (2002). *Organotransition metal chemistry*, Royal Society of Chemistry.
- Hirani, B.; Li, J.; Djurovich, P. I.; Yousufuddin, M.; Oxgaard, J.; Persson, P.; Wilson, S. R.; Bau, R.; Goddard, W. A. & Thompson, M. E. (2007). Cyclometalated iridium and platinum complexes with noninnocent ligands. *Inorg. Chem.*, 46, 3865 - 3875
- Hofmann, A.; Dahlenburg, L. & van Eldik, R. (2003). Cyclometalated analogues of platinum terpyridine complexes: kinetic study of the strong σ -donor cis and trans effects of carbon in the presence of a π -acceptor ligand backbone. *Inorg. Chem.*, 42, 6528 - 6538
- Hoogervorst, J. W.; Elsevier, J. C.; Lutz, M. & Spek, A. L. (2001). New cis- and trans-arylplatinum(II) acetylide compounds containing a bis(imino)aryl [NCN] ligand. *Organometallics*, 20, 4437 - 4440
- Hoogervorst, J. W.; Koster, A. L.; Lutz, M.; Spek, A. L. & Elsevier, J. C. (2004). trans-Arylplatinum(II) methyl compounds containing a bis(imino)aryl [NCN] ligand. *Organometallics*, 23, 1161 - 1164

- Janzen, E. D.; Vanderveer, D. G.; Mehne, L. F.; Silva, F.; da Demétrio, A.; Brédas, J. - L. & Grant, G. J. (2008). Cyclometallated Pt(II) and Pd(II) complexes with a trithiacrown ligand. *Dalton Trans.*, 1872 - 1882
- Jolliet, P.; Gianini, M.; von Zelewsky, A.; Bernardinelli, G. & Stoeckli-Evans, H. (1996). Cyclometalated Complexes of Palladium(II) and Platinum(II): cis-Configured Homoleptic and Heteroleptic Compounds with Aromatic C^N Ligands. *Inorg. Chem.*, 35, 4883 - 4888
- Kozhevnikov, V. N.; Donnio, B. & Bruce, D. W. (2008). Phosphorescent, terdentate, liquid-crystalline complexes of platinum(II): stimulus-dependent emission. *Angew. Chem., Int. Ed.*, 47, 6286-6289
- Kui, S. C. F.; Chui, S. S.-Y.; Che, C.-M. & Zhu, N. (2006). Structures, photoluminescence, and reversible vapoluminescence properties of neutral platinum(II) complexes containing extended π -conjugated cyclometalated ligands. *J. Am. Chem. Soc.*, 128, 8297 - 8309
- Kulikova, M. V.; Balashev, K. P. & Erzin, Kh. (2003). Synthesis and photophysical properties of a series of biscyclometalated platinum(II) complexes on the basis of a tridentate 2,6-diphenylpyridine. *Russ. J. Gen. Chem.*, 73, 1839 - 1845
- Kvam, P. I. & Songstad, J. (1995). Preparation and characterization of some cyclometalated Pt(II) complexes from 2-phenylpyridine and 2-(2'-thienyl)pyridine. *Acta Chem. Scand.*, 49, 313 - 324
- Kvam, P. I.; Puzyk, M. V.; Balashev, K. P. & Songstad, J. (1995). Spectroscopic and electrochemical properties of some mixed-ligand cyclometalated platinum(II) complexes derived from 2-phenylpyridine. *Acta Chem. Scand.*, 49, 335 - 343
- Lai, S.-W.; Chan, M. C.-W.; Cheung, K.-K. & Che, C.-M. (1999). Carbene and isocyanide ligation at luminescent cyclometalated 6-phenyl-2,2'-bipyridyl platinum(II) complexes: structural and spectroscopic studies. *Organometallics*, 18, 3327 - 3336
- Li, K.; Chen, Y.; Lu, W.; Zhu, N. & Che, C. - M. (2011). A cyclometalated platinum(II) complex with a pendent pyridyl motif as solid-state luminescent sensor for acidic vapors. *Chemistry - A Eur. J.*, 17(15), 4109 - 4112
- Liao, C.-T.; Chen, H.-H.; Hsu, H.-F.; Poloek, A.; Yeh, H.-H.; Chi, Y.; Wang, K.-W.; Lai, C.-H.; Lee, G.-H.; Shih, C.-W. & Chou, P.-T. (2011). Mesomorphism and luminescence properties of platinum(II) complexes with tris(alkoxy)phenyl-functionalized pyridyl pyrazolate chelates. *Chemistry - Eur. J.*, 17, 546 - 556
- Liu, J.; Yang, C.-J.; Cao, Q.-Y.; Xu, M.; Wang, J.; Peng, H.-N.; Tan, W.-F.; Lü, X.-X. & Gao, X.-C. (2009). Synthesis, crystallography, phosphorescence of platinum complexes coordinated with 2-phenylpyridine and a series of β -diketones. *Inorg. Chim. Acta*, 362, 575 - 579
- Lopez, C.; Caubet, A.; Perez, S.; Solans, X. & Font-Bardia, M. (2004). Easy access to diastereomerically pure platinacycles. *Chem. Commun.*, 540 - 541
- Lopez, C.; Solans, X. & Font-Bardia, M. (2005). The importance of the length of the $-(CH_2)_n$ -chain on the cycloplatination of the $[(\eta^5-C_5H_5)Fe\{(\eta^5-C_5H_4)-CH=N-(CH_2)_n-NMe_2\}]$ ($n = 2$ or 3) ligands and the properties of the platinacycles. *Inorg. Chem. Commun.*, 8, 631 - 634
- Lopez, C.; Caubet, A.; Perez, S.; Solans, X.; Font-Bardia, M. & Molins, E. (2006). Chiral platinum(II) compounds containing ferrocenyl Schiff bases acting as (N), (N,O)-,

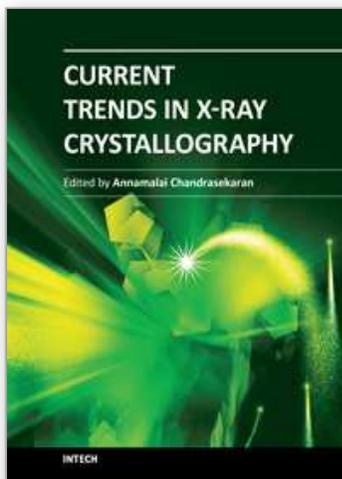
- [C(sp²,ferrocene),N]- or [C(sp²,ferrocene),N,O]²⁻ ligands. *Eur. J. Inorg. Chem.*, 3974 – 3984
- Lopez, C.; Perez, S.; Solans, X.; Font-Bardia, M. & Calvet, T. (2010). Influence of the substituent R₁ on the reactivity of [(η⁵-C₅H₅)Fe{(η⁵-C₅H₄)-CH=N(R₁)-OH}] {R₁ = -CH₂-CH₂- or 1,2-C₆H_{4}} with platinum(II) and on the properties of the complexes. *New J. Chem.*, 34, 676 – 685}
- Lopez, O.; Crespo, M.; Font-Bardia, M. & Solans, X. (1997). Activation of C-F and C-H Bonds by platinum in trifluorinated [C,N,N'] ligands. Crystal structures of [PtFMe₂{Me₂NCH₂CH₂NHCH(CH₂COMe)(2,4-C₆H₂F₂)}] and [PtMe{Me₂NCH₂-CH₂N=CH(2,3,4-C₆HF₃)}]. *Organometallics*, 16, 1233 – 1240
- Lopez-Torres, E. & Mendiola, M. A. (2010). Orthometallated versus coordination compounds for reactions of platinum(II) and palladium(II) with the ligand benzil bis(4-methyl-3-thiosemicarbazone). *Inorg. Chim. Acta*, 363, 1735 – 1740
- Lu, W.; Mi, B.-X.; Chan, M. C. W.; Hui, Z.; Che, C.-M.; Zhu, N. & Lee, S.-T. (2004). Light-emitting tridentate cyclometalated platinum(II) complexes containing σ-alkynyl auxiliaries: tuning of photo- and electrophosphorescence. *J. Am. Chem. Soc.*, 126, 4958 – 4971
- Lusby, P. J.; Mueller, P.; Pike, S. J. & Slawin, A. M. Z. (2009). Stimuli-responsive reversible assembly of 2D and 3D metallosupramolecular architectures. *J. Am. Chem. Soc.*, 131, 16398 – 16400
- Ma, B.; Djurovich, P. I. & Thompson, M. E. (2005). Excimer and electron transfer quenching studies of a cyclometalated platinum complex. *Coord. Chem. Rev.*, 249, 1501 – 1510
- Ma, B.; Li, J.; Djurovich, P. I.; Yousufuddin, M.; Bau, R. & Thompson, M. E. (2005). Synthetic control of Pt···Pt separation and photophysics of binuclear platinum complexes. *J. Am. Chem. Soc.*, 127, 28-29
- Martin, R.; Crespo, M.; Font-Bardia, M. & Calvet, T. (2009). Five- and seven-membered metallacycles in [C,N,N'] and [C,N] cycloplatinated compounds. *Organometallics*, 28, 589 – 597
- McGuire Jr., R.; McGuire, M. C. & McMillin, D. R. (2010). Platinum(II) polypyridines: A tale of two axes. *Coord. Chem. Rev.*, 254, 2574 – 2583
- Mdleleni, M. M.; Bridgewater, J. S.; Watts, R. J. & Ford, P. C. (1995). Synthesis, structure and spectroscopic properties of ortho-metallated platinum(II) complexes. *Inorg. Chem.*, 34, 2334 – 2342
- Mocanu, A. S.; Ilis, M.; Dumitrascu, F.; Ilie, M. & Cîrcu, V. (2010). Synthesis, mesomorphism and luminescence properties of palladium(II) and platinum(II) complexes with dimeric Schiff base liquid crystals. *Inorg. Chim. Acta*, 363, 729 – 736
- Nabavizadeh, S. M.; Haghighi, G. M.; Esmaeilbeig, A. R.; Raoof, F.; Mandegani, Z.; Jamali, S.; Rashidi, M. & Puddephatt, R. J. (2010). Assembly of symmetrical or unsymmetrical cyclometalated organoplatinum complexes through a bridging diphosphine ligand. *Organometallics*, 29, 4893 – 4899
- Newman, C. P.; Cave, G. W. V.; Wong, M.; Errington, W.; Alcock, N. W. & Rourke, J. P. (2001). Di-metallated platinum carbonyl complexes: platinum-platinum interactions in the solid state. *Dalton Trans.*, 2678 – 2582
- Newman, C. P.; Casey-Green, K.; Clarkson, G. J.; Cave, G. W. V.; Errington, W. & Rourke, J. P. (2007). Cyclometallated platinum(II) complexes: oxidation to, and C-H activation by, platinum(IV). *Dalton Trans.*, 3170 – 3182

- Niedermair, F.; Waich, K.; Kappaun, S.; Mayr, T.; Trimmel, G.; Mereiter, K. & Slugovc, C. (2007). Heteroleptic $\kappa^2(\text{N},\text{C}^2)$ -2-phenylpyridine platinum complexes: the use of bis(pyrazolyl)borates as ancillary ligands. *Inorg. Chim. Acta*, 360, 2767-2777
- Niedermair, F.; Kwon, O.; Zojer, K.; Kappaun, S.; Trimmel, G.; Mereiter, Kurt. & Slugovc, C. (2008). Heteroleptic platinum(II) complexes of 8-quinolinolates bearing electron withdrawing groups in 5-position. *Dalton Trans.*, 4006 - 4014
- O'Neill, M. & Kelly, S. M. (2011). Ordered Materials for Organic Electronics and Photonics. *Adv. Mater.*, 21, 556 - 584
- Pandya, S. U.; Moss, K. C.; Bryce, M. R.; Batsanov, A. S.; Fox, M. A.; Jankus, V.; Al Attar, H. A. & Monkman, A. P. (2010). Luminescent platinum(II) complexes containing cyclometallated diaryl ketimine ligands: synthesis, photophysical and computational properties. *Eur. J. Inorg. Chem.*, 1963 - 1972
- Perez, S.; Lopez, C.; Caubet, A.; Solans, X. & Font-Bardia, M. (2003). Synthesis, characterisation and study of the reactivity of the first platinum(II) complex having a [C(sp², ferrocene),N,N']- terdentate ligand. *New J. Chem.*, 27, 975 - 982
- Praefcke, K.; Bilgin, B.; Pickardt, J. & Borowski, M. (1994). Liquid-crystalline compounds, 86. The first disc-shaped dinuclear platinum mesogen. *Chem. Ber.*, 127, 1543 - 1546
- Qiu, D.; Wu, J.; Xie, Z.; Cheng, Y. & Wang, L. (2009). Synthesis, photophysical and electrophosphorescent properties of mononuclear Pt(II) complexes with arylamine functionalized cyclometalating ligands. *J. Organomet. Chem.*, 694, 737 - 746
- Qiu, D.; Feng, Y.; Wang, H.; Bao, X.; Guo, Y.; Cheng, Y. & Wang, L. (2010). Synthesis, crystal structure and photophysical properties of a novel Pt(II) complex with multi-functionalized cyclometalating ligand. *Inorg. Chem. Commun.*, 13, 613 - 617
- Quiroga, A. G.; Cubo, L.; Sanz Miguel, P. J.; Moneo, V.; Carnero, A. & Navarro-Ranninger, C. (2008). Isolation of an intermediate in the platination of p-nitroacetophenone 4-methylthiosemicarbazone: potential application as an antitumor drug. *Eur. J. Inorg. Chem.*, 1183 - 1187
- Rausch, A. F.; Monkowius, U. V.; Zabel, M. & Yersin, H. (2010). Bright sky-blue phosphorescence of [n-Bu₄N][Pt(4,6-dFppy)(CN)₂]: synthesis, crystal structure, and detailed photophysical studies. *Inorg. Chem.*, 49, 7818- 7825
- Raybov, A. D.; Ott, S.; Samuleev, P. V.; Polyakov, V. A.; Alexandrova, L.; Kazankov, G. M.; Shova, S.; Revenko, M.; Lipkowski, J. & Johansson, M. H. (2002). Structural and mechanistic look at the orthoplatination of aryl oximes by dichlorobis(sulfoxide or sulfide)platinum(II) complexes. *Inorg. Chem.*, 41, 4286 - 4294
- Riera, X.; Caubet, A.; Lopez, C.; Moreno, V.; Solans, X. & Font-Bardia, M. (2000). Activation of $\sigma(\text{C}-\text{H})$ Bonds in C₆H₅CH=NCH₂CH₂SEt induced by platinum(II). X-ray crystal structure of [Pt{C₆H₄CH=NCH₂CH₂SEt}Cl]. *Organometallics*, 19, 1384 - 1390
- Riera, X.; Lopez, C.; Caubet, A.; Moreno, V.; Solans, X. & Font-Bardia, M. (2001). Platinum(II) and palladium(II) compounds containing chiral thioimines. *Eur. J. Inorg. Chem.*, 2135 - 2142
- Rodriguez, J.; Zafrilla, J.; Albert, J.; Crespo, M.; Granell, J.; Calvet, T. & Font-Bardia, M. (2009). Cyclometallated platinum(II) compounds with imine ligands derived from amino acids: Synthesis and oxidative addition reactions. *J. Organomet. Chem.*, 694, 2467 - 2475
- Ryabov, A. D.; Kazankov, G. M.; Panyashkina, I. M.; Grozovsky, O. V.; Dyachenko, O. G.; Polyakov, V. A. & Kuz'mina, L. G. (1997). Cycloplatination of aryl and ferrocenyl

- oximes by *cis*-[PtCl₂(OSMe₂)₂] affording expected platinum(II) and unexpected platinum(IV) products. *J. Chem. Soc., Dalton Trans.*, 4385 – 4392
- Ryabov, A. D.; Kuz'mina, L. G.; Polyakov, V. A.; Kazankov, G. M.; Ryabova, E. S.; Pfeffer, M. & van Eldik, R. (1995). Kinetics and mechanism of halogen-bridge cleavage in dimethylaminomethylphenyl-C¹,N pallada- and platinacycles by pyridines. pressure effects, and crystal structures of the *N,N-cis* reaction product, its *N,N-trans* orthometallated analogue and a dimer of similar reactivity. *J. Chem. Soc., Dalton Trans.: Inorg. Chem.*, 999 – 1006
- Santoro, A.; Whitwood, A. C.; Williams, J. A. G.; Kozhevnikov, V. N. & Bruce, D. W. (2009). Synthesis, mesomorphism, and luminescent properties of calamitic 2-phenylpyridines and their complexes with platinum(II). *Chem. Mater.*, 21, 3871 – 3882
- Scaffidi-Domianello, Y. Y.; Nazarov, A. A.; Haukka, M.; Galanski, M.; Keppler, B. K.; Schneider, J.; Du, P.; Eisenberg, R. & Kukushkin, V. Y. (2007). First example of the solid-state thermal cyclometalation of ligated benzophenone imine giving novel luminescent platinum(II) species. *Inorg. Chem.*, 46, 4469 – 4482
- Schneider, J.; Du, P.; Wang, X.; Brennessel, W. W. & Eisenberg, R. (2009). Synthesis, electrochemistry, photophysics, and solvatochromism in new cyclometalated 6-phenyl-4-(*p*-R-phenyl)-2,2'-bipyridyl (R = Me, COOMe, P(O)(OEt)₂) (C^NN^N) platinum(II) thiophenolate chromophores. *Inorg. Chem.*, 48, 1498 – 1506
- Seneclauze, J. B.; Retailleau, P. & Ziessel, R. (2007). Design and preparation of neutral substituted fluorene- and carbazole-based platinum(II)-acetylide complexes. *New J. Chem.*, 31, 1412 – 1416
- Shao, P.; Li, Y. & Sun, W. (2008). Cyclometalated platinum(II) complex with strong and broadband nonlinear optical response. *J. Phys. Chem. A.*, 112, 1172 – 1179
- Sirous, J.; Zahra, M.; Nabavizadeh, S. M.; Milic, D.; Kia, R. & Rashidi, M. (2010). Cyclometalated cluster complex with a butterfly-shaped Pt₂Ag₂ core. *Inorg. Chem.*, 49, 2721 – 2726
- Siu, P. K.-M.; Ma, D.-L. & Che, C.-M. (2005). Luminescent cyclometalated platinum(II) complexes with amino acid ligands for protein binding. *Chem. Commun.*, 1025 – 1027.
- Valeur, B. (2001). *Molecular fluorescence: principles and applications*, Wiley-VCH, Verlag GmbH, Weinheim
- Vasquez-Garcia, D.; Fernandez, A.; Fernandez, J. J.; Lopez-Torres, M.; Suarez, A.; Ortigueira, J. M.; Vila, J. M. & Adams, H. (2000). New cyclometallated platinum(II) compounds with thiosemicarbazones: crystal and molecular structure of [Pt{4-MeC₆H₃C(Me)=NN=C(S)NH₂}(PPh₃)]. *J. Organomet. Chem.*, 595, 199 – 207
- Venkatesan, K.; Kouwer, P. H. J.; Yagi, S.; Muller, P. & Swager, T. M. (2008). Columnar mesophases from half-discoid platinum cyclometalated metallomesogens. *J. Mater. Chem.*, 18, 400 – 407
- Vila, M. J.; Pereira, M. T.; Ortigueira, J. M.; Lata, D.; Torres, M. L.; Fernandez, J. J.; Fernandez, A. & Adams, H. (1998). Synthesis of complexes of platinum (II) with *C,N,N'*-terdentate Schiff base donor ligands. Crystal and molecular structure of [Pt{3-Me-4-MeOC₆H₂C(H)=NCH₂CH₂NMe₂}(Me)]. *J. Organomet. Chem.*, 566, 93 – 102

- Wang, Z.; Turner, E.; Mahoney, V.; Madakuni, S.; Groy, T. & Li, J. (2010). Facile synthesis and characterization of phosphorescent Pt(N C N)X complexes. *Inorg. Chem.*, 49, 11276 - 11286
- Wang, Y. F.; Liu, Y.; Luo, J.; Qi, H. R.; Li, X. S.; Nin, M. J.; Liu, M.; Shi, D. Y.; Zhu, W. G. & Cao, Y. (2011). Metallomesogens based on platinum(II) complexes: synthesis, luminescence and polarized emission. *Dalton Trans.*, 40, 5046 - 5051
- Williams, J. A. G.; Beeby, A.; Davies, E. S.; Weinstein, J. A. & Wilson, C. (2003). An alternative route to highly luminescent platinum(II) complexes: cyclometalation with N[^]C[^]N-coordinating dipyritylbenzene ligands. *Inorg. Chem.*, 42, 8609 - 8611
- Williams, J. A. G. (2007). Photochemistry and photophysics of coordination compounds: platinum. *Top. Curr. Chem.*, 281, 205 - 268
- Williams, J. A. G.; Develay, S.; Rochester, D. L. & Murphy, L. (2008). Optimising the luminescence of platinum(II) complexes and their application in organic light emitting devices (OLEDs), *Coord. Chem. Rev.*, 252, 2596 - 2611
- Wu, Y. J.; Ding, L.; Wang, H. X.; Liu, Y. H.; Yuan, H. Z. & Mao, X. A. (1997). Synthesis, characterization and structure of ferrocenylketimine complexes of platinum(II). *J. Organomet. Chem.*, 535, 49 - 58
- Yuen, M.-Y.; Roy, V. A. L.; Lu, W.; Kui, S. C. F.; Tong, G. S. M.; So, M.-H.; Chui, S. S.-Y.; Muccini, M.; Ning, J. Q.; Xu, S. J.; & Che, C.-M. (2008). Semiconducting and electroluminescent nanowires self-assembled from organoplatinum(II) complexes. *Angew. Chem., Int. Ed.*, 47, 9895 - 9899
- Zucca, A.; Petretto, G. L.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Manassero, M.; Manassero, C.; Male, L. & Albinati, A. (2006). Dinuclear C,N,C cyclometalated platinum derivatives with bridging delocalized ligands. Fourfold deprotonation of 6,6'-diphenyl-2,2'-bipyridine, H₄L, promoted by "Pt(R)₂" fragments (R = Me, Ph). Crystal structures of [Pt₂(L)(3,5-Me₂py)₂] and {Pt₂(L)(dppe)}₂ (dppe = 1,2-bis(diphenylphosphino)ethane). X-ray powder diffraction of [Pt₂(L)(CO)₂]. *Organometallics*, 25, 2253 - 2265

IntechOpen



Current Trends in X-Ray Crystallography

Edited by Dr. Annamalai Chandrasekaran

ISBN 978-953-307-754-3

Hard cover, 436 pages

Publisher InTech

Published online 16, December, 2011

Published in print edition December, 2011

This book on X-ray Crystallography is a compilation of current trends in the use of X-ray crystallography and related structural determination methods in various fields. The methods covered here include single crystal small-molecule X-ray crystallography, macromolecular (protein) single crystal X-ray crystallography, and scattering and spectroscopic complimentary methods. The fields range from simple organic compounds, metal complexes to proteins, and also cover the meta-analyses of the database for weak interactions.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Viorel Cîrcu and Marin Micutz (2011). X-Ray Structural Characterization of Cyclometalated Luminescent Pt(II) Complexes, Current Trends in X-Ray Crystallography, Dr. Annamalai Chandrasekaran (Ed.), ISBN: 978-953-307-754-3, InTech, Available from: <http://www.intechopen.com/books/current-trends-in-x-ray-crystallography/x-ray-structural-characterization-of-cyclometalated-luminescent-pt-ii-complexes>

INTECH

open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](#), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen