N-Assisted C_{Ph}-H Activation in 3, 8-Dinitro-6-phenylphenanthridine. New C, N-Cyclometalated Compounds of Pt(II): Synthesis, Structure and Luminescence Studies.

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Dedicated to Professor Antonio Laguna on the occasion of his 65th birthday

ABSTRACT

The activation of a C_{Ph}-H bond in the phenyl ring of 3, 8-dinitro-6-phenylphenanthridine (HC^N) can be achieved by refluxing the intermediate [PtCl(η^3-2-Me-C_3H_4)(HC^N-κN)] (**1**) (η^3-2-Me-C_3H_4= η^3-2-methylallyl) in 2-methoxyethanol to render the new cyclometalated complex [{Pt(μ-Cl)(C^N)}$_2$](**2**). The cleavage of the bridging system in **2** by the neutral ligands L rendered the mononuclear complexes [PtCl(C^N)L] (L = tht **3**, PPh_3 **4**, CN^{t}Bu **5**) with the geometry (*trans* C, Cl).

The air- and temperature-stable cationic compound [Pt(C^N)(CNXyl)$_2$]ClO_4 (**6**) could be prepared from **2** by addition of CNXyl (1:4 molar ratio) after the Cl-abstraction with $AgClO_4$. Compound [Pt(C^N-κC)(tht)$_3$]ClO_4 (**7**) was prepared similarly

to **6** but using a significant excess of tht, which produces the N-dissociation of the C^N ligand. The photophysical properties of compounds **3**-**6** have been studied with the help of time-dependent-density functional theory (TD-DFT) calculations. In 2-Me-THF at low temperature (77 K) the green emission of the HC^N ligand turns in a red phosphorescence in compounds **3**-**6**, that was assigned to a mixed metal-to-ligand charge transfer/ intraligand/ ligand-to-ligand charge transfer [^{3}MLCT/^{3}IL/^{3}L'LCT] excited state. In the solid state at low temperature (77 K) the emissive behaviors are quite similar to that observed in glassy solutions with some contribution of excimeric π–π* emissions in the neutral chloro-derivatives. Compounds **4**-**6** are also emissive in the solid state at room temperature with photoluminescence quantum yields (*Φ)* between 0.032 and 0.05.

Introduction

Numerous investigations in the field of Pt(II) coordination chemistry have been recently spurred on by their attractive photophysical properties[1-11] and potential applications of triplet-emitting platinum (II) complexes as phosphors in highly efficient organic light-emitting devices (OLEDs)[12-15] or as chemosensors for oxygen,[16,17] volatile organic compounds (VOCs)[18-23] or poisonous metal cations.[24,25] Room-temperature phosphorescence is attributed to the strong spin-orbit coupling constant of the platinum atom which allows an efficient singlet-triplet intersystem crossing (ISC). The phosphorescence efficiency is favoured by a significant contribution of metal atomic orbitals to the excited state and a large energy gap between the lowest excited state and the d-d state, which promotes non-radiative decay to the ground state.

Many isolated C,N-cyclometalated complexes of platinum (II) emit from ligand-centered (IL, π-π* or n-π*) and metal-to-ligand charge transfer (MLCT) excited states and are luminescent in solution under ambient conditions. [26-27]

The photophysical properties of mononuclear heteroleptic complexes with a single cyclometalating ligand (C^N) can be fine-tuned *via* variation of the cyclometalating or even the ancillary ligands. [7,9,26-35] The electronic properties of the ligands affect the electron density at the metal center and the energy of the highest occupied molecular orbital (HOMO) and consequently the MLCT character into the lowest energy transition thus altering the radiative energy and lifetime of the excited state. On the other hand, chemical modification of the chromophoric cyclometalated ligand influences the energies of the frontier orbitals. At this point it is well known that the addition of electron-donating or –withdrawing groups in the imine fragment have the effect of raising or lowering the energy of the lowest unoccupied molecular orbital (LUMO) respectively and consequently the HOMO-LUMO energy gap.

Our interest in the chemistry of luminescent cyclometalated Pt(II) compounds led us to prepare heteroleptic benzoquinolinate Pt(II) complexes with different kinds of ancillary ligands.[36-42] For this work we focused on the synthesis of new luminescent compounds *via* variation of the cyclometalating ligand and decided to check the possibility of cyclometalation of 3, 8-Dinitro-6-phenylphenanthridine (HC^N), an organic ligand with a more extended π-conjugated system than bzq (benzoquinolinate) and electron-withdrawing groups in the imine fragment. As a result we describe the cyclometalation of 3, 8-dinitro-6-phenylphenanthridine that was achieved in two steps through the intermediate [PtCl(η^3-2-Me-C_3H_4)(HC^N-κN)]. The dinuclear cyclometalated compound [{Pt(μ-Cl)(C^N)}$_2$] was obtained and used as starting material for the synthesis of the heteroleptic mononuclear compounds [PtCl(C^N)L] (L = Tetrahydrothiophene (tht), Triphenylphosphine (PPh_3), *tert*-Butyl isocyanide (CN^tBu)) and [Pt(C^N)$(CNXyl)_2$]ClO_4 (CNXyl= 2,6-Dimethylphenyl isocyanide) that incorporate monodentate ligands with different electron-withdrawing/–donating

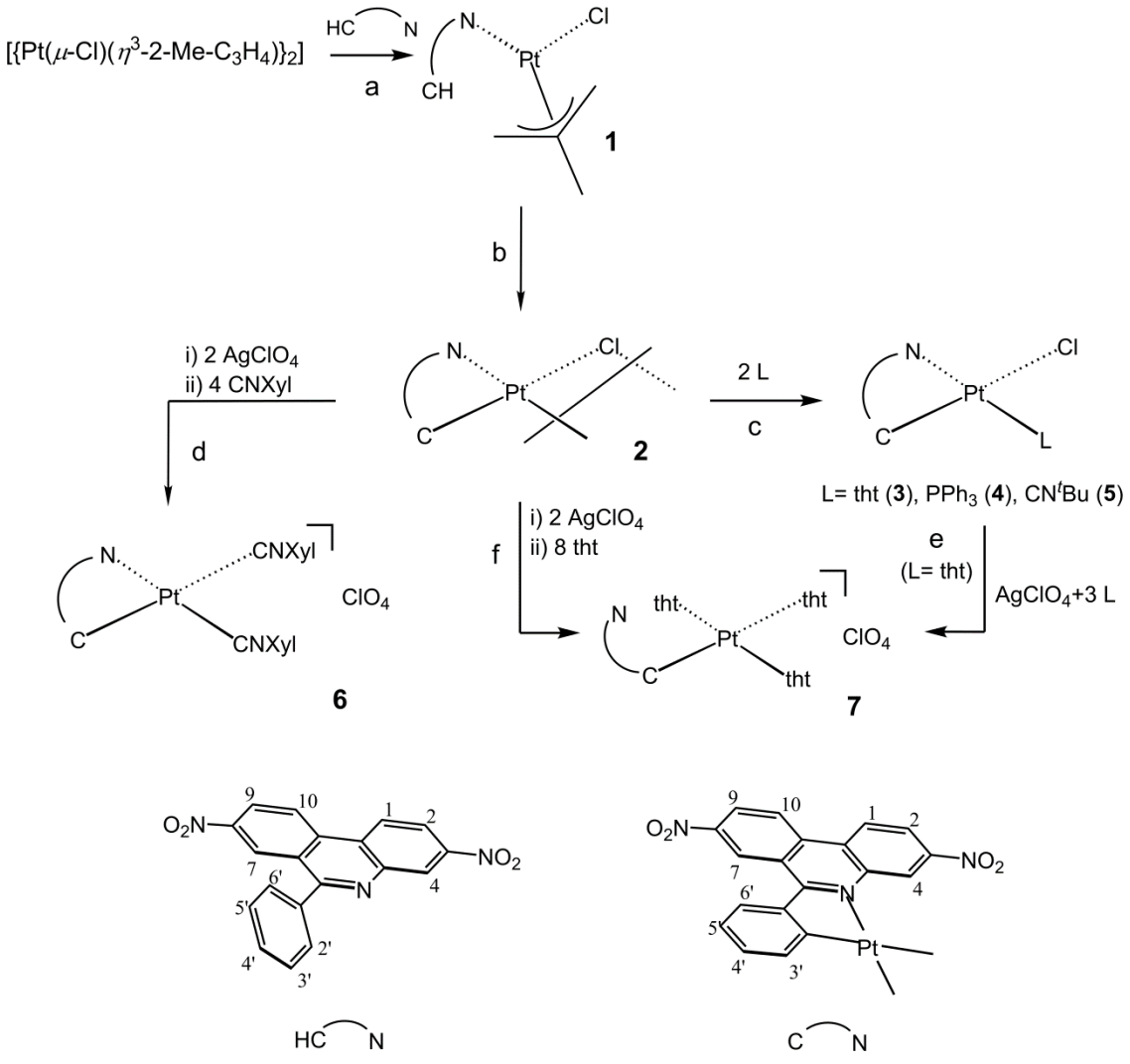
properties. Their photophysical properties were thoroughly investigated and explained with the aid of time-dependent-density functional theory (TD-DFT) calculations.

Results and Discussion

Reaction of [{Pt(μ-Cl)(η^3-2-Me-C_3H_4)}$_2$] with 3,8-dinitro-6-phenylphenanthridine (HC^N). Synthesis of [PtCl(η^3-2-Me-C_3H_4)(HC^N-κN)](1)·0.5 Me_2CO. A solution of the dichloro-bridged complex [{Pt(μ-Cl)(η^3-2-Me-C_3H_4)}$_2$] (η^3-2-Me-C_3H_4 = η^3-2-methylallyl) in acetone was treated with 3,8-dinitro-6-phenylphenanthridine (HC^N) in 1:2 molar ratio. After 2 h of stirring at room temperature, compound [PtCl(η^3-2-Me-C_3H_4)(HC^N-κN)] (**1**)·0.5 Me_2CO precipitated and was obtained as a green-yellowish air-stable solid (see Scheme 1a). The presence of acetone in the powdered samples of **1** is evident in its IR spectrum ($\upsilon_{C=O}$, 1707 cm^{-1}), and ^{1}H NMR (DMSO-d_6) that shows a singlet at 2.02 ppm (3H).An absorption at 285 cm^{-1} attributable to υ_{Pt-Cl} is consistent with a terminal Pt-Cl bond in *trans* disposition to a ligand with a large *trans* influence as η^3-2-Me-C_3H_4.[43] The ^{1}H-NMR spectrum of **1** in DMSO-d_6 shows the signals corresponding to the free ligand 3,8-dinitro-6-phenylphenanthridine suggesting that in complex **1** the monodentate HC^N-κN ligand has been substituted by a molecule of dimethylsulfoxide. All attempts to obtain a well resolved ^{1}H-NMR spectrum of **1** in other less coordinating solvent failed because of solubility issues. However, the presence in **1** of the allyl and HC^N ligands was confirmed by MALDI (+) mass spectrum (595.1 [Pt(η^3-2-Me-C_3H_4)(HC^N,-κN)]$^+$) and corroborated by X-ray diffraction study. As can be observed (Figure 1, Table 1), compound **1** crystallizes without acetone in the centrosymmetric monoclinic space group P2(1)/n which contains two molecules in the asymmetric unit (**1A** and **1B**), having similar structural details. Both, **1A** and **1B**, consist in a mononuclear highly distorted square-planar Pt(II) complex. The distortion in the platinum center is mainly

due to the bonding mode of the η^3-allyl group. The Pt-C_{allyl} distances are essentially equal to one another and similar to those found in other η^3-allyl Pt(II) complexes containing ligands of similar *trans* influence. [43] The Pt-Cl distance 2.3666 (13) Å (1A) [2.3685(12) Å (1B)] fits the bond lengths found in [Pt(η^3-2-Me-C_3H_4)(P(^{t}Bu)$_3$)Cl][44,45] and [Pt(η^3-2-Me-C_3H_4)(2-(4-Bromophenyl) imidazol[1,2a]pyridine)Cl)][43]. The Pt-N distance, 2.130 (4) Å (1A) [2.123(4) Å (1B)], is in the upper range observed in Pt(II) complexes with similar ligands[43,46,47] due to the high trans influence of the η^3-2-Me-C_3H_4 ligand.

Scheme 1. Reactions and Numerical Scheme for ^{1}H NMR Purpose



a) acetone, RT; b) 2-methoxyethanol, Δ; c) CH_2Cl_2, RT; d) i) NCMe, Δ, ii) NCMe-THF (1:10) RT; e) acetone, RT; f) i) NCMe, Δ, ii) $CHCl_3$, Δ.

The dihedral angle between the Pt coordination plane (Pt(1), Cl(1), N(1), C(20), C(22) **1A**; Pt(2), Cl(2), N(4), C(43), C(45) **1B**) and the best plane defined for the phenanthridine moiety (N(1), C(7)-C(19) **1A**; N(4), C(30)-C(42) **1B**) is 85.15(5)º (**1A**) [81.29 (5)º **1B**], probably due to the steric repulsions among the ligands.

Table 1. Selected Structural Data for 1.

1A		**1B**	
	Bond lengths [Å]		
Pt(1)-C(20)	2.105(5)	Pt(2)-C(43)	2.104(5)
Pt(1)-C(21)	2.092(5)	Pt(2)-C(44)	2.107(5)
Pt(1)-C(22)	2.099(5)	Pt(2)-C(45)	2.096(5)
Pt(1)-N(1)	2.130(4)	Pt(2)-N(4)	2.123(4)
Pt(1)-Cl(1)	2.3666(13)	Pt(2)-Cl(2)	2.3685(12)
	Bond angles (deg)		
C(22)-Pt(1)-N(1)	167.7(2)	C(45)-Pt(2)-N(4)	169.6(2)
C(20)-Pt(1)-N(1)	98.92(18)	C(43)-Pt(2)-N(4)	100.6(2)
C(22)-Pt(1)-C(20)	69.1(2)	C(45)-Pt(2)-C(43)	69.2(2)
C(22)-Pt(1)-Cl(1)	100.72(18)	C(45)-Pt(2)-Cl(2)	99.86(17)
N(1)-Pt(1)-Cl(1)	91.43(11)	N(4)-Pt(2)-Cl(2)	90.16(11)
C(20)-Pt(1)-Cl(1)	168.85(17)	C(43)-Pt(2)-Cl(2)	168.60(18)

The 3,8-dinitro-6-phenylphenanthridine is not planar with the phenyl ring forming an angle of 62.45(13)º (**1A**) [64.36(11)º (**1B**)] with the phenanthridine fragment. The

phenyl group is not orientated to the Pt atom, which rejects a Pt(1)···H(1) or Pt(2)···H(24) interaction in solid state, as observed in many examples described in the literature.[48,49]

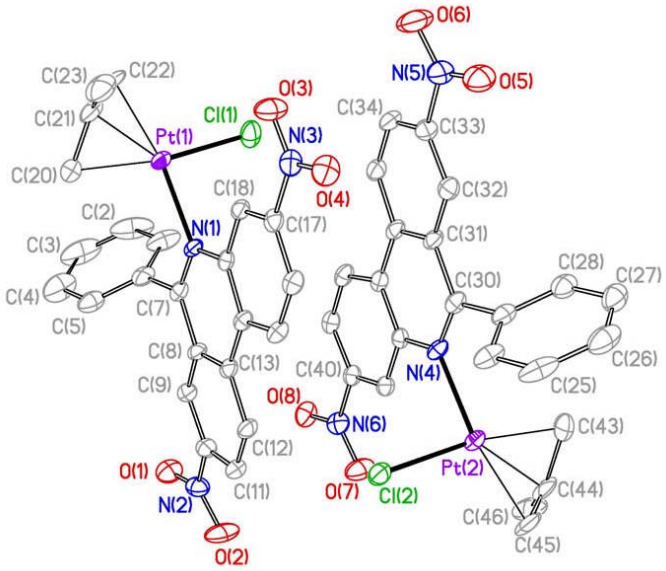


Figure 1. Molecular structure view of complexes **1A** and **1B.** All hydrogen atoms have been omitted for clarity.

Synthesis and characterization of [{Pt(μ-Cl)(C^N)}$_2$] (2) (C^N = 3,8-dinitro-6-phenylphenanthridine-H-κC,N). When a suspension of **1**·0.5 Me_2CO in 2-methoxyethanol was refluxed for 2h, it turned into a dark-brownish mixture from which compound **2** was isolated as an air stable solid although unpurified with a dark-grey and very insoluble byproduct, likely Pt(0). The ^{1}H NMR of **2** was recorded in DMSO-d_6, because of its scarce solubility in other common solvents and the signals were assigned on the basis of a ^{1}H-^{1}H COSY experiment (see Experimental Section and Figures S1 and S2). This spectrum provided direct evidence of the absence of the allyl group and the metalation of the 3,8-dinitro-6-phenylphenanthridine (HC^N) through the ortho-C of the phenyl ring (C2', see scheme 1 for numeration), since the phenyl moiety shows only four different proton signals. Apart from that, in the metalated C^N group, H_4 and H_7

undergo an important downfield shift (9.59 ppm H_4, 9.53 ppm H_7) with respect to the free ligand (8.90 ppm H_4, 8.84 ppm H_7). Attempts to obtain **2** in only one step failed; by refluxing a mixture of the allyl complex [{Pt(μ-Cl)(η^3-2-Me-C_3H_4) }$_2$] and 3,8-dinitro-6-phenylphenanthridine (1:2 molar ratio) in 2-methoxyethanol, the allyl complex decomposes. Neither pure samples nor crystals of **2** could be obtained because of solubility issues. However, **2** could be used as starting material in the synthesis of new Pt (II) compounds containing 3,8-dinitro-6-phenylphenanthridine-H-κC,N as C,N-cyclometalated ligand (see below).

Synthesis and characterization of [PtCl(C^N)(L)] (C^N = 3,8-dinitro-6-phenylphenanthridine-H-κC,N; L = tht (3), PPh_3 (4) and CN^{t}Bu (5)). Compounds **3**, **4** and **5** were obtained by reaction of the chlorine bridged compound **2** with tht, PPh_3 or CN^{t}Bu in 1:2 molar ratio in CH_2Cl_2 at room temperature (Scheme 1c). Compounds **3-5** were soluble in the reaction media and were obtained from the CH_2Cl_2 solutions as air stable solids with moderate yields and characterized by the usual techniques (See experimental Section). A similar reaction but using 2, 6-dimethylphenylisocyanide as ligand (L) renders such an insoluble solid that was not able to be characterized. All the spectroscopic data discussed below showed that in all cases only one isomer, (*trans*- C, Cl), is present in each case, which is frequently observed in this kind of compounds. Compounds **3-5** show one υ_{Pt-Cl} absorption at ca. 277 cm^{-1}, which is consistent with a terminal Pt-Cl bond trans to C. Compound **5** exhibits one absorption at 2218 cm^{-1} assignable to $\upsilon_{C\equiv NR}$, of a terminal C≡N^{t}Bu, [30,38,43,50,51] since it appears shifted to higher frequencies with respect to the free ligand (2125 cm^{-1}). ^{1}H-NMR spectra of **3-5** display the expected signals for the C^N and the ancillary ligands in 1:1 intensity ratio, which were assigned unambiguously on the basis of ^{1}H-^{1}H COSY experiments. The resonances corresponding to the phenyl ring of the C^N are clearly altered by the

coordination or nature of the ancillary ligand. In compound **4** (L = PPh_3) the phenyl signals undergo an important upfield shift ($H_{3'}$: 6.88 ppm, $H_{4'}$: 6.69 ppm) when compared with **3** ($H_{3'}$: 7.89 ppm, $H_{4'}$: 7.33 ppm) or **5** ($H_{3'}$: 7.71 ppm, $H_{4'}$: 7.32 ppm). This effect has been associated with the anisotropic shielding effect of the aromatic ring current of phenyl groups of PPh_3 near the atoms affected, [43,52-54] which is in agreement with the *cis* disposition of the Pt-C_{Ph} and Pt-P bonds in the molecule. The $^{31}P\{^1H\}$-NMR spectrum of **4** shows a singlet with platinum satellites, displaying a ^{195}Pt-P coupling constant value (4622 Hz) that corresponds to a *trans* arrangement of PPh_3 and the Pt-N bond. This value is slightly bigger than those observed in related compounds with the same geometry arrangement such as [Pt(C^N)Cl(PPh_3)] (HC^N = 2-(4-bromophenyl)imidazol[1,2-a]pyridine,[43] N, N-dimethylbenzylamine,[55] 1-trimethylsilyl-4-[(dimethylamino)-methyl]benzene,[56] 2,2'-bipyridine,[57] 2-(2'-thienyl)pyridine[58]).

Single crystal X-ray diffraction studies on **3** and **4** (see Figures 2 and 3) showed that in both complexes the Pt center adopts a square planar coordination environment highly distorted as a consequence of the small bite angle of the C^N ligand [79.18(9)º (**3**) and 79.8(2)º (**4**)], similar to those found in other five membered metalacycles of Pt

(II).[30,37,39,43,59-62]

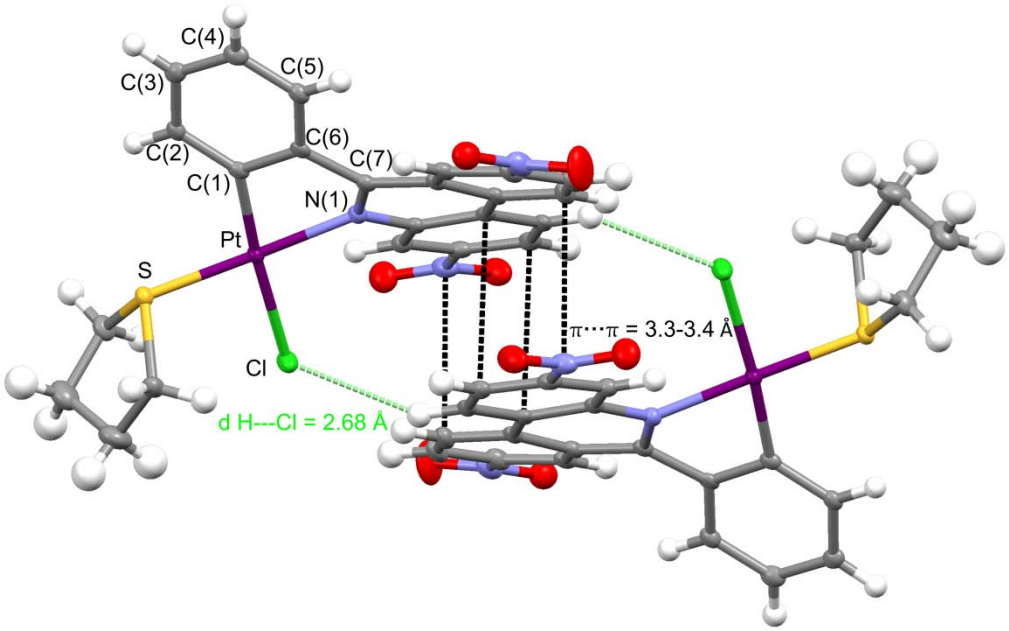


Figure 2. Molecular structure and X-ray packing view of compound **3**, solvent molecules and hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg)**:** Pt-C(1): 1.979(2); Pt-N(1): 2.062(2); Pt-S: 2.2658(6); Pt-Cl: 2.4119(7); C(1)-Pt-N(1): 79.18(9); C(1)-Pt-S: 92.47(7); N(1)-Pt-Cl: 96.69 (6); S-Pt-Cl: 90.54(2).

The larger steric demand of the bulky triphenylphosphine ligand seems to be the cause of the significant difference in the C(1)-Pt-E (E= S **3**, P **4)** angle [92.47(7)º (**3**) and 97.1 (2)º (**4**)] observed in these complexes. The Pt-E distances are in the typical range for platinum (II) compounds with these ancillary ligands in a *trans* disposition with respect to N.[30,43,46,61,63,64] Complexes **3** and **4** are not planar, the dihedral angles between the platinum coordination planes (Pt, N1, C1, Cl, S **3**; Pt, N1, C1, Cl, P **4**) and the phenanthridine moieties (N_1,C_7-C_{19}) are 48.34º (**3**) and 46.18 º (**4**). The dihedral angle between the Pt coordination plane and the phenyl moieties (C_1-C_6) are 30.31º (**3**) and 18.48º (**4**). The cyclometalated 3, 8-dinitro-6-phenylphenanthridine ligand itself is

also strongly distorted since the dihedral angles between the phenanthridine and the phenyl moieties are 39.18º (**3**) and 35.14º (**4**).

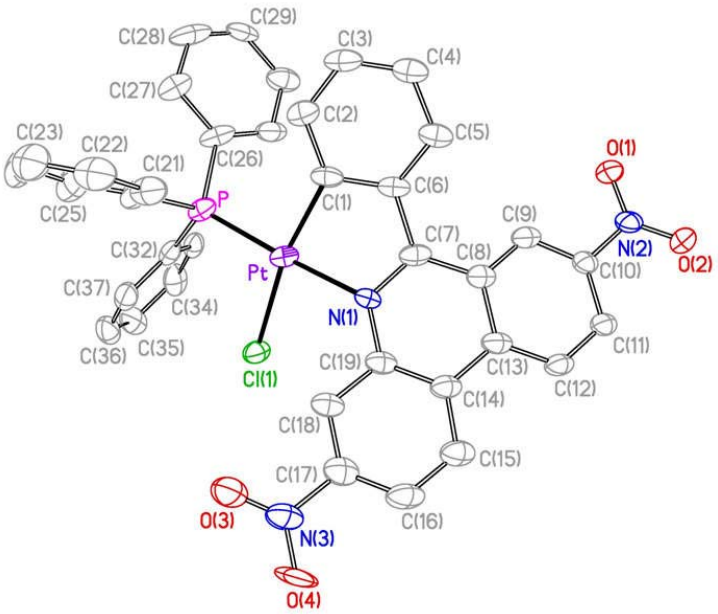


Figure 3. Molecular structure view of complex **4**. Solvent molecules and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg)**:** Pt-C(1): 2.005(7); Pt-N(1): 2.145(5); Pt-P: 2.2519(18); Pt-Cl: 2.3835(16). C(1)-Pt-N(1): 79.8(2); C(1)-Pt-P: 97.1(2); N(1)-Pt-Cl: 92.22(13); P-Pt-Cl: 90.84(6).

In compound **3** the molecules are packed in head-to-tail dimers with short [3.3-3.4 Å] interplanar separations between the phenanthridine moieties. Additionally to the intermolecular π···π interactions[38,41,57,65] (Figure 2, black dashed line) compound **3** shows weak H···Cl interactions too, with distances of 2.68 Å (Figure 2, green dashed line). In short, all the spectroscopic and structural information discussed above indicate that the cleavage of the bridging system in complex **2** by the neutral ligands tht, PPh_3 and C≡N^{t}Bu proceeds selectively (Scheme 1) generating only the (*trans*-C,Cl)-isomer. This result is the expected one on the basis of the transphobia degree (T)[36,43,66,67] of pairs of *trans* ligands, T[C(C^N)/Cl] < T[C(C^N)/L(tht, PPh_3, C≡N^{t}Bu)]. Given that in

complexes **3-5** there is no steric hindrance between pairs of *cis* ligands, the isomer obtained is that expected from the electronic preferences.

Synthesis and characterization of [Pt(C^N-*κ*C,N)(CNXyl)$_2$]ClO$_4$ (6) and [Pt(C^N-*κ*C)(tht)$_3$]ClO$_4$ (7).

Compound **6** was obtained from compound **2** in two steps, Cl-abstraction with $AgClO_4$ (1:2 molar ratio) in refluxing acetonitrile (NCMe) and subsequent addition of THF and 2,6-dimethylphenylisocyanide (CNXyl) in 1:4 molar ratio to the filtered NCMe solution at room temperature (See scheme 1d and experimental Section). Compound **6** was isolated as a yellow air-stable solid and fully characterized (see Experimental section and S.I.). The presence of two terminal isocyanide ligands in the complex is evident in the IR spectrum that shows two υ(C≡N) absorptions at about 2200 cm^{-1}, shifted to higher frequencies with respect to the free ligand (CN-Xyl: 2131 cm^{-1}).[30] The Λ_M value (Λ_M = 41.7 Ω^{-1} cm^2 mol^{-1} in a 5 × 10^{-4} M acetone solution) is lower than that expected for a 1:1 electrolyte, which seems to indicate some degree of association between the cationic complex and the counteranion. It is worth mentioning that the H_4 and $H_{3'}$ NMR signals in dicholoromethane-d_2 (9.49 ppm H_4, 7.97 ppm $H_{3'}$) appear upfield shifted with respect to those in the neutral complexes **3** (9.99 ppm H_4, 7.89 ppm $H_{3'}$) and **5** (10.21 ppm H_4, 7.71 ppm $H_{3'}$) that must be due to the anisotropic shielding effect of the isocyanide C≡N triple bond current close to these hydrogen atoms. A single crystal of compound **6** was obtained and studied by X-ray crystallography (Figure 4). The platinum (II) center shows a highly distorted square planar environment due to the small bite angle of the C^N ligand (C(1)-Pt-N(1), 79.63(0.15)º). This angle as well as the Pt-C_{C^N} and Pt-N_{C^N} bond distances are almost equal to those found in complexes **3** and **4** or in other platinum(II) compounds with cyclometalated ligands.[30,43] The coordination sphere of platinum (II) is completed with

two xylylisocyanide ligands. The Pt-C_{CNXyl} bond lengths are in the range of those observed in other Pt (II) isocyanide complexes, [50,68-76] with the Pt-C *trans* to N being slightly shorter than the other one (Pt-C(29)) in agreement with the smaller *trans* influence of N compared to the C-metalated atom. The isocyanide ligands are almost linearly coordinated. Notwithstanding, the aromatic rings of the xylylisocyanides (C_{21}-C_{26}, Xyl, and C_{30}-C_{35}, Xyl') are not coplanar with the Pt (II) coordination plane (Pt, N(1), C(1), C(20), C (29)) forming a dihedral angle of 32.32º (Xyl) and 48.85º (Xyl'). The phenanthridine (N(1), C(7)-C(19)) and phenyl moieties (C(1)-C(6)) are not coplanar to the Pt (II) coordination plane (37.05º and 19.47º phenanthridine and phenyl moieties respectively) nor between them (38.05º) like in complexes **3** and **4**. As is shown in Figure 4, there are weak interactions between the anion (ClO_4^-) and the cationic complex with a Pt-O (6) distance of 3.156 Å and a N(1)-O(6) distance of 2.993 Å. These kinds of interactions could explain the low conductivity values observed.

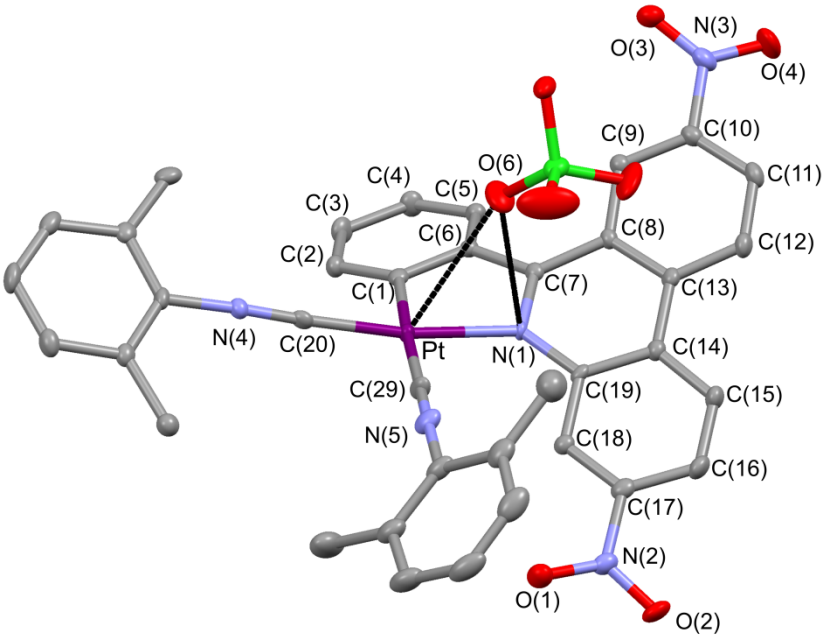


Figure 4. Molecular structure view of **6**, showing Pt-O(6) and N(1)-O(6) interactions; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg)**:** Pt-C(20): 1.895(4); Pt-C(29): 2.023(4); Pt-N(1): 2.092(3); Pt-C(1): 2.006(4);

C(1)-Pt-N(1): 79.63(15); C(20)-Pt-C(1): 91.43(16); C(20)-Pt-C(29): 90.76(17); C(29)-Pt-N(1): 98.08(15).

Attempts to prepare stable analogous complexes $[Pt(C^N)(L)_2]ClO_4$ with L = CN^tBu, PPh_3 or tht were unsuccessful. Only when L = CN^tBu, a similar compound could be obtained, but it decomposed even in the fridge (5ºC) which hindered its full characterization. These differences between the isocyanide ligands and the PPh_3 and tht might be due to the more demanding steric hindrance in the case of PPh_3 or to electronic effects for the tht, not manifested in the isocyanide ligands probably due to their π–acceptor nature.

In an effort to get $[Pt(C^N)(tht)_2]ClO_4$ harder synthesis conditions were probed: a) by reacting [PtCl(C^N)(tht)] (**3**) with $AgClO_4$ (molar ratio 1:1) and subsequent addition of tht (molar ratio 1:3) to the filtered solution and b) by refluxing a mixture of the "in situ" freshly prepared solution of $[Pt(C^N)(NCMe)_2]ClO_4$ and tht (molar ratio 1:4) in chloroform for 1 h. By either both procedures, compound $[Pt(C^N\text{-}\kappa C)(tht)_3]ClO_4$ (**7**) was obtained and isolated as an orange solid, instead of $[Pt(C^N)(tht)_2]ClO_4$ (see scheme 1e, 1f and Experimental Section).

The IR spectrum of **7** indicates the presence of the C^N ligand and of ionic perchlorate (see SI). The ^1H NMR spectrum of **7** in dichloromethane-d_2 (Figure S3) shows ten signals corresponding to the C^N ligand. The phenanthridine moiety signals appear between 9,03- 8,60 ppm, as observed in the free HC^N ligand spectrum and being clearly upfield shifted with respect to those in compounds **2 - 6**. The broadening of the $H_{3'}$ signal at the bottom (7.77 ppm,1H) due to the coupling to ^{195}Pt, indicates that the C-coordination of the phenyl moiety to the Pt (II) nucleus remains in the complex. Additionally, two different signals are shown at 2.91 ppm and 1.89 ppm, with integral

values corresponding to three tht ligands. In summary, the ^{1}H NMR spectrum of **7** in dichloromethane-d_2 shows the presence of 3 tht ligands in the coordination sphere of Pt (II) and a C-coordinated 3,8-dinitro-6-phenylphenanthridine ligand. The hemilability of the 3,8-dinitro-6-phenylphenanthridine-κC,N that leads to the N-dissociation of the ligand in the presence of excess of tht, could be attributable to the great distortion of the metalocycle "Pt(C^N)", that was observed in the X-ray structures of **3**, **4**, and **6.** The N-dissociation of C^N ligands to give monocoordinated κ^1-C ligands is not a common fact, but has been observed in the reactions of some C,N-cyclopalladated complexes with phosphines.[77] The hemilabile character of 3,8-dinitro-6-phenylphenanthridine-H is especially attractive because transition metal complexes with hemilabile ligands play a key role in homogeneous catalysis reactions.[78-80]

Photophysical Properties of compounds 3- 6.

Preliminary tests on the luminescence of complexes **1**-**7** indicate that only compounds **3**-**6** are emissive at room or low temperatures; therefore the photophysical properties have been studied only on them.

Absorption Spectra and Theoretical Calculations. The absorption spectra of [PtCl(C^N)(L)] (L = tht (**3**), PPh_3 (**4**) and CN^tBu (**5**)) and $[Pt(C^N)(CNXyl)_2]ClO_4$ (**6**) were recorded in CH_2Cl_2 at low concentration (10^{-5} M) because of their low solubility in most common solvents. The absorption spectrum of the free ligand 3,8-dinitro-6-phenylphenanthridine (HC^N) in the same conditions has been included for comparative purposes (see Fig 5 and Table S1 in Supporting information). As can be seen the UV-vis spectra of compounds **3**-**6** show intense absorptions at $\lambda \leq 390$ nm ($\varepsilon > 10^4$ M^{-1} cm^{-1}) attributable to $\pi \rightarrow \pi^*$ intraligand (IL) transitions [37,50,81-84] and weaker absorptions (ε = 9137- 15221 M^{-1} cm^{-1}) at lower energies ($390 \leq \lambda \geq 550$ nm) clearly red shifted with respect to those of the free ligand.[28,84,85] The energies of these absorptions

follow the trend **6** > **5** > **4** > **3,** in good agreement with the electron-withdrawing character of the isocyanide and PPh_3 ligands. This trend is similar to that observed previously for compounds [PtCl(bzq)(CNXyl)][38] and $[Pt(bzq)(CNXyl)_2]ClO_4$.[37]

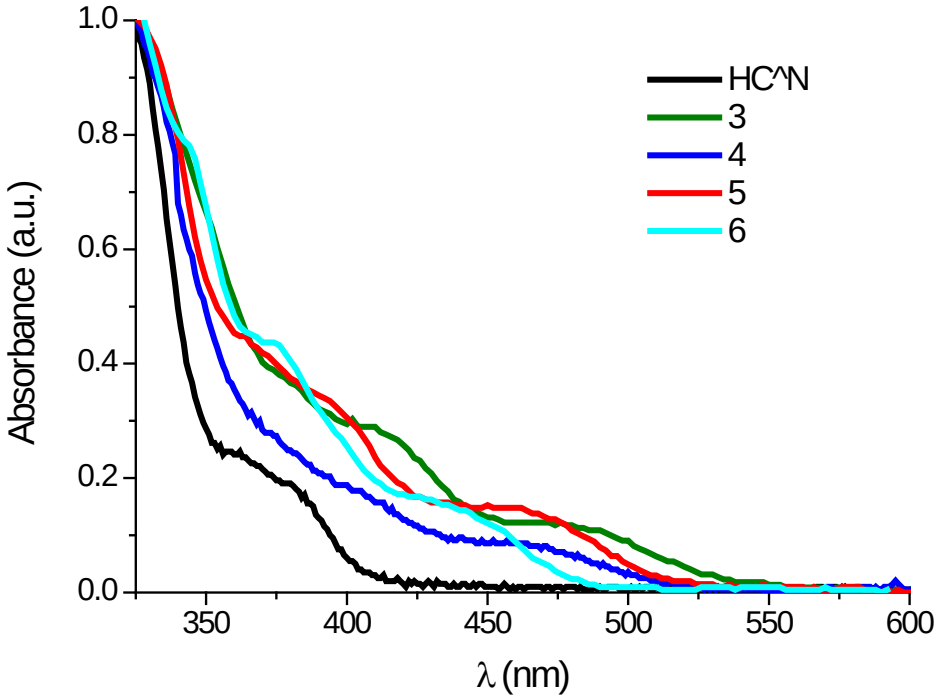
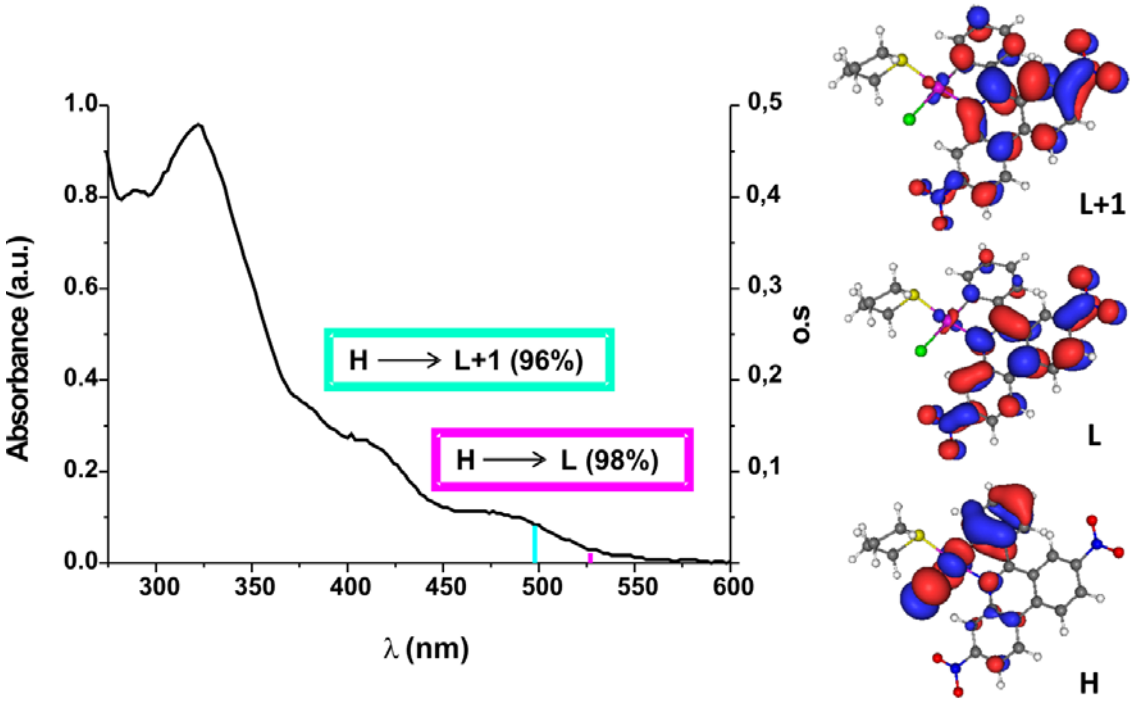


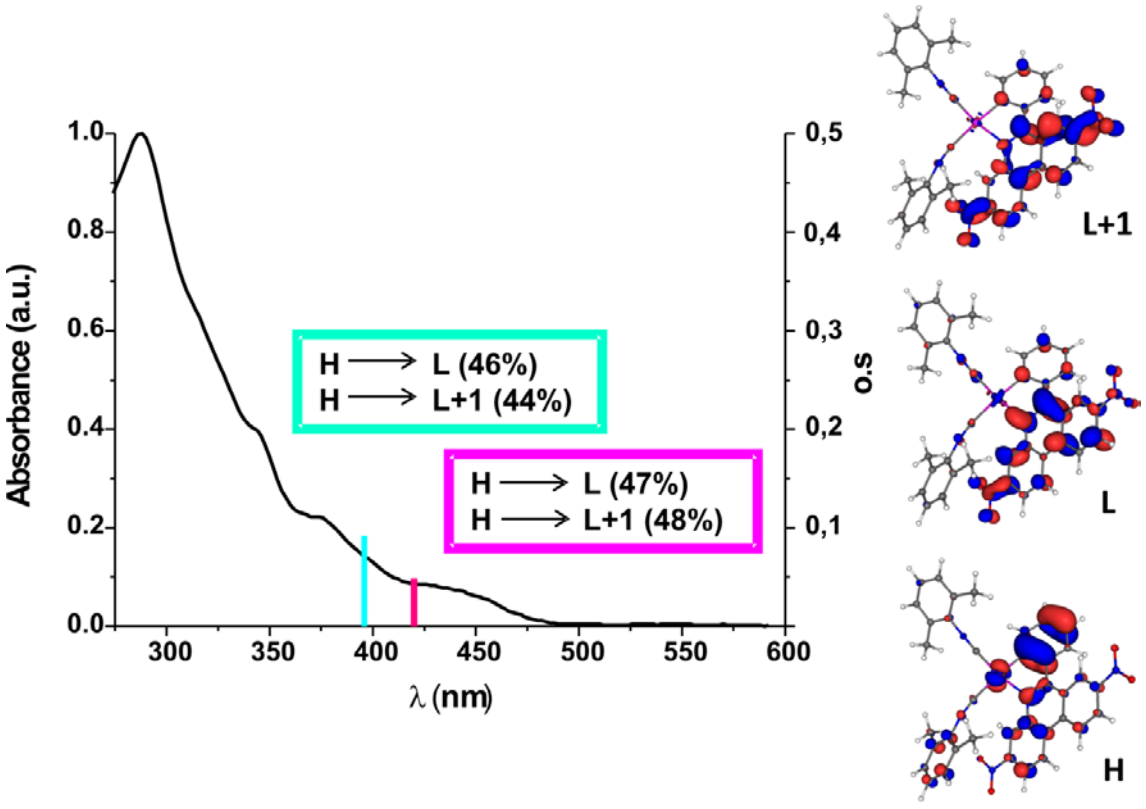
Figure 5. Normalized UV-vis spectra of HC^N and compounds **3- 6** in CH_2Cl_2 (10^{-5} M)

Time-dependent-density functional theory (TD-DFT) calculations were carried out for complexes **3, 5** and $\mathbf{6}^+$ using the B3LYP hybrid density functional. The geometric parameters of the optimized structures (Tables S2- S4 in Supporting Information) agree well with the experimental values. The molecular orbitals involved in the main excited states are depicted in Figures 6 and S4- S6 (in S.I.); the relative compositions of the different energy levels and the calculated excited states for **3, 5** and $\mathbf{6}^+$ are listed in Tables S5 and S6 (in S.I.). In dichloromethane solution the highest occupied molecular orbital (HOMO) is mainly constructed from orbitals located on the Pt (35% **3**, 32% **5**, 10% $\mathbf{6}^+$), the phenyl group of the C^N ligand (28% **3**, 24% **5**, 53% $\mathbf{6}^+$) and the chloride (25% **3**, 35% **5**) or isocyanide (10% $\mathbf{6}^+$) ligands. By contrast, the lowest unoccupied

molecular orbital (LUMO) is well located on the phenanthridine moiety of the C^N ligand (89% **3**, 97% **5**, 82% **6**). The LUMO is almost degenerate with the orbital L+1, which is also constructed from orbitals located on the C^N. Similar results were found in compounds $[Pt(bzq)(CNXyl)_2]^{+}$[37] and [Pt(bzq)Cl(CN^{t}Bu)] (bzq = benzoquinolinate)[38] which show barely any contribution of the ancillary ligands to the frontier orbitals. The calculated excited states in CH_2Cl_2 (See Figure 6a for **3** and Figure 6b for $\mathbf{6}^+$) fit well, within the accuracy of the method, with the experimental low energy absorptions. Calculations indicate that the major contributions to the two lowest-lying absorptions (λ > 460 nm) for complexes **3** and **5** involve the HOMO → LUMO (97% **3**, 98% **5**) and HOMO → L +1 (96% **3**, 97% **5**) transition respectively, indicating a mixed ligand-centered [^{1}ILCT, $\pi\rightarrow\pi^*$ (C^N)], metal-to-ligand charge transfer [^{1}MLCT (5d(Pt)→ π^* (C^N)] and ligand-to-ligand charge transfer [^{1}L'LCT, Cl→ π^* (C^N)] character. The charge transfer (CT) nature of these bands is consistent with the modest negative solvatochromism experimentally observed for **3** (Table S1, Figure S7 in S. I.).[37,43] For complex $\mathbf{6}^+$ the two lowest-lying absorptions (λ > 395 nm) involve also the HOMO → LUMO and HOMO → L+1 transitions, but they seem to have a major ligand-centered [^{1}ILCT, $\pi\rightarrow\pi^*$ (C^N)] character than in **3** and **5** along with a smaller ^{1}MLCT [(5d(Pt)→ π^* (C^N)] and ^{1}L'LCT [π (CNXyl) → π^* (C^N)] contribution.



(a)



(b)

Figure 6. a) Experimental UV-vis absorption, calculated transitions in CH_2Cl_2 (bars) and calculated molecular orbitals for compound **3**. **b)** Experimental UV-vis absorption, calculated transitions in CH_2Cl_2 (bars) and calculated molecular orbitals for $\mathbf{6}^+$.

The solid state diffuse reflectance UV/Vis spectra of **3**-**6** at 298 K show no significant differences with respect to those observed in CH_2Cl_2 solutions (Figure S8). Therefore the π-π interactions observed in the X-ray structure of **3** (at 98K) seems to have not important effects in the absorption at room temperature.

Emission Spectra. The 3, 8-dinitro-6-phenylphenanthridine ligand (HC^N) as well as the cyclometalated Pt(II) complexes (**3**-**6**) are not emissive enough in solution at room temperature (CH_2Cl_2 or 2-Me-THF) to pay attention to them. In diluted (5×10^{-5}M) glassy solutions (77 K) compounds **3**-**6** show an orange-red phosphorescence, clearly red-shifted with respect to the green emission of the free ligand (HC^N) (see Table 2 and Figure 7). These emissions show a mono-exponential decay and do not depend on the excitation wavelength. Additionally, the excitation spectra mimic in all cases the absorption ones in solution at room temperature (Figure 5). These characteristics point to assign the phosphorescence to a single emission with a mixed ^{3}MLCT/^{3}IL/^{3}L'LCT character. The longer emission lifetimes measured for **6** could be explained by a major ^{3}IL character of the excited state in this case. The emission energy and profile at higher concentration (10^{-3} M) do not change with respect to those at 5×10^{-5}M (Table 2).

In the solid state at 77K (Figure S9) the emissions of compounds **3**-**5** show a similar profile but appear red-shifted with respect to those in glassy 2-Me-THF solution. Also, their excitation spectra show peaks at $\lambda > 500$ nm different to those observed in glassy 2-Me-THF solution. Because of that we have assigned tentatively the phosphorescent emission of **3**-**5** to a mixed ^{3}MLCT/^{3}IL/^{3}L'LCT excited states with some contribution of excimeric π–π* transitions due to emissive ground-state aggregates generated by weak π–π interactions between phenanthridine groups.

Table 2. Emission Data for complexes **3**-**6** and **HC^N**.

Compound	**Media (T/K)**	**λ_{em} (λ_{exc}) [nm] *[Φ]***	**τ (μs)**
HC^N	Solid (77)	525, 565_{max}, 605_{sh} (430)	
	2-MeTHF$_d$(77)	500, 540_{max}, 575 (340)	
	2-MeTHF$_c$(77)	500, 540_{max}, 575 (380)	
3	Solid (77)	670_{max},716 (540)	7.2 (660)
	2-MeTHF$_d$(77)	632_{max}, 675 (440)	11 (632), 10.4 (675)
	2-MeTHF$_c$(77)	632_{max}, 675 (495)	10.6 (632), 10.5 (675)
4	Solid (298)	675 (460) [0.032]	9
	Solid (77)	660_{max},710 (450)	8 (660)
	2-MeTHF$_d$(77)	620, 660_{max} (450)	14.1 (620), 13.9 (660)
	2-MeTHF$_c$(77)	620, 660_{max} (490)	13.8 (620), 13.6 (660)
5	Solid (298)	670 (500) [0.047]	7.6
	Solid (77)	660, 700(500)	9 (660), 10 (700)
	2-MeTHF$_d$(77)	613, 660_{max} (450)	15 (613), 14 (660)
6	Solid (298)	600_{sh}, 670 (450) [0.052]	12.3 (670)
	Solid (77)	620, 665_{max} (450)	21.8 (620), 20.8 (665)
	CH_2Cl_2 $_d$(77)	620, 665_{max} (450)	26.6 (620), 26.3 (665)

$c = 10^{-3}$M; $d = 5 \times 10^{-5}$M

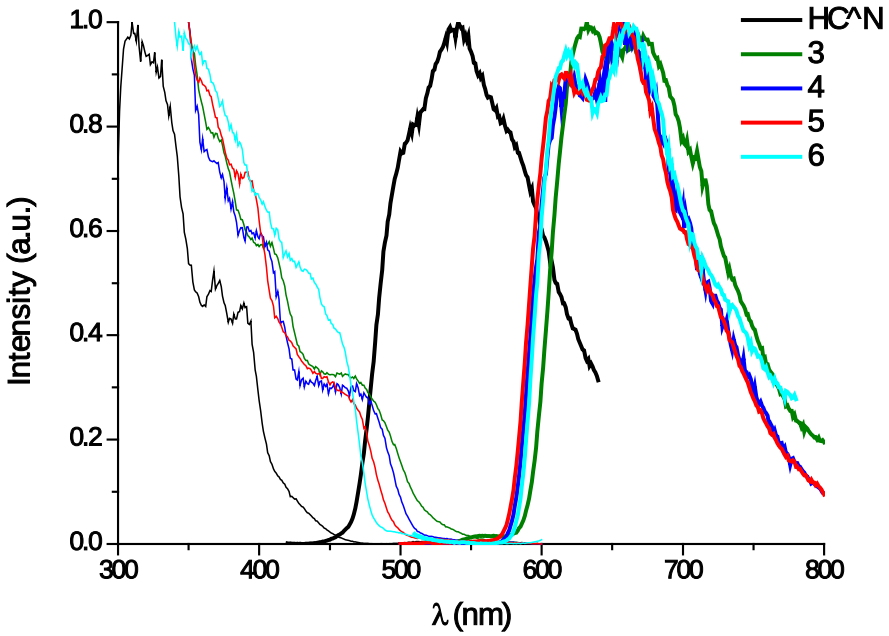


Figure 7. Normalized excitation and emission spectra of the HC^N ligand and complexes **(3-6)** in solution ($5x10^{-5}$ M, 2-Me-THF for **3-5**, CH_2Cl_2 for **6**) at 77 K.

This behavior which is frequent in square-planar Pt(II) complexes containing aromatic and non-bulky ligands[38] can be justified by the weak $\pi\pi$ interactions observed in the X-ray structure of complex **3** determined at 98 K. However no differences among the excitation and emission spectra of **6** at 77 K in the solid state (Figure S9) and those in rigid matrix of CH_2Cl_2 are observable.

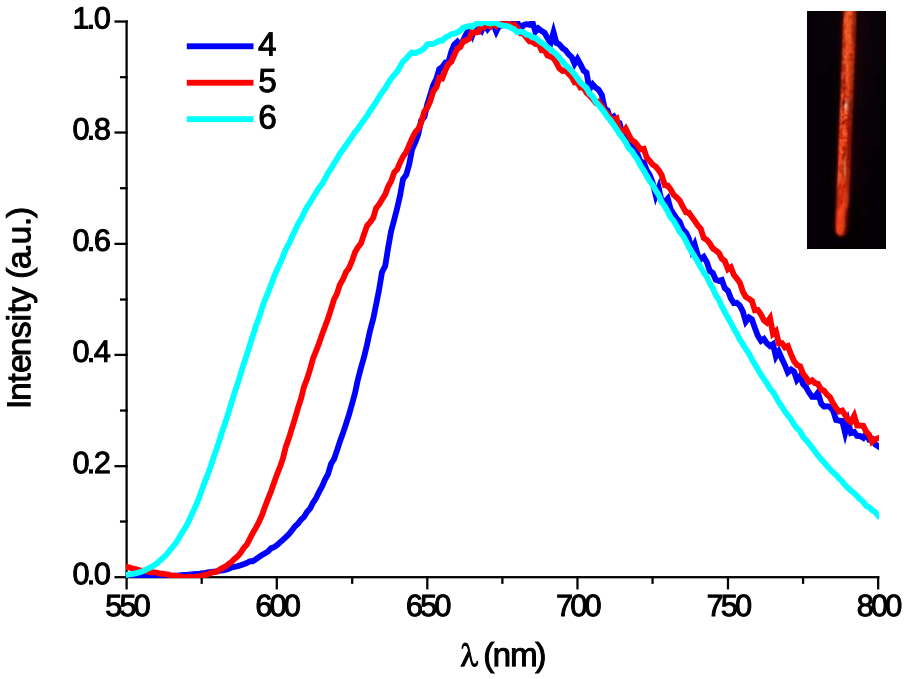


Figure 8. Normalized emission spectra in the solid state at 298 K. Right side picture, compound **6** under UV light at r.t. (λ= 365 nm).

Compounds **4**-**6** are also emissive in the solid state at room temperature (Figure 8 and Table 2). As can be seen, their phosphorescent emissions are similar, but unstructured, to those at 77 K, and can be plausibly assigned to the same excited state. In these conditions the photoluminescence quantum yields ***Φ*** are around 0.05 (see Table 2). These moderate ***Φ*** values for Pt(II) complexes are, however, good for deep red emitters[29,86] like compounds **4**-**6** (λ_{max} ca. 670 nm), according to the energy gap law.[87] The higher ***Φ*** of the emission of **6** with respect to those of **4** and **5** (See Table 2) could be justified by the presence of two strong-field ancillary ligands (CNXyl) in the complex, that increase the energy gap between the lowest-lying excited state and the higher-lying d-d one, along with the absence of excimers, which prevent the nonradiative decay processes.[88,89]

Conclusions

The activation of a C_{Ph}-H bond in the phenyl ring of 3,8-dinitro-6-phenylphenanthridine (HC^N) by [{Pt(μ-Cl)(η^3-2-Me-C_3H_4)}$_2$] (η^3-2-Me-C_3H_4= η^3-2-methylallyl) could not be achieved in one step but in two. Complex [PtCl(η^3-2-Me-C_3H_4)(HC^N-κN)] (**1**) was the intermediate to get the cyclometalated compound [{Pt(μ-Cl)(C^N)}$_2$] (**2**). Compound **2** could be used as starting material for the synthesis of new neutral and cationic cyclometalated complexes as [PtCl(C^N)L] (L= tht, PPh_3, CN^tBu) and [Pt(C^N)(CNXyl)$_2$]ClO_4 with the C^N group coordinated in a chelate fashion. Compound [Pt(C^N-κC)(tht)$_3$]ClO_4 containing 3,8-dinitro-6-phenylphenanthridine-H-κC was also obtained from **2** by the Cl-abstraction with $AgClO_4$ and using a significant excess of tht. This result shows the hemilabile character of the 3,8-dinitro-6-phenylphenanthridine-κC,N which could be attributed to the great distortion of the metalocycle "Pt(C^N)". Therefore, the 3,8-dinitro-6-phenylphenanthridine (HC^N) has been revealed as a versatile ligand with different kinds of coordination modes, since we have obtained complexes with the neutral ligand N-coordinated (HC^N-κN) and the anionic C^N as κC,N or κC. The chemical shifts of the H atoms close to the platinum center (H4 and H3') result very sensitive to the coordination mode and to the electronic characteristics of the ancillary ligands.

At 77 K in rigid matrix of 2-Me-THF or CH_2Cl_2 or in the solid state, compounds **3-6** show a red phosphorescence that was assigned to a mixed ^{3}MLCT/^{3}IL/^{3}L'LCT excited state. At room temperature compounds **4-6** are emissive in the solid state with moderately good photoluminescence quantum yields (Φ, ca. 0.05) for deep red emitters.

Experimental Section

All the information about materials, instrumentation methods used for characterization and photophysical studies, Crystal data and structure refinement of **1, 3,**

4 and **6** (Tables S6-S9) together with the full IR data corresponding to HC^N and complexes **1**-**7** is given in the Supporting Information.

3,8-dinitro 6-phenylphenanthridine (**HC^N**). ^{1}H NMR (400 MHz, DMSO, 298 K,δ_H) 9.30 (d, 1H, $^{3}J_{9\text{-}10}$= 9.0 Hz, H_{10}), 9.21 (d, 1H, $^{3}J_{1\text{-}2}$= 9.0 Hz, H_1), 8.90 (d, 1H, $^{4}J_{2\text{-}4}$= 2.3 Hz, H_4), 8.84 (d, 1H, $^{4}J_{7\text{-}9}$= 2.2 Hz, H_7), 8.78 (dd, 1H, $^{3}J_{9\text{-}10}$= 9.0 Hz, $^{4}J_{7\text{-}9}$= 2.2 Hz, H_9), 8.56 (dd, 1H, $^{3}J_{1\text{-}2}$= 9.0, $^{4}J_{2\text{-}4}$= 2.3 Hz, H_2), 7.84 (m, 2H, $H_{2',6'}$), 7.69 (m, 3H, $H_{3',4',5'}$). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K,δ_H) 9.09 (dd, 1H, $^{4}J_{2\text{-}4}$= 2.4 Hz, $^{5}J_{1\text{-}4}$= 0.3 Hz, H_4), 9.08 (dd, 1H, $^{4}J_{7\text{-}9}$= 2.3 Hz, $^{4}J_{7\text{-}10}$= 0.4 Hz, H_7), 8.93 (d, 1H, $^{3}J_{9\text{-}10}$= 9.0 Hz, H_{10}), 8.84 (d, 1H, $^{3}J_{1\text{-}2}$= 9.0 Hz, H_1), 8.73 (dd, 1H, $^{3}J_{9\text{-}10}$= 9.0 Hz, $^{4}J_{7\text{-}9}$= 2.3 Hz, H_9), 8.61 (dd, 1H, $^{3}J_{1\text{-}2}$= 9.0, $^{4}J_{2\text{-}4}$= 2.4 Hz, H_2), 7.80 (m, 2H, $H_{2',6'}$), 7.67 (m, 3H, $H_{3',4',5'}$).

Preparation of [PtCl(η^3-2-Me-C_3H_4)(HC^N-κN)](1)·0.5 Me_2CO. 3, 8-dinitro 6-phenylphenanthridine (0.987 g, 2.80 mmol) was added to a golden colored solution of the dichloro-bridged complex [{Pt(η^3-2-Me-C_3H_4)(μ-Cl)}$_2$] (0.8 g, 1.4 mmol) in acetone (65 mL). The solution turned into a green-yellowish suspension immediately. The mixture was stirred for 2 h at room temperature and then, the suspension was filtered-off and the green-yellowish solid was washed with acetone (3x5 mL) and Et_2O (3x5 mL) to give **1**. Yield: 1.3362 g, 75%. Calcd for $C_{23}ClH_{18}N_3O_4$ Pt· 0.5 Me_2CO: C, 44.59; H, 3.21; N, 6.37. Found: C, 44.66; H, 3.25; N, 6.4. MS (MALDI+): m/z 595.1 [Pt(η^3-C_4H_7) (HC^N)]$^+$.

Preparation of [{Pt(μ-Cl)(C^N)}$_2$] (2). A green suspension of **1·0.5 Me_2CO** (0.800 g, 1.212 mmol) in 2-methoxyethanol (50 mL) was refluxed for 2 h. The resulting brown precipitate was filtered and washed with methanol (10 mL) and Et_2O (15 mL) to give **2**. Yield: 0.5378 g, 77%. ^{1}H NMR (400 MHz, DMSO, 298 K, δ_H) 9.59 (d, 1H, $^{4}J_{2\text{-}4}$= 2.2 Hz, H_4), 9.53 (d, 1H, $^{4}J_{7\text{-}9}$= 2.1 Hz, H_7), 9.25 (d, 1H, $^{3}J_{9\text{-}10}$= 9.2 Hz, H_{10}), 9.11 (d, 1H, $^{3}J_{1\text{-}2}$= 9.2 Hz, H_1), 8.90 (dd, 1H, $^{3}J_{9\text{-}10}$= 9.2 Hz, $^{4}J_{7\text{-}9}$= 2.1 Hz, H_9), 8.52 (dd, 1H, $^{3}J_{1\text{-}2}$=

9.2 Hz, $^4J_{2\text{-}4}$= 2.2 Hz, H_2), 8.31 (dd, 1H, $^3J_{3'\text{-}4'}$= 7.8 Hz, $^4J_{3'\text{-}5'}$= 1.0 Hz, $H_{3'}$), 8.00 (dd, 1H, $^3J_{5'\text{-}6'}$= 7.5 Hz, $^4J_{4'\text{-}6'}$= 1.3 Hz, $H_{6'}$), 7.41 (ddd, 1H, $^3J_{5'\text{-}6'}$= $^3J_{4'\text{-}5'}$= 7.5 Hz, $^4J_{3'\text{-}5'}$= 1.0 Hz, $H_{5'}$), 7.34 (ddd, 1H, $^3J_{3'\text{-}4'}$= $^3J_{4'\text{-}5'}$= 7.8 Hz, $^4J_{4'\text{-}6'}$= 1.3 Hz, $H_{4'}$).

Preparation of [PtCl(C^N)(tht)] (3). THT (0.031 mL, 0.348 mmol) was added to a brownish suspension of **2** (0.200 g, 0.174 mmol,) in CH_2Cl_2 (30 mL). The reaction mixture was stirred for 24 h at room temperature and then filtered through Celites. The resulting red solution was evaporated to dryness. Et_2O (5 mL) was added to the solid residue and then it was filtered and washed with Et_2O (3x5 mL) to give **3** as an orange solid. Yield: 0.134 g, 58.0%.Anal. Calcd for $C_{23}ClH_{18}N_3O_4PtS$: C, 41.67; H, 2.74; N, 6.34. Found: C, 41.82; H, 2.81; N, 6.31. MS (MALDI+): m/z 627.2.1 $[Pt(C^N)(tht)]^+$. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K, δ_H) 9.99 (d, 1H, $^4J_{2\text{-}4}$= 2.2 Hz, H_4), 9.66 (s, 1H, H_7), 8.80 (m, 2H, H_9, H_{10}), 8.63 (d, 1H, $^3J_{1\text{-}2}$= 9.0 Hz, H_1), 8.42 (dd, 1H, $^3J_{1\text{-}2}$= 9.0 Hz, $^4J_{2\text{-}4}$= 2.2 Hz, H_2), 7.89 (m, 2H, $^3J_{Pt\text{-}3'}$= 44.33 Hz, $H_{3',6'}$), 7.33 (m, 2H, $H_{4',5'}$), 3.84 (m, 2H, $^3J_{Pt\text{-}H}$= 72.1 Hz, S-CH$^{\alpha}$-), 3.12 (m, 2H, $^3J_{Pt\text{-}H}$= 50 Hz, S-CH$^{\alpha'}$-), 2.38 (s, 2H, -CH_2^{β}-), 2.08 (s, 2H, -$CH_2{}^{\beta'}$-).

Preparation of [PtCl(C^N)(PPh_3)] (4). PPh_3 (91.3 mg, 0.348 mmol) was added to a brownish suspension of **2** (0.200 g, 0.174 mmol,) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 22 h at room temperature and then filtered through Celite. The resulting orange solution was evaporated to dryness. Et_2O (5 mL) was added to the solid and then it was filtered and washed with Et_2O (3x5 mL) to give **4** as an orange solid. Yield: 0.175 g, 60.1%. Calcd for $C_{37}ClH_{25}N_3O_4PPt$: C, 53.08; H, 3.01; N, 5.02. Found: C, 52.76; H, 3.43; N, 4.70. MS (MALDI+): m/z 801.1 $[Pt(C^N)(PPh_3)]^+$. ^{1}H NMR (400 MHz, CH_2Cl_2, 298 K, δ_H) 10.00 (d, 1H, $^4J_{2\text{-}4}$= 2.2 Hz, H_4), 9.77 (d, 1H, $^4J_{7\text{-}9}$ = 2.1 Hz, H_7), 8.88 (d, 1H, $^3J_{9\text{-}10}$= 9.1 Hz, H_{10}), 8.82 (dd, 1H, $^3J_{9\text{-}10}$= 9.1 Hz, $^4J_{7\text{-}9}$= 2.1 Hz, H_9), 8.68 (d, 1H, $^3J_{1\text{-}2}$= 9.0 Hz, H_1), 8.42 (dd, 1H, $^3J_{1\text{-}2}$= 9.0 Hz, $^4J_{2\text{-}4}$= 2.2 Hz, H_2), 7.84 (m,

7H, 6H$_o$, PPh$_3$, H$_{6'}$), 7.50 (m, 3H, H$_p$, PPh$_3$), 7.43 (m, 6H, H$_m$, PPh$_3$), 7.15 (m, 1H, H$_{5'}$), 6.88 (dd, 1H, $^3J_{Pt\text{-}3'}$= 52.6 Hz, $^3J_{3'\text{-}4'}$= 7.5 Hz, $^4J_{3'\text{-}5'}$= 2.7 Hz, H$_{3'}$), 6.69 (m, 1H, H$_{4'}$). ^{31}P NMR{^{1}H} (162 MHz, CH_2Cl_2, 298 K, δ_p) 20.75 (s, $^1J_{Pt\text{-}P}$ = 4622 Hz).

Preparation of [PtCl(C^N)(CN^{t}Bu)] (5). *tert*-butylisocyanide (49.19 μL, 0.435 mmol) was added to a stirred suspension of **2** (0.250 g, 0.217 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was stirred for 14 h at room temperature and then filtered through Celite. The resulting solution was evaporated to dryness and the solid was washed with Et_2O (3x5 mL), yielding **5** as a yellow solid. Yield: 0.138 g, 48.2%. Calcd for $C_{24}ClH_{19}N_4O_4Pt$: C, 43.81; H, 2.91; N, 8.52. Found: C, 43.54; H, 2.75; N, 8.41. MS (MALDI+): m/z 622.1 [Pt(C^N)(CN^{t}Bu)]$^+$ ^{1}H NMR (400 MHz, CH_2Cl_2, 298 K, δ_H) 10.21 (d, 1H, $^4J_{2\text{-}4}$= 2.2 Hz, H$_4$), 9.72 (d, 1H, $^4J_{7\text{-}9}$= 2.2 Hz, H$_7$), 8.87 (d, 1H, $^3J_{9\text{-}10}$= 9.0 Hz, H$_{10}$), 8.83 (dd, 1H, $^3J_{9\text{-}10}$= 9.0 Hz, $^4J_{7\text{-}9}$= 2.2 Hz, H$_9$), 8.70 (d, 1H, $^3J_{1\text{-}2}$= 9.0 Hz, H$_1$), 8.50 (dd, 1H, $^3J_{1\text{-}2}$= 9.0 Hz, $^4J_{2\text{-}4}$= 2.2 Hz, H$_2$), 7.96 (dm, 1H, $^3J_{5'\text{-}6'}$= 7.9 Hz, H$_{6'}$), 7.71 (dd, 1H, $^3J_{Pt\text{-}3'}$= 67.8 Hz, $^3J_{3'\text{-}4'}$= 7.5 Hz, $^4J_{3'\text{-}5'}$= 1.2 Hz, H$_{3'}$), 7.39 (ddd, 1H, $^3J_{5'\text{-}6'}$= 7.9 Hz, $^3J_{4'\text{-}5'}$= 7.5 Hz, $^4J_{5'\text{-}3'}$= 1.2 Hz, H$_{5'}$), 7.32 (ddd,1H, $^3J_{3'\text{-}4'}$= $^3J_{4'\text{-}5'}$= 7.5 Hz, $^4J_{4'\text{-}6'}$= 1.4 Hz, H$_{4'}$), 1,71 (s, 9H, Me, CN^{t}Bu).

Preparation of [Pt(C^N)(CNXyl)$_2$]ClO$_4$ (6). $AgClO_4$ (72 mg, 0.347mmol) was added to a stirred suspension of **2** (200 mg, 0.174mmol) in CH_3CN (100 mL). The reaction mixture was refluxed 2h, and filtered through Celites. The resulting solution was concentrated to a volume of 3 mL, then THF (30 mL) and 2, 6-dimethylphenyl isocyanide (91 mg, 0.690 mmol) were added to it. The orange mixture was stirred for 18h at room temperature to afford a yellow precipitate which was filtered and washed with Et_2O (3 x 5 mL), yielding **6** as a pure yellow solid. Yield: 0.1770 g, 56 %. Anal. Calcd for $C_{37}ClH_{28}N_5O_8Pt$: C, 49.31; H, 3.13; N, 7.77. Found: C, 49.00; H, 3.28; N, 7.65. MS (MALDI+): m/z 801.2 [Pt(C^N)(Xyl)$_2$]$^+$, 670.2 [Pt(C^N)(Xyl)]$^+$. Λ_M (5 × 10^{-4}

M acetone solution): 41.7 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ_H 9.80 (d,1H, $^4J_{7\text{-}9}$=2.2 Hz, H_7), 9.49 (d, 1H,$^4J_{2\text{-}4}$=2.1Hz, H_4), 9.12 (d, 1H, $^3J_{9\text{-}10}$=8.8 Hz, H_{10}), 9.01 (d, 1H, $^3J_{1\text{-}2}$= 9.0 Hz, H_1), 8.99 (dd, 1H, $^4J_{9\text{-}10}$=8.8 Hz, $^3J_{7\text{-}9}$= 2.2 Hz, H_9), 8.6 (dd, 1H,$^3J_{1\text{-}2}$= 9.0 Hz, $^4J_{2\text{-}4}$=2.1 Hz, H_2), 8.14 (ddd, 1H,$^3J_{5'\text{-}6'}$= 7.6 Hz, $^4J_{4'\text{-}6'}$= 1.4 Hz, $^5J_{3'\text{-}6'}$= -0.6 Hz, $H_{6'}$), 7.97 (ddd, 1H, $^3J_{3'\text{-}4'}$= 7.0 Hz, $^4J_{3'\text{-}5'}$= 1.5 Hz, $^5J_{3'\text{-}6'}$= -0.6 Hz, $^3J_{Pt\text{-}H}$=52.2 Hz, $H_{3'}$), 7.58 (ddd, 1H, $^3J_{3'\text{-}4'}$= 7.0 Hz, $^3J_{4'\text{-}5'}$= 7.3 Hz, $^4J_{4'\text{-}6'}$= 1.4 Hz, $H_{4'}$), 7.54 (ddd, 1H, $^3J_{4'\text{-}5'}$= 7.3 Hz, $^3J_{5'\text{-}6'}$= 7.6 Hz, $^4J_{3'\text{-}5'}$= 1.5 Hz, $H_{5'}$), 7.44 (t, 1H, $^3J_{p\text{-}m}$= 8.0 Hz, H_p), 7.35 (t, 1H, $^3J_{p'\text{-}m'}$= 7.6 Hz, $H_{p'}$),7.30 (d, 2H, $^3J_{p\text{-}m}$= 7.6 Hz, H_m), 7.17 (d, 2H, $^3J_{p'\text{-}m'}$= 7.6 Hz, $H_{m'}$), 2.58 (s, 6H, Me, Xyl), 2.28 (s, 6H, Me, Xyl').

Preparation of [Pt(C^N-*κ*C)(tht)$_3$]ClO$_4$ (7). Method A) $AgClO_4$ (0.051 g, 0.246 mmol) was added to a red solution of compound **3** (0.163 g, 0.246 mmol) in acetone (20 mL) and then tht (65 µL, 0.738 mmol) was added to the resulting orange solution. The reaction mixture was stirred for 75 min. and then filtered through Celites. The orange solution was evaporated to dryness and the oily residue was treated with Et_2O (10 mL) and cooled with liquid N_2. The resulting orange solid was then washed with Et_2O (3x5 mL) yielding **7**.Yield: 0.1841 g, 82.8 %. **Method B**) $AgClO_4$ (57 mg, 0.275 mmol) was added to a stirred suspension of **2** (159 mg, 0.137 mmol) in CH_3CN (100 mL). The reaction mixture was refluxed 2 h, and filtered through Celites. The resulting solution was evaporated to dryness, then, $CHCl_3$ (80 mL) and tht (98 µL, 1.10 mmol) were added to it. The reaction mixture was refluxed for 1 h and then filtered through celites. The resulting orange solution was evaporated to dryness and treated with Et_2O to yield an orange solid, **7**. Yield 0.17 g, 68 %. Anal. Calcd for $C_{31}ClH_{34}N_3O_8PtS3$: C, 41.22; H, 3.79; N, 4.65. Found: C, 40.86; H, 3.88; N, 4.57. MS (MALDI+): m/z 627.2.1 $[Pt(C^N)(tht)]^+$. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K,δ_H) 9.03-8.77 (m, 5H, H_1, H_4, H_7,

H_9, H_{10},), 8.60 (d, 1H, $^3J_{1\text{-}2}$= 8.2 Hz, H_2), 7.77 (s, 1H, $H_{3'}$), 7.43-7.37 (m, 3H, $H_{4',5',6'}$), 2.91 (s, 12 H, S-CH_2^{α}-), 1.890 (s, 12H, -CH_2^{β}-).

X-**ray Structure Determinations.** Suitable crystals for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into concentrated solutions of the complexes (**1**, **3**, **4** and **6**) in CH_2Cl_2. Crystal and structure refinement data are summarized in Table S7. The crystals were mounted in a quartz fibre in a random orientation and held in place with fluorinated oil. Data collection was performed at 100 K temperature on a Oxford Diffraction Xcalibur CCD diffractometer using graphite monochromated Mo-Kα radiation (λ= 0.71073 Å) with a nominal crystal to detector distance of 5.0 cm. The diffraction frames were integrated and corrected for absorption using the Crysalis RED package.[90] Lorentz and polarisation corrections were applied. The structure was solved by direct methods. All non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealised geometries and assigned isotropic displacement parameters equal to 1.2 times (1.5 times for methyl H atoms) the U_{iso} values of their respective parent carbon atoms. A disordered *n*-hexane half molecule was found during the refinement process of compound **1** and were refined with restrains in its geometry and thermal displacement parameters Very diffuse solvent were found during the refinement process of compound **4** and were refined as a CH_2Cl_2 and a Me_2CO molecules with occupancy 0.3 in both cases. Restrains in the geometry and thermal displacement parameters of these moieties were applied. The structure was refined using the SHELXL-97 program.[91]

Computational Methods.

Density functional calculations were performed using the B3LYP[92,93]and M06[94]hybrid density functional under the Gaussian09 package.[95] The SDD pseudopotential and associated basis set[96] was used for platinum, and the 6-31G(d)[97,98] basis set was used for

all other atoms. Geometry optimisations were performed under no symmetry restrictions, using initial coordinates derived from X-ray data. Frequency calculations were used to confirm the stationary points were true minima. The time-dependent density-functional(TD-DFT) calculations were performed using the polarized continuum model approach (PCM) implemented in the Gaussian 09 software. Molecular orbitals were visualized using the Molekel program package.[99]

Supporting Information Available: Experimental, Computational and Crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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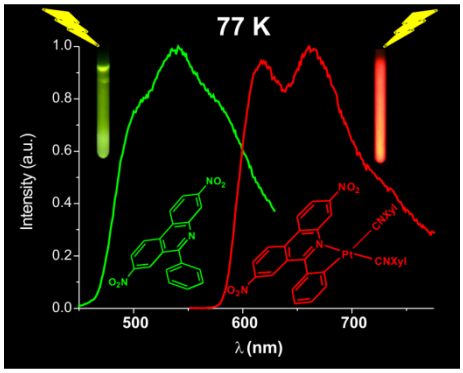
77 K
Intensity (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
500
600
700
λ (nm)
NO2
O2N
N
NO2
CNXyl
Pt
CNXyl
O2N