PhD degree in Chemical Science and Technology

XXXIII Cycle

New complexes of transition metal ions, Pd(II), Pt(II), Au(III), and terrae rare, Y(III), La(III) , Sm(II), with N-heterocyclic aromatic ligands.

Scientific Disciplinary Sector: **CHIM/03**

PhD student: Dr. Sara Pischedda

Coordinator: Prof. Stefano Enzo

Supervisor: Prof. Antonio Zucca

Co-Supervisor: Prof. Sergio Stoccoro

Final exam academic year 2019/2020

Thesis discussed in the exam session of May 2021

To my mum and my brother.

Dr. Sara Pischedda gratefully acknowledges Sardinian Regional Government for the financial support of this PhD scholarship (P.O.R. Sardegna F.S.E.- Operational Programme of the Autonomous Region of Sardinia, European Social Fund 2014-2020 – Axis III Education and Training Thematic goal 10, Investment Priority 10ii, Specific Goal 10.5) and the Mobility Grants Erasmus+Placedoc.

TABLE OF CONTENTS

Introduction…….5

Result and discussion.....11

Synthesis and characterization of ligands with imidazo[1,5-*a*]pyridine nucleus

Synthesis and characterization of Pd(II) and Pt(II) complexes

Synthesis and characterization of Pd(II) and Pt(II) organometallic complexes

Reactivity

Theoretical analysis

Synthesis and characterization of Au(III) complexes

Synthesis and characterization of Y(III), La(III) and Sm(II) complexes

Cyclometalated rollover complexes of Pt(II).

Conclusion…….....70

Experimental part…….....72

Introduction

This doctoral project represents the study of synthesis and characterization of a news coordination compounds with different classes of N-heterocyclic aromatic ligands. It is a result of a collaboration between the Universities of Sassari, Manchester and Leicester. Most of the work was done in the University of Sassari under the supervision of Prof. A. Zucca and Prof. S. Stoccoro while the other parts were done in the University of Manchester under the supervision of Dr. D. Mills and in the University of Leicester under the supervision of Dr. F. Ortu.

In our research group we have long been interested in the coordination behaviour of nitrogen ligands with metal ions in d^8 configuration, such as Pd(II), Pt(II) and Au(III), and the possible application of the corresponding complexes.

Precious metals play a crucial role in modern synthetic chemistry, especially for their extensive use in homogeneous catalysis. Pd complexes are used in cross-coupling reactions, for which Suzuki, Heck and Negishi were jointly awarded the Nobel Prize for Chemistry in 2010.[1]

In particular, the aim of our research is the isolation of cyclometalated species (classical or roll-over) *via* intramolecular C-H

[1] a) M. Lakshmi Kantam, P. Srinivas, J. Yadav, Pravin R. Likhar, Suresh Bhargava, *J. Org. Chem.*, **2009**, 74, 4882; b) M. Ohff, A. Ohff, M. E. van der Boom, D. Milstein, *J. Am. Chem. Soc.* **1997**, 119, 48, 11687.

bond activation using a variety of nitrogen-based ligands, such as 2,2' bipyridine and phenanthrolines.[2]

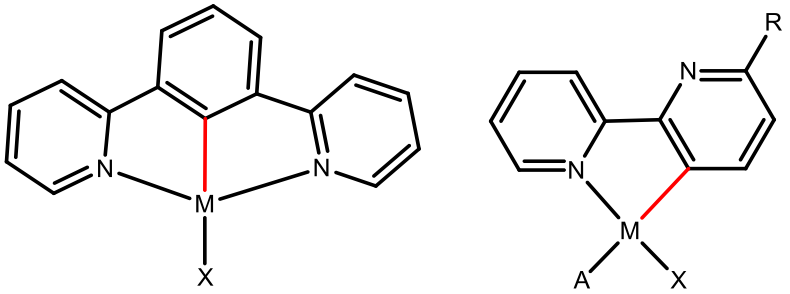


Figure 1. *Classical cyclometallated and rollover species*

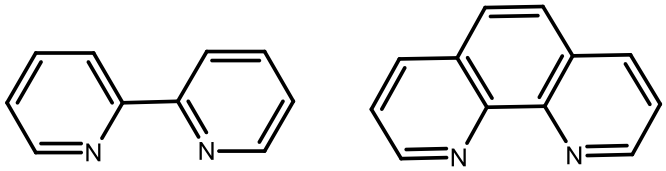


Figure 1'. *2,2'-bypiridine and 1,10 phenantroline*

A cyclometalated species is a complex where the metal is a member of a cycle; more in detail, it is a complex with a connection of σ-E-M-C bonds, where E is an atom that can donate an electron pair, M is a metal atom and C is a carbon atom "bonded" with E. Several reaction mechanisms have been proposed for the cyclometalation reaction, such as oxidative addition of a C-H fragment from a ligand E-(C-H), already coordinated to a metal M, generating a new M-C bond and a new M-H bond.

[2] a) G. Minghetti, S. Stoccoro, M. A. Cinellu, B. Soro, A. Zucca, *Organometallics*, **2003**, 23, 4770; b) S. Stoccoro, L. Maidich, T. Ruiu, M. A. Cinellu, G. J. Clarkson, A. Zucca, *Dalton Trans*., **2015**, 44, 18001-18011.

After the formation of the cyclometalated species a reductive elimination often occurs.

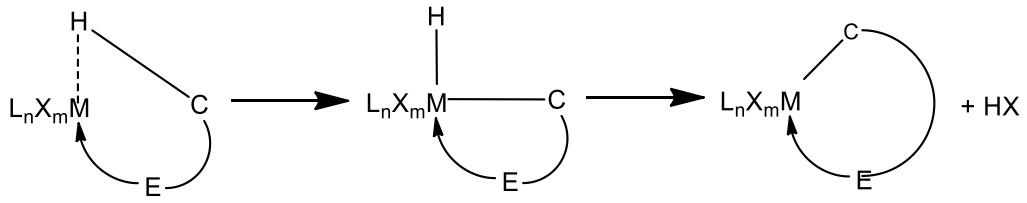


Figure 2. *General scheme of cyclometallation reaction*

In addition, the *rollover reaction* is an interesting and special C-H bond activation possible if the ligand has particolary properties. This is the case of 6- substitued-2,2'-bypiridines:

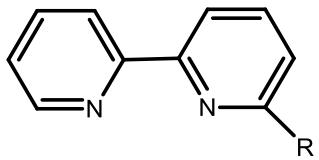


Figure 3. *6-substituted-2,2'-bypiridines*

With this class of nitrogen ligands is possible to observe firstly rotation of the substituted pyridine ring and after the activation of C*(sp³)*-H bond with electronrich derivatives of Pt(II).[3,4]

[3] G. Minghetti, S. Stoccoro, M. A. Cinellu, B. Soro, A. Zucca, *Organometallics* **2003,** *22,* 4770-4777.
[4] a) A. Zucca, L. Maidich, M. I. Pilo, S. Pischedda, M. Sedda and S. Stoccoro, *Applied Sciences*, **2020,** 10, 6665; b) A. Zucca; M.I. Pilo, *Molecules* **2021**, 26, 328.

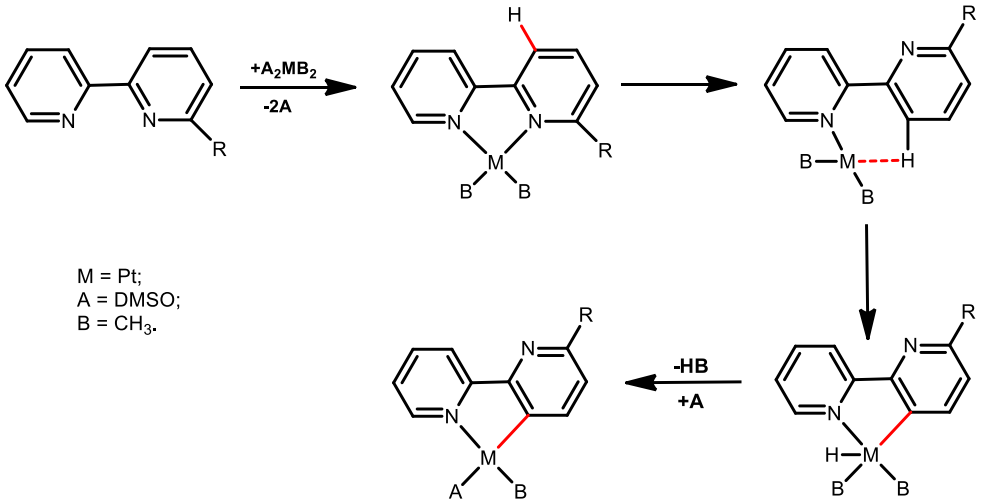


Figure 4. *General scheme of rollover reaction*

Following our continuous interest in the comprehension of the reactivity of bidentate nitrogen ligands, such as 6-substituted 2,2'bipyridines, with d^8 transition metal ions (e.g. Pd(II), Pt(II) and Au(III)), we decided to investigate the coordinating behaviour of another series of N-heterocyclic aromatic ligands, in particular 3-substituted 1-(pyridin-2-yl)imidazo[1,5-a]pyridines, containing the imidazo[1,5-*a*]pyridine skeleton[5], see figure 5:

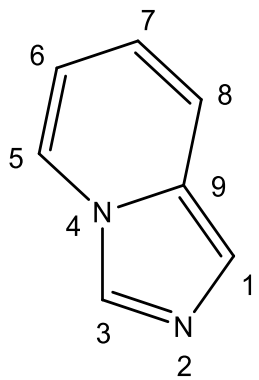


Figure 5. *imidazo [1,5-a]pyridine skeleton*

[5] G. Hajos; Z. Riedl, *Science of Synthesis*, **2002**, 12, 613.

These *N,N*-bidentate ligands with mixed five and six-membered heterocycles are a desirable class of compounds in the pursuit of structural diversity for property performance. In particular, 1-pyridylimidazo[1,5-*a*]pyridines possess a bidentate structural feature with a pyridyl unit directly next to a fused imidazole and have emerged as a new class of ligands.[6]

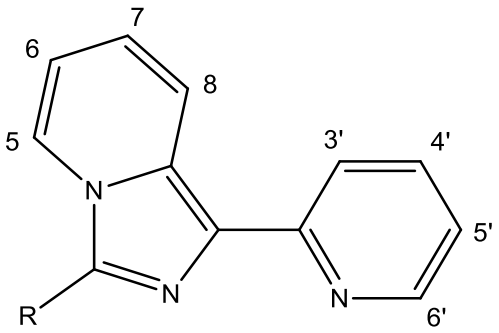


Figure 6. *1-pyridylimidazo[1,5-a]pyridine ligand*

Moreover these ligands were chosen for their ability to form chelate complexes with different metal ions with peculiars properties; in fact, the imidazo[1,5-a]pyridine nucleus is known in literature also for its photophysical activity[7] and for the potential applications in the field of OLEDs[8] and organic thin-layer field-effect transistors (FETs).[9]

---

[6] a) A. G. Ligtenbarg; A. L. Spek; R. Hage ; B. L. Feringa, *J. Chem. Soc., Dalton Trans.* **1999**, 659; b) M. E. Bluhm; M. Ciesielski; Walter, O. Go ̈rls, M. Do ̈ring, *Inorg. Chem*. **2003**, *42*, 8878.

[7] E. Yamaguchi, F. Shibahara, T. Murai, *J. Org. Chem.* **2011**, *76*, 6146–6158, and references cited therein.

[8] a) M. Nakatsuka and T. Shimamura, *Jpn. Kokai Tokkyo Koho* JP 2001035664; *Chem. Abstr.* **2001**, *134*, 170632; b) G. Tomin- aga, R. Kohama, A. Takano, *Jpn. Kokai Tokkyo Koho* JP 2001006877; *Chem. Abstr.* **2001**, *134*, 93136; c) D. Kitazawa, G. Tominaga, A. Takano, *Jpn. Kokai Tokkyo Koho* JP 2001057292; *Chem. Abstr.* **2001**, *134*, 200276.

[9] H. Nakamura, H. Yamamoto, *PCT Int. Appl*. WO 2005043630; *Chem. Abstr.* **2005**, *142*, 440277.

So different 1-pyridylimidazo[1,5-*a*]pyridines, have been coordinated to transition metals to produce highly luminescent coordination compounds based on Re(I)[10], Zn(II)[11,12], Ag(I)[13], Cd(II)[14], Ru(II) and Os(II)[15] metal centers.

Furthermore, the coordination of small organic molecules often produces a significant effect on their biological activities. Within this context, we synthesized heterocyclic imidazo[1,5-a]pyridine derivatives owing also to their huge biological and medicinal applications[16].

For these reasons, these ligands, with imidazo[1,5-*a*]pyridine skeleton, seemed very interesting to us and apparently very similar to 2,2'bipyridines 6-substituted.

Also, these molecules can be a lot very attractive because they might behave in different modes: as *neutral ligands*, using only nitrogen atoms to chelate the metal ions or as *anionic ligands* with the activation of C-H bonds in different positions.

---

[10] a) L. Salassa, A. Albertino, C. Garino, G. Volpi, C. Nervi, R. Gobetto, K. I. Hardcastle, *Organometallics* **2008**, *27*, 1427– 1435; b) C. Garino, T. Ruiu, L. Salassa, A. Albertino, G. Volpi, C. Nervi, R. Gobetto, K. I. Hardcastle, *Eur. J. Inorg. Chem.* **2008**, 3587–3591.

[11] a) G. Volpi, E. Priola, C. Garini, A. Daolio; R. Rabezzana, P. Benzi, A. Giordana, E. Diana, R. Gobetto, *Inorg. Chim. Acta*, 509, **2020**; b) G. A. Ardizzoia, S. Brenna, S. Durini, B. Therrien and M. Veronelli, *Eur. J. Inorg. Chem*., **2014**, 4310–4319; c) G. A. Ardizzoia, S. Brenna, S. Durini and B. Therrien, *Polyhedron*, **2015**, 90, 214–220.

[12] a) K.P. Thakor, M.V. Lunagariya, B.S. Bhatt, M.N. Patel, *Luminescence* 34, **2019**, 113–124; b) L. Ronconi, P.J. Sadler, *Coord. Chem. Rev*. 251, **2007**, 1633–1648.

[13] S. Durini, G. A.Ardizzoia, B. Therrienc and S. Brenna, *New J. Chem*., **2017**, 41, 3006-3014.

[14]N. Kundu, S. M. Towsif Abtab, S. Kundu, A. Endo, S. J. Teat, M. Chaudhury, *Inorg. Chem.* **2012**, *51*, 2652–2661.

[15]A. L. Guckian, M. Doering, M. Ciesielski, O. Walter, J. Hjelm, N. M. O'Boyle, W. Henry, W. R. Browne, J. J. McGarvey, J. G. Vos, *Dalton Trans.* **2004**, 3943–3949.

[16] a) K.P. Thakor, M.V. Lunagariya, B.S. Bhatt, M.N. Patel, *Luminescence* 34 ,**2019**, 113–124; b) L. Ronconi, P.J. Sadler, *Coord. Chem. Rev*. 251, **2007**, 1633–1648; c) D.A. Kanthecha, B.S. Bhatt, M. N. Patel *Heliyon* 5, **2019**, e01968.

In my work: *New complexes of transition metal ions, Pd(II), Pt(II), Au(III), and terrae rare, Y(III), La(III), Sm(II), with N-heterocyclic aromatic ligands*, is reported an unprecedent study between this particular class of ligands and precious metals in d^8 configuration and terrae rare, currently unexplored.

In particular, it is reported the synthesis of new species of Pd(II), Pt(II), Au(III); Y(III), La(III) and Sm(II); their spectroscopic characterization (including infrared, ^{1}H NMR, mono and two-dimensional and X-Ray diffraction), elemental analysis with their reactivity and potential applications.

Results and discussion

Synthesis and characterization of ligands with imidazo[1,5-a]pyridine nucleus

The first goal of this work was the synthesis and characterization of a class of N-heterocyclic aromatic ligands, chosen as a class of interest, characterized by the presence of the imidazo[1,5-a]pyridine nucleus. In particular, we decided to study:

- *3-substituted (pyridin-2-yl)imidazo[1,5-a]pyridines;*
- *1-substituted 3-(pyridin-2-yl)imidazo[1,5-a]pyridines* ;
- *bis-imidazo[1,5-a]pyridin-3-yl)benzenes.*

In the Figure 7, are reported the ligands synthesized with their molecular structures, still characterized by the presence of the imidazo[1,5-a]pyridine skeleton.

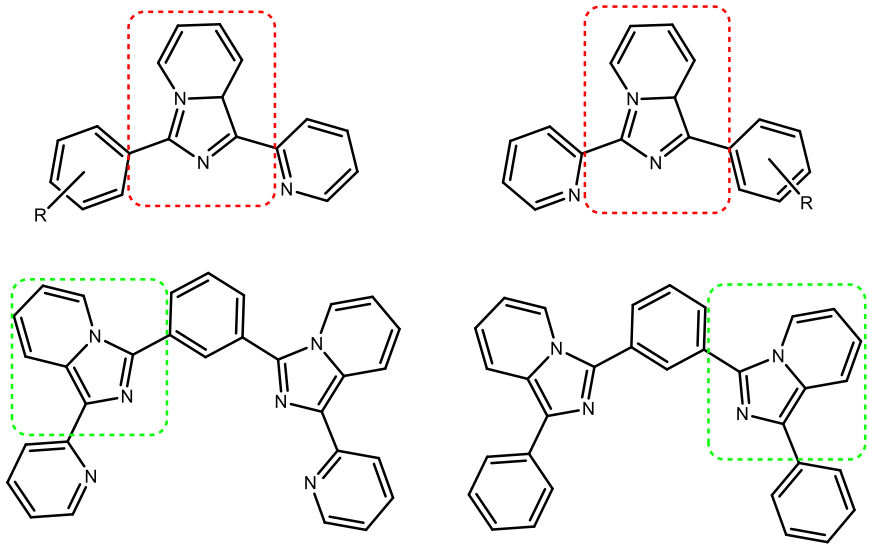


Figure 7. *substituited 1-(pyridin-2-yl)imidazo[1,5-a]pyridine*

The first attempt concerned the synthesis of *3-substituited 1-(pyridin-2-yl)imidazo[1,5-a]pyridines*, where the substituent in 3 position is an arylic ring and it was conducted according to Xin R. Bu and coworkers[17].

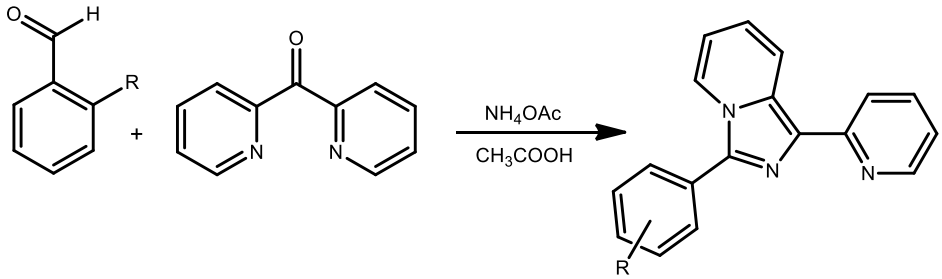


Figure 8. *General synthesis for 3-arylic-1-pyridilimidazo-[1,5-a]pyridine*

The procedure proposed is a one-pot synthesis that does not require any catalyst or Lewis acid; furthermore, it is possible to use a wide

[17] a) J. Wang, L. Dyers Jr., R. Mason Jr., P. Amoyaw, X. R. Bu, *J. Org. Chem.* **2005**, *70*, 2353–2356; b) J. Wang, R. Mason, D. Van Derveer, K. Feng, X. R. Bu, *J. Org. Chem.* **2003**, *68*, 2415–2418.

range of different aldehydic substrates. The proposed mechanism of reaction assumes that the ammonium acetate converts the aldehyde into the corresponding imine, that can then react with the 2,2'-dipyridylketone, as in the scheme reported in Figure 9.

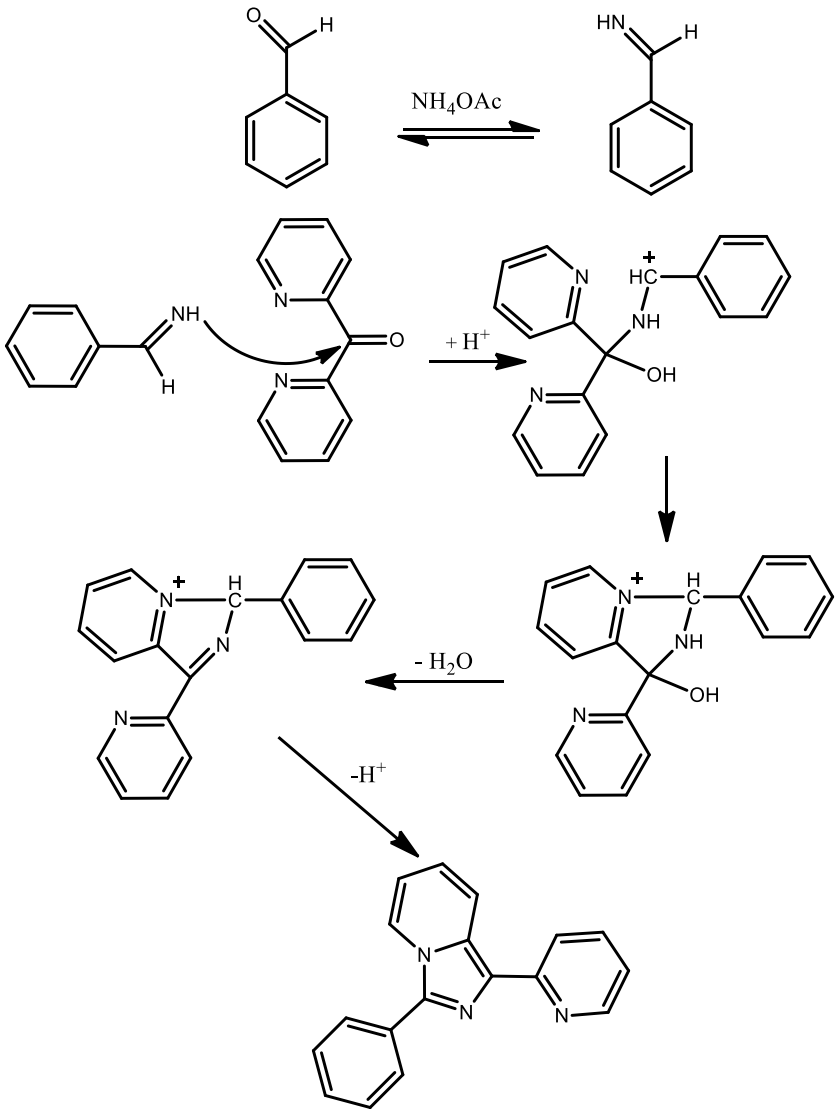


Figure 9. *General mechanism proposed*

Therefore, with this method it was possible to synthesize six different ligands:

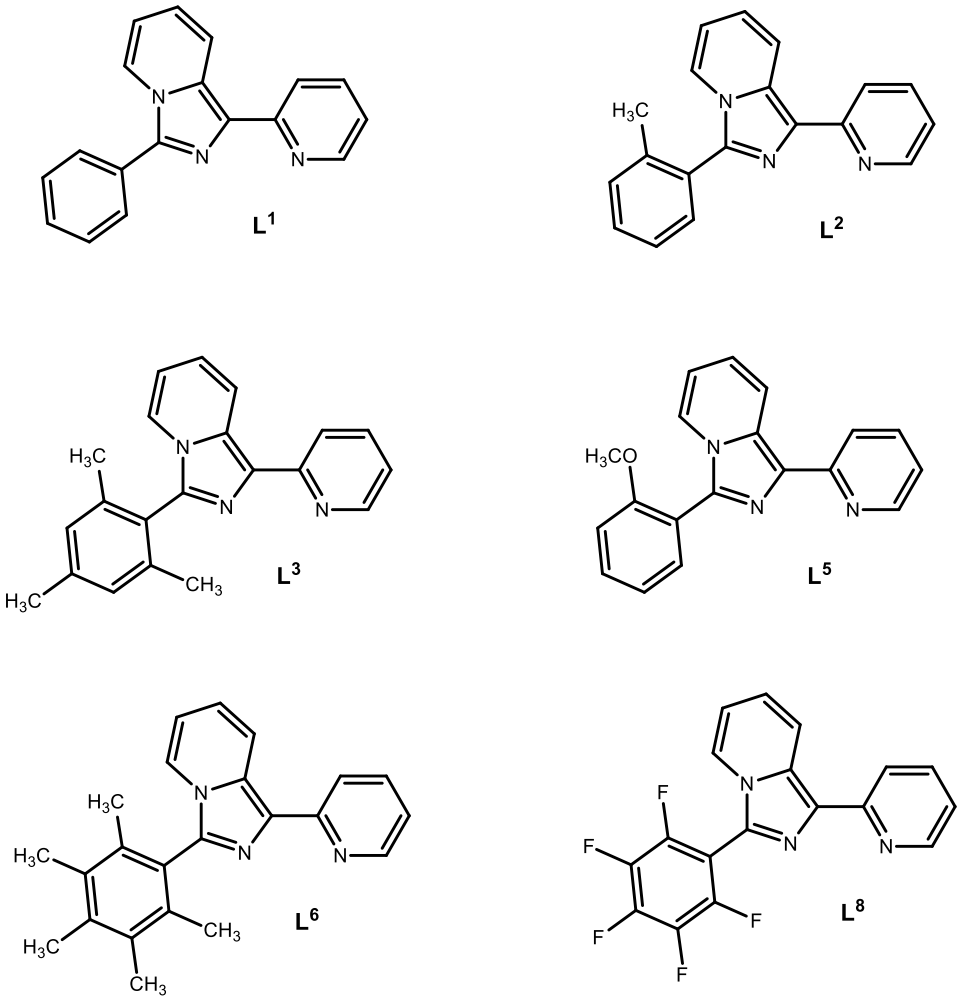


Figure 10. *Arylic ligands (L^1, L^2, L^3, L^5, L^6 and L^8)*

Conversely the synthesis for *3-substituted 1-(pyridin-2-yl)imidazo[1,5-a]pyridines*, where the substituent in 3 position is a benzylic ring, was conducted according to R. Grigg and coworkers :[18]

[18] R. Grigg, P. Kennewell, V. Savic, V. Sridharan, *Tetrahedron*, **1992**, 10423-10430

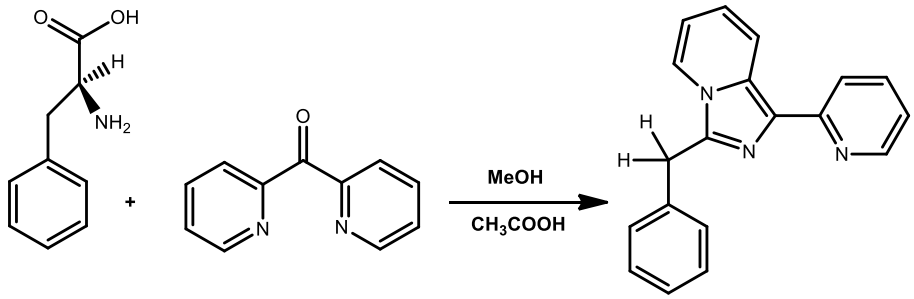


Figure 11. *General synthesis for 3-benzylic-1-pyridilimidazo-[1,5-a]pyridine*

According to this method it was possible to synthesize L^4:

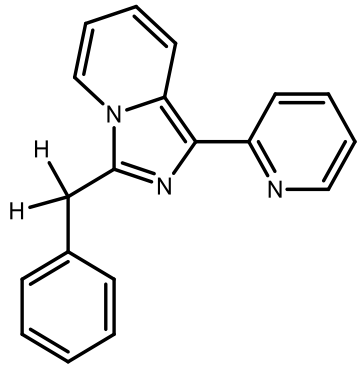


Figure 12. *Ligand L^4*

These products were purified by column chromatography and characterized in detail in solution by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, mono and two-dimensional. In this way the signals of all the protons were assigned (see **Table 1**).

Table 1. ^{1}HNMR selected data of L^n in $CDCl_3$.

L^n	H8	H6'	H5	H3'	Har	H4'	H5'	H6	H7	Other
L^1	8.70; d	8.64; d	8.26; d	8.24; d		7.72; td	7.10; dd	6.92; dd	6.65; td	
L^2	8.71; d	8.64; d	7.64; d	8.23; d		7.70; t	7.09; dd	6.60; t	6.93; t	2.26; s, CH_3
L^3	8.94; d	8.89; d	7.61; d	8.48; d		7.95; td	7.33; dd	6.82; dd	7.17; t	2.62; s, CH_3para 2.27; s, CH_3ortho

L⁴	8.62; d	8.60; d	7.59; d	8.17; d		7.71; td	7.07; dd	6.52; dd	6.84; t	4.51; s, CH_2
L⁵	8.70; d	8.62; d	7,62; d	7.69; d		7.50; t	7.0 7; t	6.94; t	6.61; t	3.81; s, OCH_3
L⁶	8.70; d	8.64; d	8.25; d	7.34; d		7.70; td	7.09; t	6.92; t	6.55; t	2.33; s, CH_3para 2.27; s, CH_3meta 1.90; s, CH_3ortho
L⁸	8.80; d	8.65; d	8.20; d	7.69; d		7.75; t	7.16; t	7.07; t	6.81; t	

The interpretation of ^{1}H NMR spectra of L^n in $CDCl_3$ is not easy and the existence of three different spin systems involving 4, 4, and a variable number of protons depending on the substituent in 3, was clearly identified by 2D NMR techniques (COSY, and NOESY)[19].

In the case of L^1 these spin systems include 4 (●), 4 (○), and 5 (◆) protons respectively (see in Figure 13), the signal at 7.26 ppm being due to the solvent ($CHCl_3$). This information however was not sufficient for explain unequivocally the structural assignment with the attribution of all the signals.

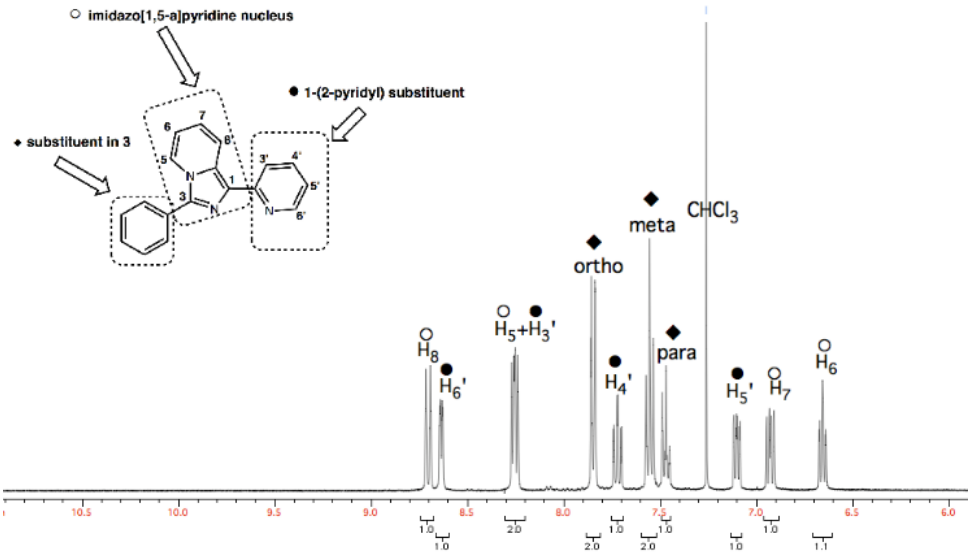


Figure 13. *Spin systems present in the ligand L^1*

[19] S. Albano; G. Olivo; L. Mandolini; C. Massera; F. Ugozzoli and S. Di Stefano, *J. Org. Chem.*; **2017**, 82, 3820–3825.

In the ^{1}H NMR spectrum of L^{1} the signal at lower field has been attributed to the H8 proton: an anomalous position, for example with respect to the signal of the H5 proton, also considering the proximity to the nitrogen atom in position 4 of the imidazo[1,5-a] pyridine skeleton.

In our opinion, this is due to the interaction of H8 with the nitrogen atom of the pyridinic substituent in position 1.

This fact has been confirmed with the synthesis of corresponding isomeric ligand for L^{1}: *1-phenyl-3-(2-pyridyl)-imidazo[1,5-a]pyridine* **(L^{7})**, in which the 2-pyridyl group the phenyl exchanged their position.

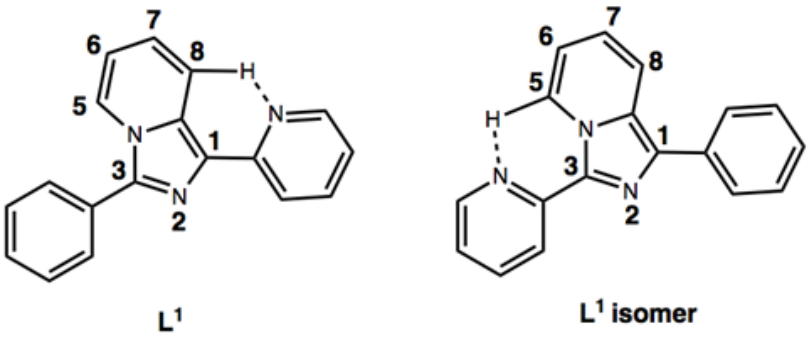


Figure 14. *Long-range N--H interaction*

As can clearly be seen in the ^{1}H NMR spectrum of L^{7} ligand the most deshielded proton now turns out to be H5.

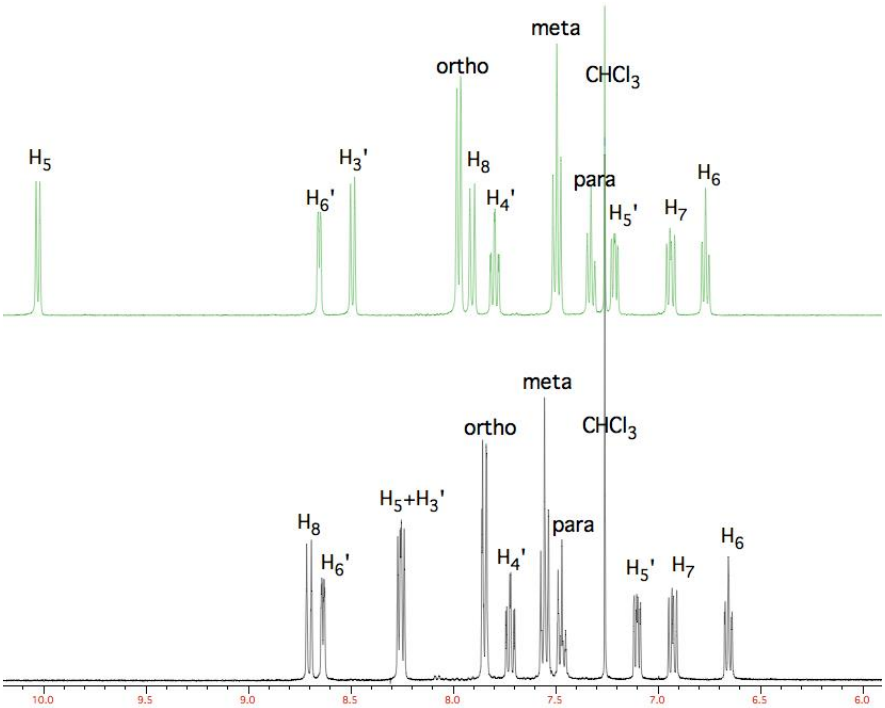


Figure 15. *Comparison ^{1}H NMR L^7(green) vs L^1(blue)*

The synthesis for *1-substituited 1-(pyridin-2-yl)imidazo[1,5-a]pyridines* **(L^7)**, was conducted according to J. Chang.[20]

Also, in this case, the synthetic approach is available for different substrates, and is operationally simple because it proceeds in a single step and can be conveniently carried out on a gram scale, according to the reaction scheme reported in Figure 16:

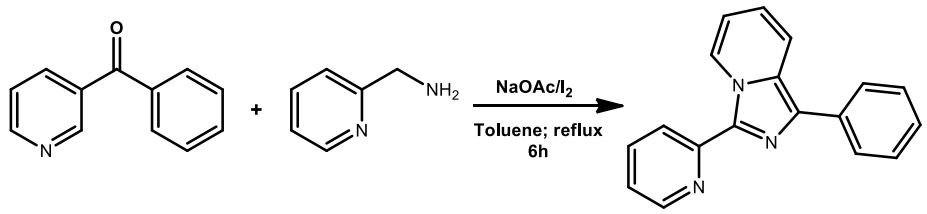


Figura 16. *General synthesis for 1-substituited 1-(pyridin-2-yl)imidazo[1,5-a]pyridines*

[20] Z. Hu, J. Hou, J. Liu, W. Yu, J. Chang, *Org. Biomol. Chem*., **2018**,16, 5653

The ligand L^7, isolated as a yellow solid, was purified by column chromatography, and characterized in detail in solution by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, mono and two-dimensional.

The two groups of ligands, just described, are particularly interesting because they can potentially coordinate the metal ions in different modes: as *neutral ligands*, chelating the metal ions, to give *adduct* species, or as *anionic ligands* with the activation of a C-H bond.

Generally, the activation of C-H bond can be split into three main mechanism: *electrophilic C-H bond activation*, *oxidative addition,* and *σ-bond metathesis.* The electronic configuration at the metal centre together with the nature of the C-H bond, in particular the hybridization at carbon, decisively determine which mechanism may be most probable.

Electrophilic C-H bonds activation are generally observed with electron-poor late transition metals, for example: palladium(II), and platinum(II). And can be considered as an analogue mechanism of organic electrophilic aromatic substitution.

While oxidative addition is a bond activation *via* C-H (or C-R) possibly if the metal centre is an electron-rich. It is most common for cyclometallations using iridium(I) and rhodium(I), as well as for some osmium(II) precursors, and it seems to prevail in most C_{alkyl} -H bond activations with late transition metals.

Finally, cyclometalation reactions involving *σ*-bond metathesis have been considered as the predominant pathway when C-H bond activation is accomplished with electron-poor metal centres such as

high-valent early transition metals, and perhaps also with carbonyl complexes.[21]

For this reason, if the ligands coordinate the metal ions like *anionic ligand* with the activation of a C-H bond (electrophilic C-H bonds activation), there is a possibility to obtain two different products:

1) *cyclometalated roll-over* species with the activation of a *C(sp^2)-H* bond in the pyridine ring;
2) *classical cyclometalated* species N^N^C, with the activation of a C-H bond in the arylic or benzylic substituent in 1 or 3 position respectively.

The choice of arylic (with methyl, methoxy or halogen group as substituents in different positions or simply phenyl) or benzylic substituent was not unintentional, because this determines either electron density on the ring and consequently the properties and the possibility to active a C-H bond or the size of cyclometalated ring.

In fact, ligands L^1 and L^7 could potentially give a five membered ring with the activation of a C*(sp^2)*-H bond. Also, with L^4 there is a possibility of obtaining a six-term cycle by activating a C*(sp^3)*-H *bond (*see Figure 17*)*.

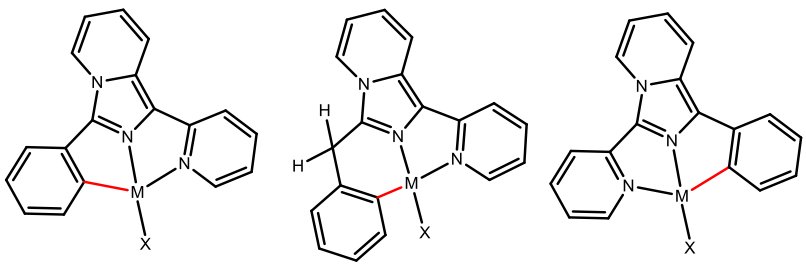


Figure 17. *Activation of C-H bond for L^1, L^4 and L^7*

[21] Martin Albrecht, *Chem. Rev.* **2010**, *110,* 576–623

While the other ligands could potentially give a six membered ring with the activation of C*(sp^3)*-H bond, less tensioned than the five-membered one.

The last group of N-heterocyclic aromatic ligands considered in this thesis was that of bis-imidazo[1,5-a]pyridin-3-yl)benzenes.

The synthesis was conducted according to G. Volpi[22], as the following scheme shows:

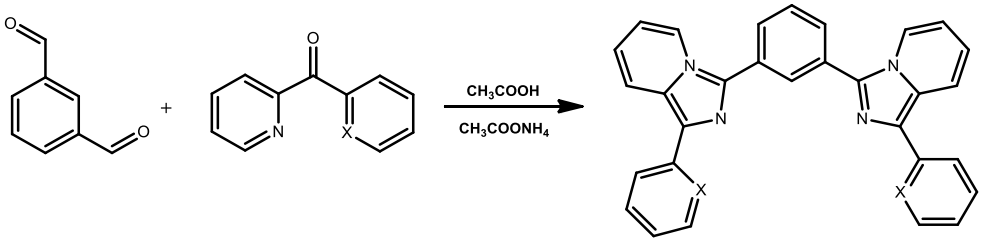


Figure 18. *General synthesis of bis-imidazo[1,5-a]pyridin-3-yl)benzene*

The procedure is a facile double condensation available to different ketone substrates, operationally simple because it proceeds in a single step and can be conveniently carried out on a gram scale.

Therefore, with this method it was possible to synthesize two different potential pincer ligands:

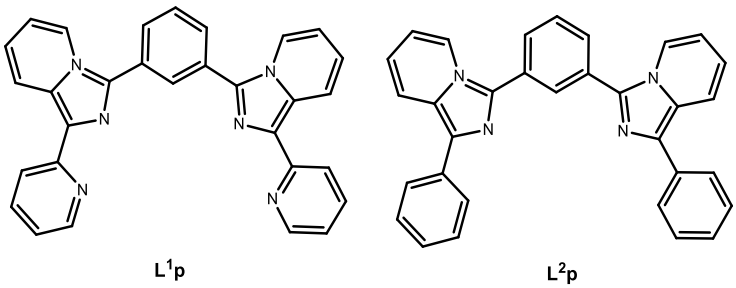


Figure 19. *Pincer ligands.*

[22] G. Volpi, C. Garino, E. Conterosito, C. Barolo , R. Gobetto, G. Viscardi, *Dyes and Pigments* 128, **2016**, 96-100.

These ligands, isolated as yellow solids, were purified by column chromatography, and fully characterized in solution by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, mono and two-dimensional.

In Figure 20, it is reported, as an example, the 2D-COSY spectrum of L^{1}_{p}. The signals of all protons were assigned (*see experimental part*).

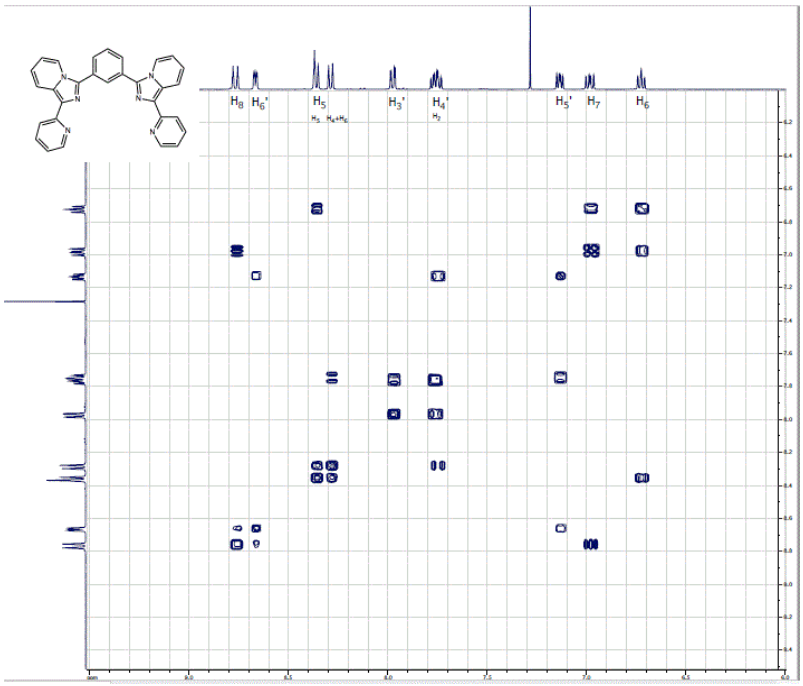


Figure 20. *2D-COSY of L^{1}_{p}*

The choice of synthesizing two different pincer ligands is due to the fact that potentially they should behave like *anionic ligands* with the activation of C-H bonds, generating new interesting cyclometalated species N^C^N.

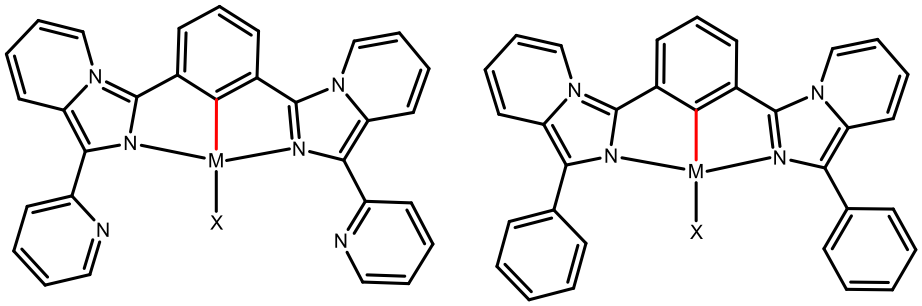


Figure 21. *Activation of C(sp^2)-H bond for L^1_p and L^2_p*

Once the ligands were synthesized and fully characterized, it was possible to proceed with the synthesis of the complexes with metal ions in d^8 configuration and with terrae rare, with the main objective being to obtain new cyclometalated species.

Synthesis and characterization of Pd(II) and Pt(II) complexes

The goal of this research work was the study of the behaviour of these N-heterocyclic aromatic ligands, previously described, towards to transition metals ions in d^8 configuration, such as: Pd(II), Pt(II) and Au(III).

The first synthesis was conducted in acetic acid using $Pd(OAc)_2$ in stochiometric ratio (1:1) using the *3-substituted 1-(pyridin-2-yl)imidazo[1,5-a]pyridines* ligand, in particular: $L^{1\text{-}4,6}$. After exchange with LiCl several Pd(II) adducts, $[PdL^nCl_2]$ (**1-4,6**), were obtained.

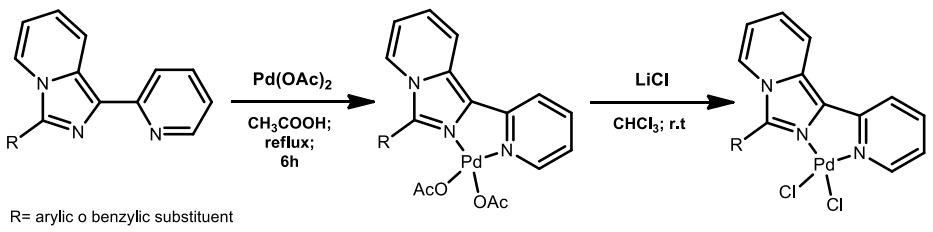


Figure 22. *General synthesis for Pd(II) adducts, (**1-4,6**)*

Using L^5 ligand, the reaction was conducted in a different mode starting from $[Pd(CH_3CN)_2Cl_2]$ in stoichiometric ratio (1:1), in acetonitrile, always obtaining the corresponding adduct $[PdL^5Cl_2]$, **(5).**

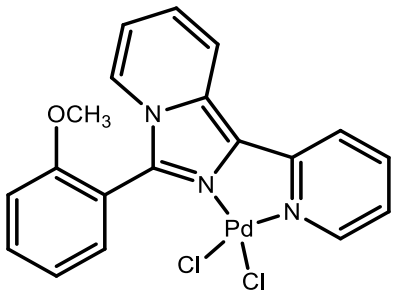


Figure 23. $[PdL^5Cl_2]$ *adduct*

All adducts were obtained in good yields as yellow solids, with melting points above 250 °C.

In these adducts the ligands L^n, n=1-6, act as a classic chelating N^N ligands, despite the best reaction conditions used to obtain activation of the C*(sp²)*-H or C*(sp³)*-H bond respectively in position *ortho* of the substituent.[23]

The spectroscopic investigation confirms the presence in solution of adducts excluding the formation cyclometalated species.

[23] a) A. D. Ryabov, *Chem. Rev.*, **1990**, 90, 403; b) M. Albrecht, *Chem. Rev.*, **2010**, 110, 576.

In the ^{1}H NMR spectra, it was possible to observe that the number of protons, compared with the value obtained from the integral of the ^{1}H NMR spectra of the free ligands, is unchanged highlighting that no cyclometalated species had been obtained.

In the ^{1}H NMR spectra it is also evident a shift towards lower field of the proton H6'**,** about 1 ppm compared to free ligand, of the pyridine ring due to the proximity to a chlorido[24] and a shift towards higher field of the proton H8, by the coordination effect of the metal centre. Other protons do not show any significant changes.

For complexes: [PdL^{2}Cl$_2$]**, (2)**, [PdL^{3}Cl$_2$]**, (3),** [PdL^{5}Cl$_2$]**, (5),** and [PdL^{6}Cl$_2$]**, (6),** the signals of the methyl or methoxy groups protons of the substituent arylic in 3 position, are not very different from those present the free ligand indicating, in solution, a conformation in which they are far from the metal centre. Most probably the aromatic rings of the arylic substituent is arranged perpendicular to the metal coordination plane.

Infrared spectra of the imidazo [1,5-a]pyridine palladium(II) complexes show the typical pattern of the ligands with sharp and intense bands in the range from 1515 to 1615 cm^{-1} with another band at about 1640 cm^{-1} ($\nu_{C=N}$). These bands are slightly shifted to higher frequencies than those of the free ligand due to the coordination to the metal.

Finally, the elementary analyses are in perfect agreement with the [PdL^{n}Cl$_2$] proposed formulation.

In **Table 2** are reported the ^{1}H NMR signals for all adducts.

[24] P.K. Byers and A.J. Canty, *Organometallics*, **1990,** 9, 210-220

Table 2. ^{1}H NMR data in CD_2Cl_2 of [PdL^{n}Cl$_2$]

L^n	H6'	H5'	H3'	H8	H4'	H$_{ar}$	H5	H7	H6	Other
1	9.10	7.22	7.85	7.82	7.78	7.55	7.25	7.12	6.80	
2	9.25	7.41	7.85	8.05	7.85	7.35	7.15	6.80	6.80	2.17, CH_3ortho
3	9.26	7.33	7.43	7.96	8.03	7.08	7.35	7.35	6.90	2.44, CH_3para 2.15, CH_3ortho 2.05, CH_3ortho
4	9.27	7.27	7.91	7.91	8.00	7.37	7.28	7.28	6.90	4.43, CH_2
5	9.24	7.67	7.59	7.86	7.97	7.42-7.06	7.13	7.13	7.03	3.86, OCH_3
6	9.23	7.84	7.36	7.92	7.99		7.29	7.29	6.82	2.35, CH_3para 2.27, CH_3meta 1.90, CH_3ortho

Also, it was possible to obtain crystals suitable for X-Ray structure resolution [PdL^{5}Cl$_2$], **(5)**, *via* slow evaporation of the solvent from a CH_2Cl_2 solution.

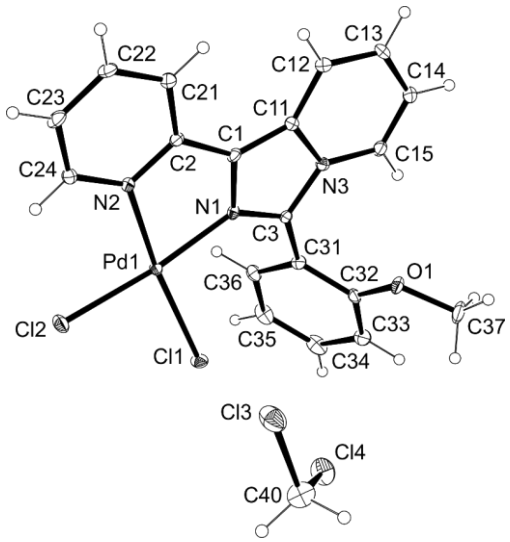


Figure 24. *X-Ray structure of* [PdL^{5}Cl$_2$]

X-ray analysis shows that the system is orthorombic with a square planar geometry around the Pd centre, tipical of this ion and with

bond lengths and angles comparable with structures of similar complexes, reported in literature.[25]

The pyridyl-imidazopyridine ligand acts as a bidentate donor [Pd1−N1 = 2.026(3) Å; Pd1−N2 = 2.049(3) Å] and the metal centre is perfectly placed on the mean calculated between the four donor atoms. Two chlorine atoms are bound to the metal centre in *cis* position [Pd1–Cl1 = 2.2912(10) Å; Pd1–Cl2 = 2.2914(11) Å].

It is possible to notice that the methoxy group is as far as possible from the metal centre, as expected from results of the ^{1}H NMR spectrum, in which it was not observed any change in the chemical shift for methoxy group protons compared with free ligand. From the structure it also is evident that the 2-methoxyphenyl ring and the imidazopyridine system are orthogonal. The structure is the definitive evidence that no cyclometalated species were formed.

Also with the *1-substituted 1-(pyridin-2-yl)imidazo[1,5-a]pyridines* ligand **(L^7)**, the same synthesis methods were used to obtain unsuccessfull the Pd(II) corresponding adduct: the desired product was in this case not isolated.

Thereafore, two new methodologies were used, starting from Na_2PdCl_4 in methanol or $[PdCl_2(PhCN)_2]$ in chloroform. In this way, it was possible to isolate the desired adduct of Pd(II), compound $[PdL^7Cl_2]$, **(7)**.

[25] D. Kovala-Demertzi; J.R. Miller; N. Kourkoumelis; S.K. Hadjikakou; M.A. Demertzis, Palladium(II) and Platinum(II) Complexes of Pyridine-2-Carbaldehyde Thiosemicarbazone with Potential Biological Activity. Synthesis, Structure and Spectral Properties. Extended Network via Hydrogen Bond Linkages of [Pd(PyTsc)Cl]. *Polyhedron* **1999**, *18* (7), 1005–1013.

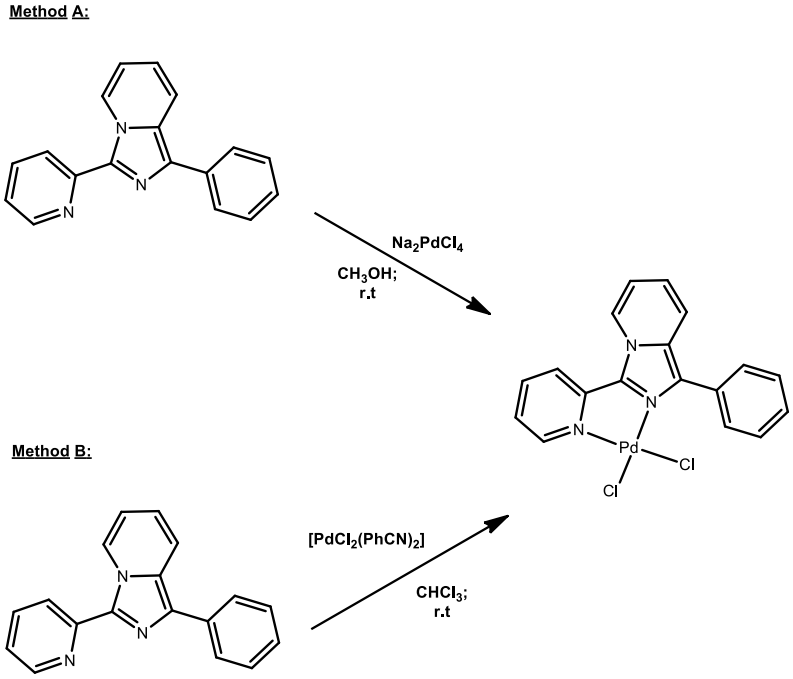


Figure 25. *Methods to obtain [PdL^{7}Cl$_2$] adduct*

The adduct, **(7)**, was obtained as an orange solid, in a good yield. Also, in this case, L^7 shows the classic chelating N^N behaviour despite the best reaction conditions used to obtain activation of the C*(sp^2)*-H bond in *ortho* position of the substituent.

In the ^{1}H NMR spectrum, it was possible to observe the same number of protons, as in ^{1}H NMR spectrum of the free ligand excluding any metalation process. In the spectrum can be seen a shift towards lower field of the proton H6' of the pyridine ring due to the proximity to an electronegative chlorido and a shift towards higher field of the proton H5 for the reasons already discussed above. All signals were assigned (*see experimental part*): the other protons do not show any significant changes compared to the free ligand. Infrared spectra, and elemental analysis confirm the structure proposed.

Also for the last group of N-heterocyclic aromatic ligands considered in this work namely bis-imidazo[1,5-a]pyridin-3-yl)benzene, the syntheses were conducted in acetic acid with Na_2PdCl_4 in stochiometric ratio (1:1), with the aim of obtaining pincer complexes by activating the C(*sp*^{2})-H bond of the benzene ring.

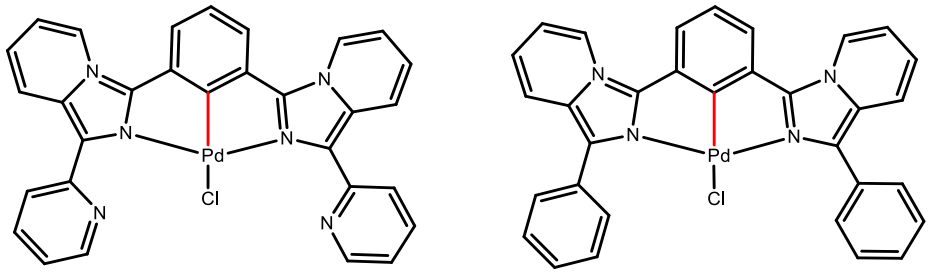


Figure 26. Pincer complexes

For L^2_p no palladium(II) species was isolated, while for L^1_p it was possible to obtain and characterize a new adduct $[Pd(L^1_p)Cl_2]$, **(8)**

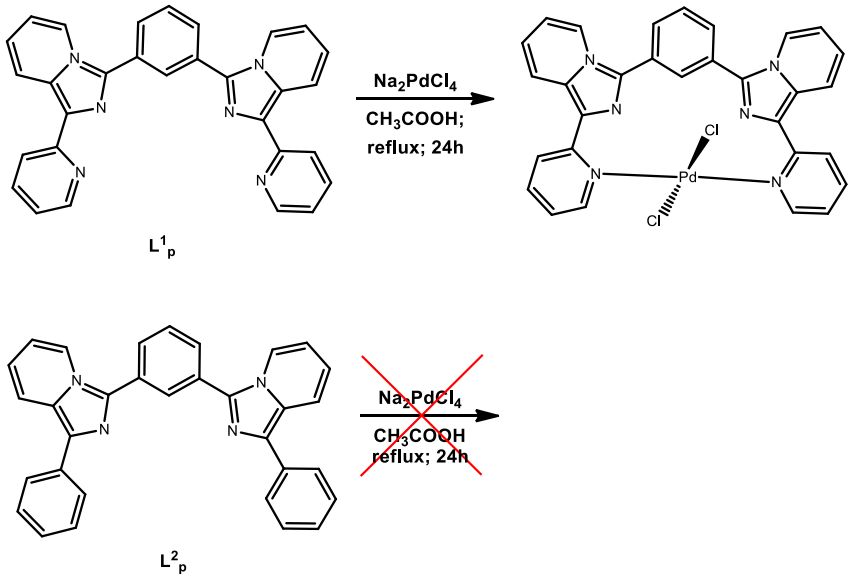


Figure 27. *General scheme of reaction for pincer ligand*

It was obtained as a yellow solid, and in a good yield. Unfortunately, also in this case, the potential pincer ligand, L^1_p, acts as a classic chelating N^N ligand, by means of the pyridine groups of the imidazopyridine fragment in position 1 and 3. Under the same conditions, the corresponding pincer complex of the similar ligand 1,3-dipyridylbenzene was obtained quite easily.[26]

The NMR data (all signals were assigned, *see experimental part*), in fact exclude, also in this case, the formation, of cyclometalated pincer derivatives. The number of protons, compared to value obtained from the integral in the ^{1}H NMR spectrum of the free ligand, is unchanged.

In the spectrum it is also evident a shift towards lower field of the proton H6' of the pyridine ring caused by the proximity to an electronegative chlorido; other protons do not show any significant changes.

To exclude the formation of palladium(II) cyclometalates in the synthesis that involves the use of $Pd(OAc)_2$, considered the best precursor of palladium for this type of process, the corresponding acetate derivatives $[PdL^n(OAc)_2]$ were isolated and characterized.

In this case, the syntheses were conducted in dichloromethane in stochiometric ratio (1:1), as in the scheme:

[26] B. Soro, S. Stoccoro, G. Minghetti, A. Zucca, M. A. Cinellu, S. Gladiali, M. Manassero and M. Sansoni, *Organometallics* **2005**, 24, 1, 53–61.

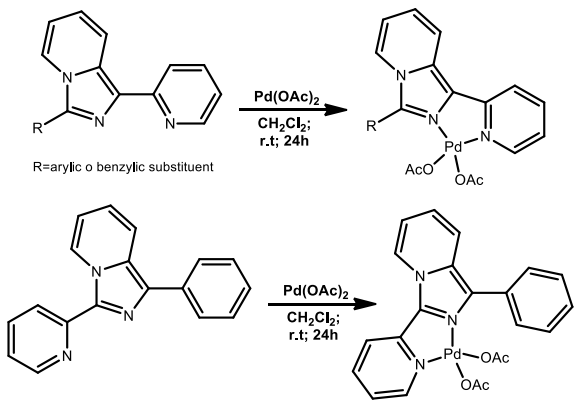


Figure 28. *General reaction scheme for [PdL^n(OAc)$_2$]*

All species obtained, as yellow-orange powders in a good yield, were extensively characterized in solution and in solid state (infrared spectra and elemental analyses).

In **Table 3** the attributions of the ^{1}H NMR signals are shown: different chemical shift for methyl protons of the acetate can be seen given the non-equivalence of the two nitrogen halves. The acetate with the methyl signal (singlet) at higher fields is certainly attributed to the one in *trans* at pyridinic group, close to the aryl substituent. Arranging itself perpendicularly to the metal plane the aromatic ring of the aryl shields these protons, compared to those of the other acetate in *trans* to the imidazolic nitrogen. This fact is less pronounced in the case of the [PdL^4(OAc)$_2$], **(4')**, complex given the presence of the spacer CH_2.

In the ^{1}H NMR spectra it is also evident a slight shift towards lower field of the proton H6' of the pyridine ring caused by the proximity to oxygen of the acetate group and a shift towards higher field of the proton H8, due to the coordination effect of the metal centre. The

other protons do not show any significant changes compared to the spectra of free ligands.

Table 3. ^{1}H NMR data in $CDCl_3$ of $[PdL^n(OAc)_2]$

	H6'	H5'	H3'	H8	H4'	Har	H5	H7	H6	Other
1'	8.12	7.24	7.80	7.91	7.98	7.67-7.60	7.85	7.29	6.86	1.99, CH_3(OAc); 1.13, CH_3(OAc)
2'	8.14	7.25	7.51	7.89	7.98	7.50-7.40	7.79	7.31	6.86	2.18, CH_3ortho; 1.98, CH_3(OAc) 1.11, CH_3(OAc)
3'	8.14	7.30	7.40	7.89	7.98	7.04	7.77	7.24	6.85	2.35, CH_3para; 2.09, CH_3ortho 1.98, CH_3(OAc); 1.11, CH_3(OAc)
4'	8.07	7.16	7.74	7.84	7.92	7.35-7.23	7.84	7.16	6.77	4.60, CH_2; 2.14, CH_3(OAc) 1.89, CH_3(OAc)
5'	8.27	7.18	7.53	8.27	8.09	7.26-7.10	7.53	6.81	6.72	3.96, OCH_3; 2.09, CH_3(OAc) 1.34, CH_3(OAc)
6'	8.15	7.27	7.79	7.90	7.98		7.37	7.15	6.80	2.27, CH_3para; 2.26, CH_3meta 2.07, CH_3(OAc); 1.99, CH_3ortho 1.12, CH_3(OAc)
7'	9.07	7.52	7.65	8.13	8.24	7.65-7.52	8.38	7.08	7.08	2.13, CH_3(OAc) 1.26, CH_3(OAc)

After palladium complexes the interest of our research was moved to the platinum(II) chemistry using K_2PtCl_4 as starting compound. With this specific salt, using 6-substituted 2,2'-bipyridines, the corresponding cyclometalated complexes were obtained[27], in conditions of reaction known as *"Morgan Conditions"*[28].

Therefore, the syntheses were conducted in water and hydrochloric acid (2M), to solubilize the ligand, using a molar ratio K_2PtCl_4/L^{1-7} of (1:1).

[27] E. Constable, R. P.G. Henney, T. A. Leese and D. A. Tocher, *J. Chem. Soc. Chem Comm*., **1990**, 513-515

[28] G. Morgan and F. H. Burstall, J. *Chem. Soc.,* **1934**, 965.

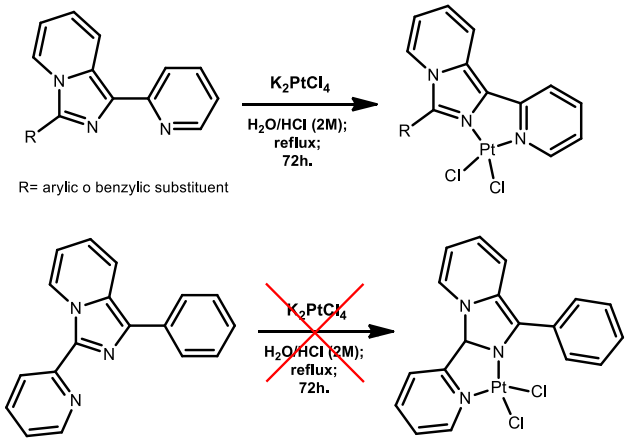


Figure 29. *General scheme for [PtL^{n}Cl$_2$]*

Also in this case the corresponding Pt(II) adducts, [PtL^{n}Cl$_2$], n=1÷6, **(9-14)**, were isolated and characterized while, with the ligand (L^7), no product was isolated, maybe for the acidic reaction conditions

These syntheses of the Pt(II) adducts have been further optimized using a microwave conditions[29] reducing the reaction times and significantly improving the yields.

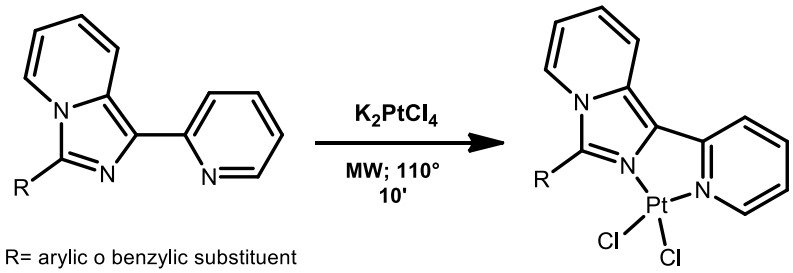


Figure 30. *General scheme for [PtL^{n}Cl$_2$] in MW.*

All platinum adducts obtained, were characterized in solution via NMR spectroscopy.

[29] N. Godbert, T. Pugliese, I. Aiello, A. Bellusci, A. Crispini, and M. Ghedini, *Eur. J. Inorg. Chem.*, **2007**, 5105–5111.

As can be seen in **Table 4**, the ^{1}H NMR data are in complete agreement with the proposed formulation. With the number of protons, equal to that of the free ligand confirming that the absence of cyclometalated species even in traces. In particular, the H6' proton signals are more deshielded than those of the corresponding palladium complexes most likely due to the greater electronegativity of platinum[30].

The coupling constants $^{3}J_{Pt-H}$ confirm the successful coordination of the pyridine ring on the platinum atom. It is also evident a shift towards higher field of the proton H8, due to the coordination effect of the metal centre. The other protons do not show, in general, significant shifts compared to free ligands.

Table 4. ^{1}H NMR data in $CDCl_3$ of $[PtL^{n}Cl_2]$

	H6'	H5'	H3'	H8	H4'	Har	H5	H7	H6	Other
9	9.51; $^{3}J_{Pt-H}$=36Hz	7.33	7.84	7.95	8.05	7.66	7.84	7.33	6.92	
10	9.63; $^{3}J_{Pt-H}$=34Hz	7.62	7.86	7.96	8.07	7.62-7.28	7.62	7.62	6.91	2.22, CH_3ortho
11	9.63; $^{3}J_{Pt-H}$=37Hz	7.31	7.87	7.97	8.07	7.07	7.43	7.37	6.91	2.42, CH_3para 2.03, CH_3ortho
12	9.39; $^{3}J_{Pt-H}$=37Hz	7.51	8.22	8.33	8.22	7.51-7.22	8.33	7.22	7.12	5.41, CH_2
13	9.61; $^{3}J_{Pt-H}$=38Hz	7.75	7.90	7.75	7.90	7.56	7.56	7.09	6.81	3.77, OCH_3
14	9.61; $^{3}J_{Pt-H}$=38Hz	7,32	7.86	7.96	8.05		7.32	7.32	6.85	2.36, CH_3para 2.27, CH_3meta 1.91, CH_3ortho

[30] a) J. E. Huheey, E.A. Keiter, and R.L. Keiter in *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th edition, Harper Collins, New York, USA, **1993**; b) J. B. Mann, T. L. Meek, E. T. Knight, J. F. Capitani and L. C. Allen, *J. Am. Chem. Soc.*, **2000**, 122, 5132-5137.

For two adducts [PtL^{1}Cl$_2$], **(9)**, and [PtL^{4}Cl$_2$], **(12)**, was possible to obtain crystals suitable for X-Ray structure resolution by slow diffusion of di-isopropyl ether into a chloroform solution at room temperature.

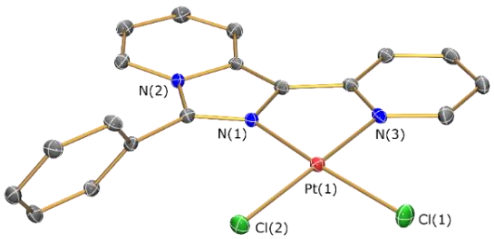


Figure 31. *X-Ray structure of [PtL^{1}Cl$_2$]*

The structure of the complex [PtL^{1}Cl$_2$], **(9)**, belonging to monoclinic system shows the expected square planar geometry around the Pt centre with bond lengths and angles comparable with those of similar complexes.[31] The pyridyl-imidazopyridine ligand acts as a bidentate donor [Pt1−N1 = 2.020(2) Å; Pt1−N3 = 2.023(2) Å] and the metal centre perfectly placed on the mean calculated between the four donor atoms. Two chlorine atoms are bound to the metal centre in *cis* position [Pt1–Cl1 = 2.2896(8) Å; Pt1–Cl2 = 2.2869(7) Å].

[31] a) K. Ha, *Z. Kristallogr.-New Cryst. Struct.* **2011**, 577; b) A. N. Chernyshev, N. A. Bokach, Y. A. Izotova, M. Haukka, *Acta Crys- tallogr., Sect. E* 2009, *65*, m60; **2009**, *44*, 1921–1925

The aryl substituent, arranged perpendicular to the plane of the metal, moves the aromatic protons as far as possible from the centre of the metal itself, making any activation process more difficult. This could be one of the reasons for the lack of cyclometalation.

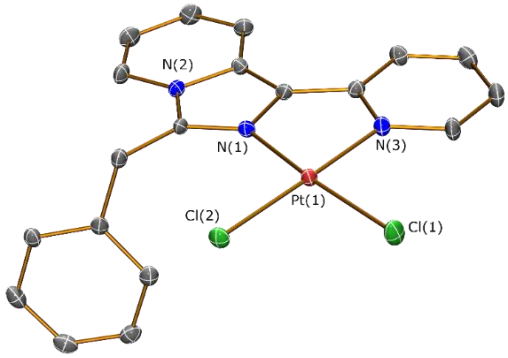


Figure 32. *X-Ray structure of [PtL^{4}Cl$_2$]*

Analogous considerations are possible for the adduct [PtL^{4}Cl$_2$], **(12)**, whose structure belongs to monoclinic system.

The X-Ray structure shows a square planar geometry around the Pt centre [Σ_{E-Pt-E} = 360.0(2)°], featuring a pyridyl-imidazopyridine ligand which acts as a bidentate donor [Pt1−N1 = 2.029(2) Å; Pt1−N3 = 2.028(3) Å] and the metal centre perfectly placed on the mean calculated between the four donor atoms. Two chlorine atoms are bound to the metal centre in *cis* position [Pt1–Cl1 = 2.2883(9) Å; Pt1–Cl2 = 2.2961(11) Å].

The X-Ray structure of complex, **(12),** points out a hydrogen interaction of one hydrogen of the methylenic group (CH_2) of the

benzylic substituent with the chlorine in *trans* to the nitrogen of the pyridine ring. The CH_2 acts as a spacer by moving the aromatic protons away from the metal center and reducing the possibility of activation and, as we will see later, the shielding effect of the ring current.

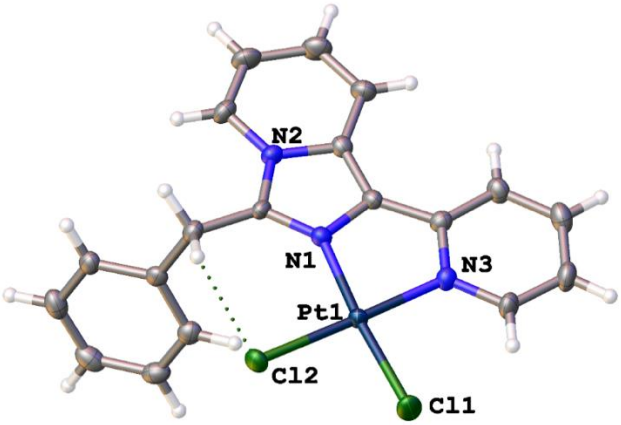


Figure 32'. *alternative X-Ray structure of [PtL^{4}Cl$_2$]*

Synthesis and characterization of Pd(II) and Pt(II) organometallic complexes

Pursuing the aim of obtaining cyclometalate species of Pd(II) and Pt(II) we tried to change starting intermediates using organometallic complexes such as [Pd(COD)(CH_3)Cl], [Pt(DMSO)$_2$(CH_3)Cl] and [Pt(DMSO)$_2$(CH_3)$_2$] more electron rich than Pd(OAc)$_2$ and K_2PtCl_4 previously used.

These starting materials were selected with the expectation that, by working on the methyl group directly linked to the metal, or operating on the chloride, to create a coordinative unsaturation there was the possibility to force activation a C-H bond of the substituent in position 3 of the L^n ligands.

[Pd(COD)(CH_3)Cl][32] was reacted with ligands, L^{1-6}, at room temperature in molar ratio (1:1) see the scheme reported in Figure 33:

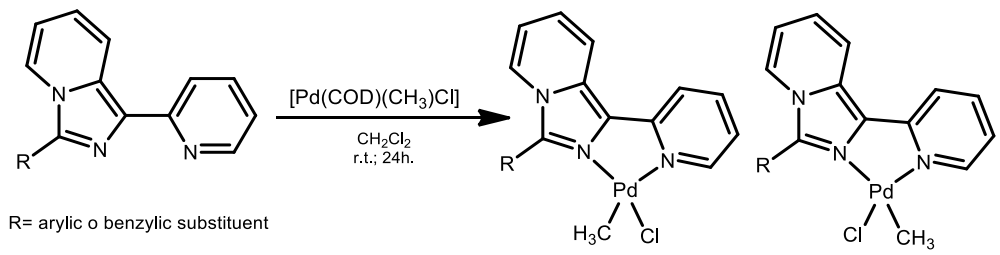


Figure 33. *General scheme for [PdL^n(CH_3)Cl]*

In this way, it was possible to isolate six news species, with general formula [PdL^n(CH_3)Cl], **(15-20)**, obtained as yellow solids, in a good yields.

The obtained products have been extensively characterized as adducts in which the nitrogen ligands act as a chelating and due to the non-equivalence of the two nitrogen halves and the planar square geometry, typical of the Pd(II) systems, two stereoisomers are expected (see Figure 33): one with the methyl group in *trans* to pyridine nitrogen the other with the methyl group in *trans* to imidazole nitrogen. It has been possible to observe a marked preference for the stereoisomer with the pyridine donor *trans* the methyl group. (*Major stereoisomers*: **(15-20);** *minor stereoisomers*: **(15'-20')**).

In the ^{1}H NMR spectra, the signals related to the protons of the M-CH_3 and the proton H6' of the coordinated pyridine ring were very diagnostic in the confirmation of the proposed structures. For these

[32] R. E. Riilke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen and K.Vrieze, *Inorg. Chem.,* **1993**, *32,* 5769-5778

complexes δ(Pd-Me) occurs in the range 1.05-0.35 ppm and protons of the donors ring *cis* to the halogen are discerned by the marked downfield shift; e.g. H6' proton adjacent to chloro in [PdL^1(CH$_3$)Cl], **(15)**, occurs at 9.11 ppm compared with 8.51 for the same proton adjacent to Pd-Me, **(15')**. When going to the complex with the benzylic substituent [PdL^4(CH$_3$)Cl], **(18)** the only stereoisomer present in solution, it is the one with the methyl group in *trans* to the imidazole ring, most likely for a matter of steric bulk.

In **Table 5** are reported ^{1}H NMR data of Pd(II) derivatives [PdL^n(CH$_3$)Cl], n=1-6, **(15-20)**.

Table 5. ^{1}H NMR selected data in CDCl$_3$ of [PdL^n(CH$_3$)Cl]

	H6'	CH$_3$ of the arylic substituent in 3 (L^2, L^3,L^5,L^6) or CH$_2$ (L^4)	Pd-CH$_3$	%
15	9.11, d		0.35, s	85
15'	8.51, d		1.05, s	11
16	9.15, d	2.17, s [3H], ortho	0.35, s	95
16'	8.53, d	2.27 s [3H], ortho	1.03, s	5
17	9.18, d	2.02, s [6H] ortho; 2.41, s [3H] para	0.39, s	98
17'	8.52, d	2.03, s [6H] ortho; 2.38, s [3H] para	1.02, s	2
18'	8.56,d	5.15, s [2H]	1.17, s	90
18	9.23	5.36, s [2H]	1.26, s	10
19	9.13, d	3.81, s [3H]	0.38, s	84
19'	8.51, d	5.30, s [3H]	1.03, s	16
20	9.13,d	2.34, s [3] para; 2.26 s [6] meta; 1.90, s [3H] ortho	0.36, s	89
20'	8.70, d	2.34, s [3] para; 2.26 s [6] meta; 1.90, s [3H] ortho	1.28, s	11

The complex [PdL^1(CH$_3$)Cl] is present in solution as a mixture of two diastereoisomers (85%; 11%) with that having the methyl in *trans* to the pyridine ring, **(15)**, present in greater quantity. This can be inferred either from the chemical shift of the proton H6' very

deshielded compared to the free ligand, due to the presence of chlorido on the metal or from the chemical shift of the methyl bound to the palladium at δ 0.35, very shielded by the action of the phenyl substituent in position 3 that, placing almost perpendicularly to the metal plane, shields the methyl protons. A third species (4%) could very probably be the dichloro species [PdL^1Cl_2], **(1)**, due to reaction of complex [$PdL^1(CH_3)Cl$] with the chlorinated solvent.[33] The same trend can be reported for the other complexes, [$PdL^2(CH_3)Cl$], [$PdL^3(CH_3)Cl$], [$PdL^5(CH_3)Cl$], [$PdL^6(CH_3)Cl$], with an increase in the percentage of the stereoisomer prevailing with the increase in the steric hindrance of the substituent.

The ^1H NMR spectrum of the complex with L^4 ligand, [$PdL^4(CH_3)Cl$], shows a behavior in contrast with what has already been observed. The prevailing stereoisomer, **(18')**, is the one with the methyl in *trans* to the imidazole nitrogen as it can be easily deduced by the chemical shift of the proton H6' (see **Table 5**). With the spacer, the shield effect operated by the aromatic ring of the substituent on the Pd-CH_3 is less effective than that observed in the cases seen above (δ 1.26 ppm vs δ 1.17 ppm).

It was possible to obtain crystals, suitable for X-Ray structure resolution of two adducts [$PdL^2(CH_3)Cl$] and [$PdL^3(CH_3)Cl$] via slow evaporation of the solvent from a CH_2Cl_2 solution.

[33] A. Abo-Amer, M. S. McCready, F. Zhang, and R. J. Puddephatt, *Can. J. Chem.*, **2012**, 90, 46–54 and references therein.

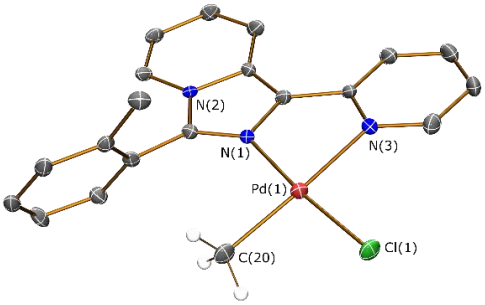


Figure 34. *major stereoisomer of [PdL^2(CH$_3$)Cl],* ***(16)***

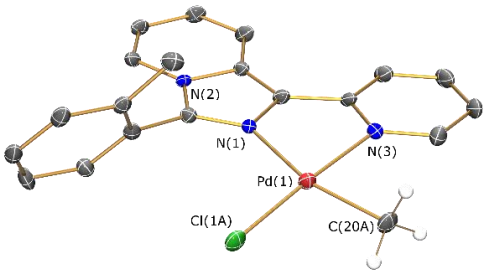


Figure 34'. *minor stereoisomer of [PdL^2(CH$_3$)Cl],* ***(16')***

The X-Ray structure resolution shows that the system is orthogonal with a square planar geometry around the Pd centre [Σ_{E-Au-E} = 360.0(4)°], featuring a pyridyl-imidazopyridine ligand which acts as a bidentate donor [Pd(1)−N(1) = 2.143(5) Å; Pd(1)−N2 = 2.067(5) Å] and the metal centre perfectly placed on the mean calculated between the four donor atoms. The methyl carbon C(20) is position in *trans* with respect to pyridyl nitrogen N(3) [Pd1−C(20A) = 2.114(5) Å], whilst chlorine atom Cl(1) is positioned in *trans* to the imidazolyl

nitrogen N(1) [Pd1−Cl(1) = 2.295(2) Å]. Additionally, a second isomer is present, in which the positions of the chloride and methyl ligands are swapped (Figure 34'); this is only a minor component, with occupancy of approximately 15%. Owing to the low occupancy of the second isomer and large statistical uncertainty of its metric parameters, a rigorous comparison cannot be drawn with the main component.

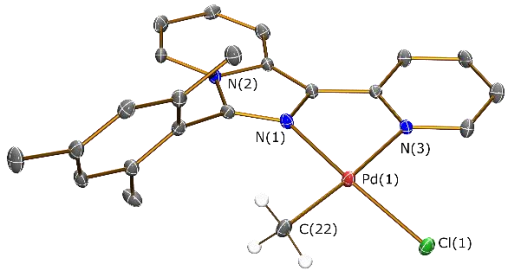


Figure 35. *major stereoisomer of [PdL^3(CH$_3$)Cl],* ***(17)***

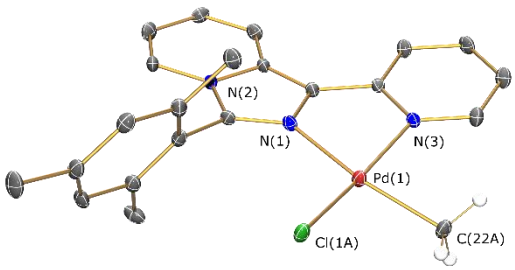


Figure 35'. *minor stereoisomer of [PdL^3(CH$_3$)Cl],****(17')***

Analogous considerations are possible for the adduct [PdL^3(CH$_3$)Cl]. Also in this case, it is evident that the system is orthogonal. The X-

Ray structure displays a square planar geometry around the Pd centre [Σ_{E-Pt-E} = 359.9(3)°], featuring a pyridyl-imidazopyridine ligand which acts as a bidentate donor [Pd(1)−N(1) = 2.055(3) Å; Pd(1)−N(3) = 2.148(4) Å] and the metal centre perfectly placed on the mean calculated between the four donor atoms. One chlorine atom is bound to the metal centre [Pd(1)–Cl(1) = 2.3064(13) Å], with an additional methyl ligand coordinated in *cis* [Pd(1)–C(22) = 2.049(5) Å; Cl(1)–Pd(1)–C(22A) = 89.22(14)°]. A second isomer can also be identified (see Figure 35'), with the chlorine and methyl ligands positioned swapped. Although the presence of the second isomer is unequivocal, this species accounts for less than 5% of the structure, therefore its metric parameters cannot be discussed due to the large error of the measurement.

In the case of Pt(II), the starting complex was *trans*-[Pt(DMSO)$_2$(CH$_3$)Cl][34] which in chloroform solution is actually a mixture of the *cis* and *trans* isomers in equilibrium, and of two more aqua-species, the *cis* and *trans* [Pt(DMSO)Cl(CH$_3$)(OH$_2$)] as extensively studied by the Romeo's research group.[35]

Trans-[Pt(DMSO)$_2$(CH$_3$)Cl] was reacted with the ligands, in particular L$^{1-6}$, at room temperature in molar ratio (1:1), as in the scheme reported in Figure 36:

---

[34] a) C. Eaborn, K. Kundu, A. J. Pidcock, *J. Chem. Soc., Dalton Trans.* **1981**, 933-938; b) R. Romeo, L. Monsu Scolaro, *Inorg. Synth.* **1998**, *32*, 153; c) R. Romeo, L. Monsu` Scolaro, N. Nastasi, B. E. Mann, G. Bruno and F. Nicolo, *Inorg. Chem.,* **1996**, *35,* 7691.

[35] R. Romeo; L. Monsù Scolaro; N. Nastasi; B. E. Mann; G. Bruno; F. Nicolò, *Trans* -Chloromethylbis(Dimethyl Sulfoxide)Platinum(II): X-Ray Structure, Mechanism of Isomerization, and Its Use as a Precursor to Organoamine Complexes of Variable Geometrical Configurations. *Inorganic Chemistry* **1996**, *35* (26), 7691–7698.

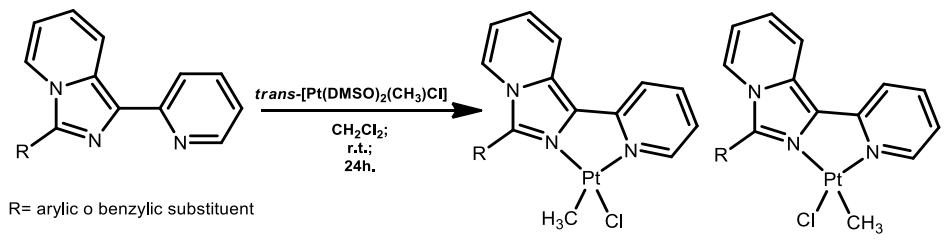


Figure 36. *General scheme for [PtL^n(CH$_3$)Cl]*

In this way, it was possible to obtain a six different new adducts: [PtL^n(CH$_3$)Cl],n=1-6, **(21-26)**, as yellow solids and in a good yields (except the complex with L^4).

In general for these complexes, it is possible to do the same considerations for the analogous complexes of Pd(II). Also in this case, the nitrogen ligands act as chelating donors and due to the non-equivalence of the two nitrogen halves and the planar square geometry, two stereoisomers are expected (see Figure 36) with a marked preference for the stereoisomer with the pyridine donor *trans* the methyl group.

All these adducts were extensively characterized in solution with ^{1}H NMR spectroscopy which, as in the case of the palladium complexes, excluded the formation of cyclometalate derivatives.

Unlike the palladium complexes, in this case it is possible to observe $J_{Pt\text{-}H}$ coupling constants with the nucleus NMR active ^{195}Pt, and this is the reason why some signals show satellites. For example, the methyl groups are clearly visible, as singlets with satellites generally around δ 1.20, ^{2}J(Pt-H)= 80 Hz and δ 0.57, ^{2}J(Pt-H) = 79 Hz, where the one more intense is also the one more shielded confirming the structure for the major stereosisomer. Another evidence arises from

the chemical shift of the H6 'proton of the coordinated pyridine ring: a comparison with the ^{1}H NMR spectrum of the free-ligand, shows for the major stereoisomer a shift towards lower field of this proton caused by the proximity to a chlorido atom.

These complexes could be an interesting starting compound for generate cyclometalated species.

The most significant ^{1}H NMR data are reported in **Table 6.**

Table 6. ^{1}H NMR selected data in $CDCl_3$ of $[PtL^n(CH_3)Cl]$

	H6'	CH_3 of the arylic or benzylic substituent in 3	Pt-CH_3	%
21	9.49		0.51, s, $^2J_{Pt-H}$=78.1 Hz	71
21'	8.96		1.09, s, $^2J_{Pt-H}$=80.4 Hz	20
22	9.50	2.15, s [3H] ortho	0.51, s, $^2J_{Pt-H}$=78.1 Hz	63
22'	8.96	2.23, s [3H] ortho;	1.07, s, $^2J_{Pt-H}$=78.8 Hz	21
23	9.43	2.02, s [6H] ortho; 1.93 s [3H] para	0.53, s, $^2J_{Pt-H}$=71.4 Hz	98
23'	8.71	2.20, s [6H] ortho; 2.41 s [3H] para	1.15, s, $^2J_{Pt-H}$=71.2 Hz	2
24	9.04	5.30, s [2H] CH2	1.24, s, $^2J_{Pt-H}$=80.1Hz	100
25	9.53	3.81, s [3H]	0.57, s, $^2J_{Pt-H}$=80.0 Hz	67
25'	9.00	2.62, s [3H]	1.20, s, $^2J_{Pt-H}$=78.0 Hz	33
26	9.46	2.35, s [3H] para; 2.28 s [6H] ortho; 1.90 [6] meta	0.40, s, $^2J_{Pt-H}$=80.0 Hz	100

X-Ray quality crystals of compound $[PtL^2(CH_3)Cl]$ were obtained by slow evaporation of the solvent from a CH_2Cl_2 solution.

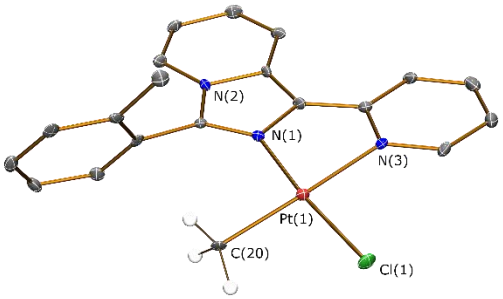


Figure 37. *major stereoisomer of [PtL^2(CH$_3$)Cl],* ***(22)***

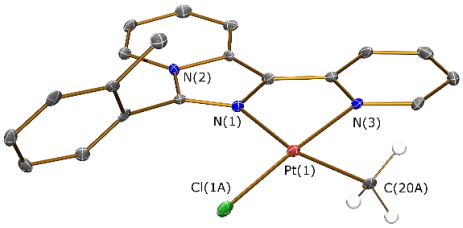


Figure 37'. *minor stereoisomer of [PtL^2(CH$_3$)Cl],* ***(22')***

The structure belonging to monoclinic system, displays the expected square planar geometry around the Pt centre [Σ_{E-Au-E} = 360.0(6)°], featuring a pyridyl-imidazopyridine ligand which acts as a bidentate donor [Pt1−N1 = 1.952(4) Å; Pt1−N2 = 2.110(4) Å] and the metal centre perfectly placed on the mean calculated between the four donor atoms. The methyl carbon C(20) is position in *trans* with respect to pyridyl nitrogen N(3) [Pt1−C20 = 2.068(11) Å], whilst

chlorine atom C(1) is positioned in *trans* to the imidazolyl nitrogen N(1) [Pt1−Cl1 = 2.217(8) Å]. Noteworthy, a second isomer is present, in which the positions of the chloride and methyl ligands are swapped (Figure 37'); this is only a minor component, with occupancy of approximately 15%. Owing to the low occupancy of the second isomer and large statistical uncertainty of its metric parameters, a rigorous comparison cannot be drawn with the main component.

The last complexes synthetized were the $[PtL^n(CH_3)_2]$, n=1-6, **(27-32).** Unlike the previous syntheses, these were conducted in acetone, by reaction of $[Pt(DMSO)_2(CH_3)_2]$[36] with the ligands, L^{1-6}, in molar ratio (1:1), at room temperature, see Figure 38:

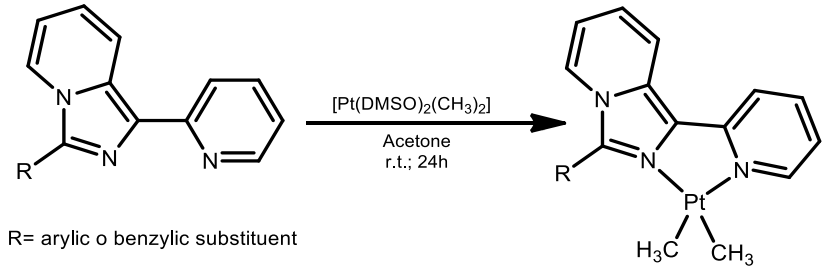


Figure 38. *General scheme for $[PtL^n(CH_3)_2]$*

The choice of this solvent was justified by the fact that the new dimethylplatinum(II) complexes can react with dichloromethane and chloroform to give products of oxidative addition of the solvent, generating the corresponding Pt(IV) complexes.

[36] a) C. Eaborn, K. Kundu, A. J. Pidcock, *J. Chem. Soc., Dalton Trans.* **1981**, 933-938; b) E.A. Baquero, A. Rodríguez-Zúñiga,; J.C. Flores, M. Temprado, E. de Jesús, *J. Organomet. Chem.* **2019**, *896*, 108–112.

In the case of compound [PtL^5(CH$_3$)$_2$], **(31)**, in CH$_2$Cl$_2$ three possible isomers were generated as observed following the reaction in an NMR tube for several days. It was possible to notice how all the possible isomers were produced almost immediately, but in the end, the more stable thermodynamically isomer prevailed over the others two.

The first isomer formed (kinetic product), is probably the product of the *cis*-oxidative addition, but the more stable thermodynamically is the product of *trans* addiction with the CH$_2$Cl group *trans* to the chlorine atom.[37]

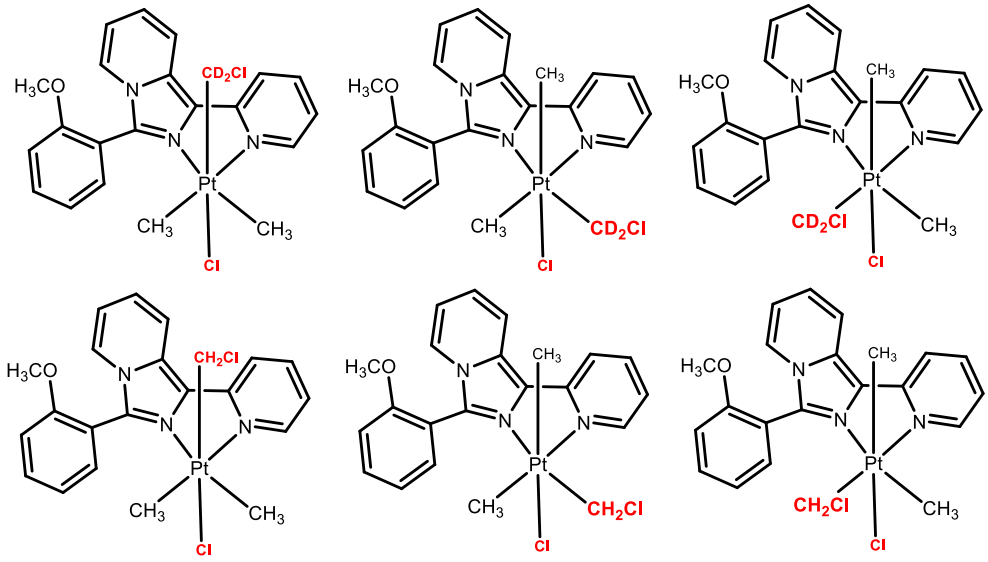


Figure 39. *Complexes of Pt(IV)*

To obtain clean adducts, [PtL^n(CH$_3$)$_2$], and avoid activation of the chlorinated solvent, the reactions were carried out in acetone and the NMR spectra always recorded in deuterated acetone.

[37] A. Abo-Amer; M.S. McCready; F. Zhang; R.J. Puddephatt, The Role of Solvent in Organometallic Chemistry Oxidative Addition with Dichloromethane or Chloroform. *Canadian Journal of Chemistry* **2012**, *90* (1), 46–54.

The adducts, **(27-32),** were obtained as yellow solids, in a good yields extensively characterized in solution and solid state.

Even in this case no cyclometalated species were obtained, during the synthesis as confirmed from the integral in the ^{1}H NMR spectra

In the 1H NMR spectra two peaks are clearly visible for the methyl groups, generally around δ 0.77, $^{2}J(Pt\text{-}H)$ = 92 Hz, attributable to methyl in *trans* to the imydazole ring, and δ 0.25, $^{2}J(Pt\text{-}H)$ = 88 Hz, attributable to methyl in *trans* to the pyridine ring.(see **Table 7)**

Table 7. ^{1}H NMR in acetone-d^{6} of $[PtL^{n}(CH_3)_2]$

	H6'	CH_3 of the arylic or benzylic substituent in 3	Pt-CH_3
27	9.04, d $^{3}J_{Pt\text{-}H}$=28.1 Hz		0.76, s, $^{3}J_{Pt\text{-}H}$=90.0 Hz 0.26, s, $^{3}J_{Pt\text{-}H}$=89.4 Hz
28	9.03, d $^{3}J_{Pt\text{-}H}$=16.0 Hz	2.21, s [3H] ortho	0.75, s, $^{3}J_{Pt\text{-}H}$=88.5 Hz 0.24, s, $^{3}J_{Pt\text{-}H}$=90.6 Hz
29	9.03, d $^{3}J_{Pt\text{-}H}$=16.0Hz	2.38, s [3H] para; 2.01, s [6H] ortho	0.24, s, $^{3}J_{Pt\text{-}H}$=88.5 Hz 0.28, s, $^{3}J_{Pt\text{-}H}$=90.6 Hz
30	9.04	4.90, s [2H]	1.10, s, $^{3}J_{Pt\text{-}H}$=87.0 Hz 0.91, s, $^{3}J_{Pt\text{-}H}$=87.9 Hz
31	9.03, d $^{3}J_{Pt\text{-}H}$=16.0Hz	3.85, s [3H]	0.76, s, $^{3}J_{Pt\text{-}H}$=88.0 Hz 0.30, s, $^{3}J_{Pt\text{-}H}$=88.0 Hz
32	9.04, d $^{3}J_{Pt\text{-}H}$=16.0Hz	2.35, s [3H] para; 2.29, s [6H] meta; 1.91, s [6H] ortho	0.75, s, $^{3}J_{Pt\text{-}H}$=88.0 Hz 0.24, s, $^{3}J_{Pt\text{-}H}$=92.0 Hz

In an attempt to promote the cyclometalation reaction, by the reductive elimination of ethane and oxidative addition of a C-H bond of the coordinated ligand, an acetone solution of the complex $[PtL^{5}(CH_3)_2]$, **(30)**, was heated, but, no changes were observed.

Since with the previously discussed synthesis no cyclometalated species were obtained, we tried to force a cyclometalation reaction with the creation of a coordinative unsaturation, in a poorly

coordinated solvent, by abstracting either chlorine or methyl with a suitable reagent from the platinum centre.

Reactivity

To remove the chlorine atom from the complexes [PtL^2(CH$_3$)Cl], **(22)** and [PtL^5(CH$_3$)Cl], **(25)**, it was used a silver salt with weakly coordinating anion such as [PF$_6$]. It is well-known the ability of AgPF$_6$ to abstract halide ligands from metal complexes, that leads to the formation of a solvato species and the corresponding silver halide; [PF$_6$] behaves as counter ion for the cationic metal complex.

The hope was that conducting these reactions in a weakly coordinating solvent, the imidazo-pyridine ligand has to fulfil that vacancy via the activation of C-H bond of the substituent in 3 position.

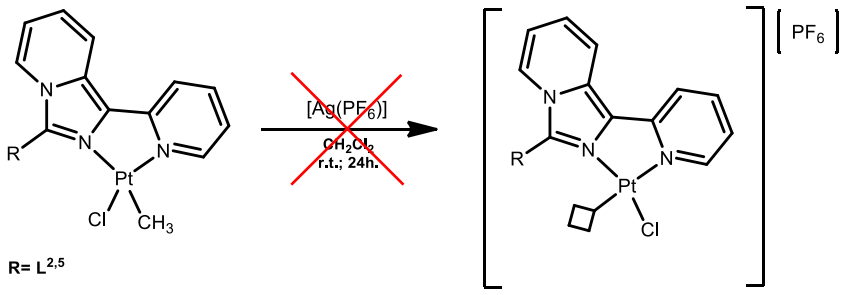


Figure 40. *General scheme of reaction with AgPF$_6$*

No cyclometalated species were obtained despite several attempts made: only mixtures of complexes, hard to resolve, were obtained.

Another attempt was that to try to abstract the methyl group from complex [PtL^5(CH$_3$)$_2$], **(31)**, using a carbocation, such as [Ph$_3$C] in

[Ph_3C][BF_4]. Unfortunately, a mixture of unidentified derivatives was obtained.[38]

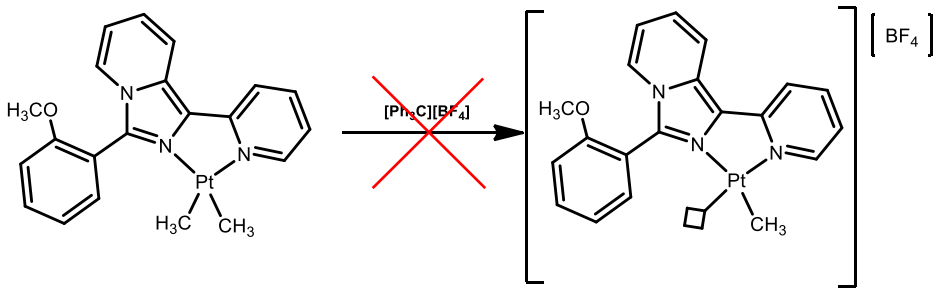


Figure 41. *Scheme of reaction with [Ph_3C][BF_4]*

To try to remove the chlorine atom from complexes [$PdL^n(CH_3)Cl$] and to force cyclometallation reaction it was thought to use strong reaction conditions and a selective salt such as [$(Et_3Si)_2H$][$B(C_6F_5)_4$]. In particular, this attempt was done in a NMR tube with [$PdL^1(CH_3)Cl$] and [$PdL^3(CH_3)Cl$] complexes in deutered benzene, see the scheme reported in Figure 42:

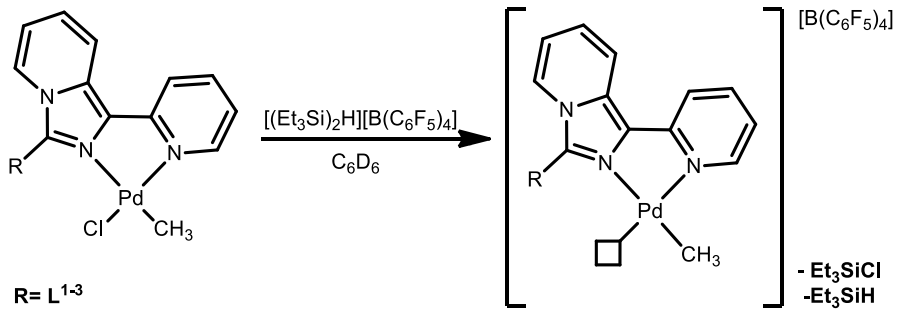


Figure 42. *General scheme of reaction with [$(Et_3Si)_2H$][$B(C_6F_5)_4$] .*

[38] Synthesis, characterization and catalytic activity of Pd(II) and Pt(II) complex with 3-(2-methoxyphenil)-1-(pyridin-2-yl)imidazo[1,5-a]pyridine as ligand. Thesis of Dr. Riccardo Polese. Academic year **2017-2018**.
.

No activation of C-H bond was observed but it was possible to isolate a cationic complexes of palladium(II) in which two molecules of ligand are coordinated with the metal ion as evidenced by the preliminary X-Ray solution of the two structures. In fact, it was possible to obtain a preliminary crystal structure for these new compounds $[Pt(L^1)_2CH_3][B(C_6F_5)_4]$ and $[Pt(L^1)_2Cl][B(C_6F_5)_4]$.

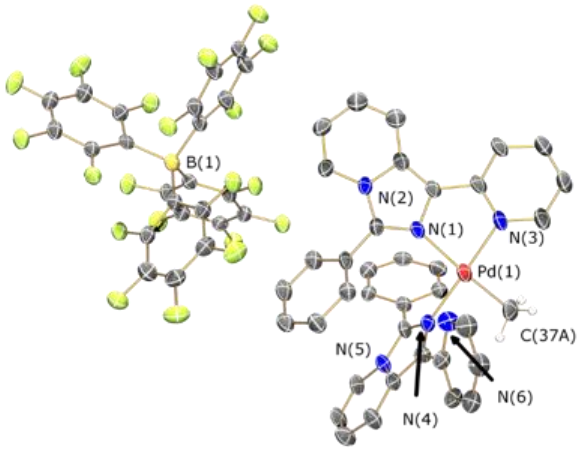


Figure 43. *Preliminary X-Ray structure for $[Pd(L^1)_2CH_3][B(C_6F_5)_4]$.*

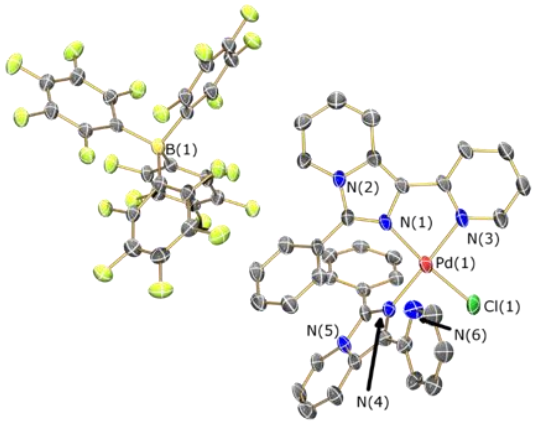


Figure 43'. *Preliminary X-Ray structure for $[Pd(L^1)_2Cl][B(C_6F_5)_4]$.*

To complete the study for the reactivity on the organometallics compounds of palladium(II), it was used another strong reagent to try to remove the chlorine atom from complexes [$PdL^n(CH_3)Cl$] and force cyclometallation reaction.

In this way, complexes [$PdL^5(CH_3)Cl$] and [$PdL^6(CH_3)Cl$] were reacted with $B(C_6F_5)_3$. This prove was done in NMR tube using deuterated benzene, that was left to sonicate for 1hour to dissolve completely reagents, such as in the scheme reported in Figure 44:

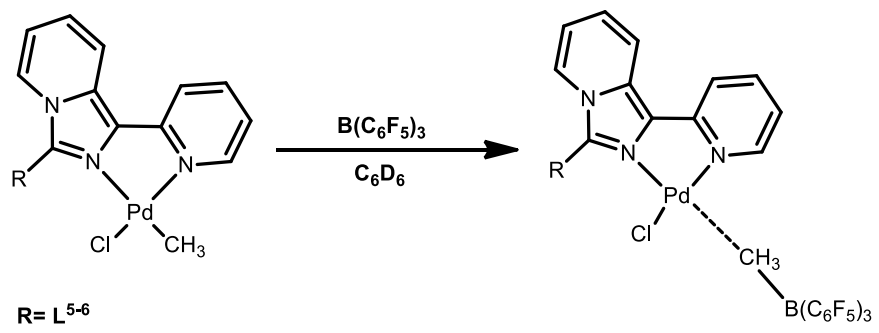


Figure 44. *General scheme of reaction with $B(C_6F_5)_3$.*

For these reactions there are no data to propose because it wasn't possible to characterize the possible products due to the pandemic of Covid 19.

Theoretical analysis

Part of the thesis have been dedicated to theoretical analysis to comprehend the reasons why no cyclometalated was observed.

Taking advantage of the X-Ray structure of the [Pt(**L^n**)Cl_2] series and to understand the nature of this phenomenon we performed a theoretical prediction of the Gibbs energy associated with the metalation of the four Pt adducts ([(Pt(**L^n**)Cl_2]$_{aq}$ → [(Pt(**L^n**-H)Cl]$_{aq}$ + HCl_{aq}) comparing the values with the thermodynamics of the complex formed by the similar ligand 6-(1-phenylbenzyl)-2,2'-bipyridine (bipy)[39] In **Table 8** is summarized a comparison of X-Ray and DFT (M06/6-311g(d,p)/SDD+f[ECP]) selected parameters, the little deviations demonstrate that the selected DFT level of theory guarantees accurate performances in the structural prediction of this kind of complexes. Furthermore the method appear robust and was successfully applied in literature for high accuracy energy prediction of transition metal complexes.[40]

Table 8. Selected bond lengths, angles and dihedral for the complexes [Pt(L^1)Cl_2], [Pt(L^2)Cl_2] and [Pt(L^4)Cl_2].

	[Pt(L^1)Cl_2]		**[Pt(L^2)Cl_2]**		**[Pt(L^4)Cl_2]**	
Parameter [a]	Exptl.[b]	Calcd.	Exptl.[b]	Calcd.	Exptl.[b]	Calcd.
Pt(II)-N(1)	2.023	2.070	2.026	2.056	2.029	2.069
Pt (II)-N(2)	2.020	2.072	2.110	2.074	2.028	2.068
Pt (II)-Cl(1)	2.290	2.317	2.285	2.319	2.288	2.319
Pt (II)-Cl(2)	2.287	2.320	2.217	2.319	2.296	2.327
N(1)-Pt(II)-N(2)	80.60	79.19	79.48	79.29	80.44	79.17
N(1)-Pt(II)-Cl(2)	97.47	98.03	101.87	97.17	98.00	98.89
N(2)-Pt(II)-Cl(1)	94.19	93.84	95.54	94.09	94.24	93.83
Cl(1)-Pt(II)-Cl(2)	87.69	88.88	84.05	89.45	87.31	88.11
N(1)–X(α)–X(β)–X(γ)	66.99	58.45	63.68	83.04	96.126	107.53
X(α)–X(β)–X(γ)	--	--	--	--	113.57	112.94
X(α)–X(β)–X(γ)–X(δ)	--	--	--	--	132.60	122.08

Distances in Å and angles in degrees. [b] structural data from this work.

[39]S. Stoccoro; L. Maidich, T. Ruiu, M. A. Cinellu, G.J. Clarkson, A. Zucca; *Dalton Transactions,* **2015,***44* (41), 18001-18011.

[40] S. Shil; D. Bhattacharya; S. Sarkar;A. Misra, Performance of the Widely Used Minnesota Density Functionals for the Prediction of Heat of Formations, Ionization Potentials of Some Benchmarked First Row Transition Metal Complexes. *The Journal of Physical Chemistry A* **2013,** *117* (23), 4945-4955.

The results summarized in **Table 9** clearly show that the hypothetical reaction is associated, for all the ligands, with ΔG_{aq} values considerably higher respect the homologous reaction of [(Pt(**bipy**)Cl_2].

Particularly $\Delta\Delta G_{aq}$ values ranging from 7.10 to 17.31 kcal·mol^{-1} highlight thermodynamics inertia of the metallatation for the [(Pt(**L^n**)Cl_2] series.

Table 9. Theoretical relative ΔG_{aq} calculations for the cyclometallation reaction of the synthetized adducts: [(Pt(**L^n**)Cl_2]$_{aq}$ → [(Pt(**L^n**-H)Cl]$_{aq}$ + HCl_{aq} .

Complex	$\Delta\Delta G_{gas}$[a]	$\Delta\Delta G_{aq}$[a],[b]
[(Pt(**L^1**-H)Cl]	21.15	17.31
[(Pt(**L^2**-H)Cl]	16.84	13.41
[(Pt(**L^3**-H)Cl]	14.08	11.12
[(Pt(**L^4**-H)Cl]	13.97	7.10

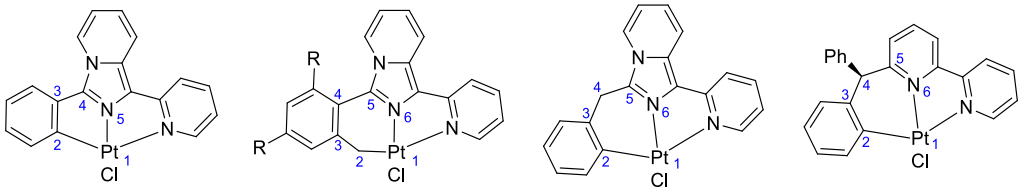
[a] Values in kcal·mol^{-1} referred to the value obtained for the bypi complex taken as a zero[39]. [b] Gibbs free energy computed with the following formulae: $\Delta G_{aq} = \Delta G_{gas} + \Delta G_{sol}([(Pt(\mathbf{L^n}\text{-H})Cl]) - \Delta G_{sol}([(Pt(\mathbf{L^n})Cl_2]) + \Delta G_{sol}(HCl) + RTlnV$.

An accurate structural analysis of the hypothetical cyclometallated complexes unveils the reasons behind the high $\Delta\Delta G_{aq}$ associated with the cyclometallation. The 5-member and 6-member rings formed by the ligands **L$^{1-4}$** presents a high angle steric strain in comparison with the characterized bipyridine complex.

As it can be seen in **Table 10**, the mean of the deviation from the ideal angles ranges from 4.35º to 8.51º for the ligands synthetized in this work versus 2.94º computed for the stable complex [Pt(**bipy**-H)Cl]. In addition, the distances Pt(II)-N play a critical role, in fact the

cyclometallation forces these bonds to became smaller respect to the ideal values increasing the potential energy of the compounds.

Table 10. Selected bond lengths and bond angles on the formed ring in cyclometallation reaction. In parenthesis is reported the absolute deviation from the ideal value in angstrom and degrees respectively.



[Pt(L^1-H)Cl] R=H, [Pt(L^2-H)Cl] R=CH_3, [Pt(L^3-H)Cl] [Pt(L^4-H)Cl] [Pt(bipy-H)Cl]

	[Pt(L^1-H)Cl] [a]	**[Pt(L^2-H)Cl]** [a]	**[Pt(L^3-H)Cl]** [a]	**[Pt(L^4-H)Cl]** [a]	**[Pt(bipy-H)Cl]** [a]
Angles [b],[c]	5-member ring	6-member ring	6-member ring	6-member ring	6-member ring
1-2-3	112.05 (7.95)	116.88 (7.38)	116.44 (6.94)	123.61 (3.61)	120.27 (0.27)
2-3-4	114.18 (5.82)	125.44 (5.44)	124.73 (4.73)	127.76 (7.76)	122.70 (2.70)
3-4-5	113.93 (6.07)	120.29 (0.29)	118.29 (1.71)	118.64 (9.14)	115.51 (6.01)
4-5-1(6)	126.28 (6.28)	123.28 (3.28)	123.22 (3.22)	126.37 (6.37)	119.34 (0.66)
5-1(6)-2(1)	73.56 (16.44)	130.11 (10.11)	128.79 (8.79)	131.17 (11.17)	124.30 (4.30)
6-1-2	--	90.36 (0.36)	89.28 (0.72)	92.09 (2.09)	93.67 (3.67)
Mean dev.	*8.51*	*4.48*	*4.35*	*6.69*	*2.94*
Distances [b],[c]					
Pt(II)-N(1)	1.933 (0.090)	1.978 (0.045)	1.980 (0.043)	1.982 (0.041)	2.041 (0.018)
Pt (II)-N(3)	2.313 (0.293)	2.198 (0.178)	2.211 (0.191)	2.196 (0.176)	2.154 (0.134)
Mean dev.	*0.192*	*0.112*	*0.117*	*0.109*	*0.076*

[a] DFT computed structural data from this work. [b] Angles in degrees. [c] Distances

Synthesis and characterization of Au(III) complexes

The study of the interaction of these ligands with ion of transition metals was extended to Au(III). Considering our experience in this

field,[41] $Na[AuCl_4]$ was reacted with the ligands, L^n, n=1-4,6, and an excess of KPF_6 at room temperature in a (1:1) molar ratio, as in the scheme reported in Figure 45:

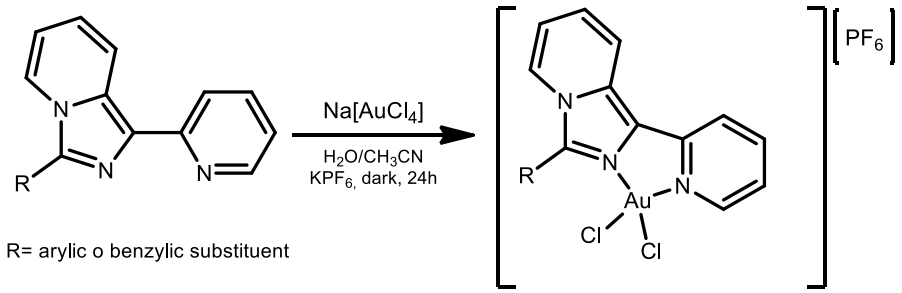


Figure 45. *General scheme for $[AuL^nCl_2][PF_6]$*

In this way, it was possible to obtain five different new compounds, $[AuL^nCl_2][PF_6]$, **(33-37)**, as dark green solids and in a good yields.

Also, in this case, the ligands act as a classic chelating N^N ligand, and the spectroscopic investigation confirms the presence in solution of a cationic adducts, excluding the formation of cyclometalated species.

By the ^1H NMR spectrum it is possible to observe that the number of protons, compared to the value obtained from the integral in the ^1H NMR spectrum of the free ligand, is unchanged, confirming the formation of cationic adducts N^N. It is also evident a shift towards lower field of the proton H6' of the pyridine ring caused by the proximity to a chlorine atom, and a shift towards higher field of the proton H8, generated by the coordination effect of the metal centre. Other protons do not show any significant changes.

[41] M. A. Cinellu, G. Minghetti, M. V. Pinna, S. Stoccoro, A. Zucca and M. Manassero*, J. Chem. Soc., Dalton Trans.*, **2000,** 1261-1265.

In addition, the existence of a cationic adduct is confirmed by the presence of anion [PF_6]. In fact with ^{31}P NMR and infrared spectrum (characteristic band at 840 cm^{-1}) is possible to see the signals attributable at this species. Finally, the elementary analyses are in perfect agreement with the proposed formulation.

In the **Table 11** were reported the signals for all compounds, [AuL^nCl_2][PF_6], n= 1-4,6, **(33-37)**.

Table 11. ^1H NMR in acetone-d^6 of [AuL^nCl_2][PF_6]

	H6'	H5'	H3'	H8	H4'	H_{ar}	H5	H7	H6	Other
33	9.42	7.83	8.79	7.94	8.65	7.94-7.89	8.29	7.69	7.43	
34	9.29	7.79	8.50	7.93	8.50	7.57*7.38	8.65	7.70	7.30	2.12, CH_3ortho
35	9.44	7.93	8.64	8.00	8.64	7.18	8.79	7.84	7.47	2.43, CH_3para 2.10, CH_3ortho
36	9.49	7.78	8.74	8.61	7.92	7.41	8.61	7.41	7.41	5.58, CH_2
37	9.03	7.59	8.48	8.51	8.41		7.92	7.75	7.32	2.37,CH_3para; 2.29,CH_3meta; 1.97,CH_3ortho

X-Ray quality crystals of compound [AuL^3Cl_2][PF_6], **(35)**, were obtained by slow evaporation of the solvent from a CH_3CN solution.

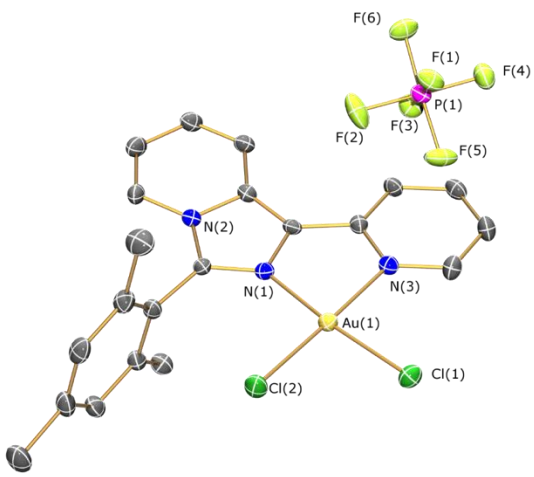


Figure 46. *X-Ray structure for [AuL^{3}Cl$_2$][PF$_6$]*

The system is monoclinic and the cation displays a square planar geometry around the Au centre [Σ_{E-Au-E} = 360.0(3)°], featuring a pyridyl-imidazopyridine ligand which acts as a bidentate donor [Au1−N1 = 2.028(3) Å; Au1−N3 = 2.050(3) Å] and the metal centre perfectly placed on the mean calculated between the four donor atoms. The chlorine Cl(2) is position in *trans* with respect to pyridyl nitrogen N(3) [Au1−Cl(2) = 2.2563(10) Å], whilst chlorine atom Cl(1) is positioned in *trans* to the imidazolyl nitrogen N(1) [Au1−Cl(1) = 2.2579(10) Å].

The same reactions were repeated, in more severe conditions under reflux, to try to force the cyclometallated reactions. So same ligands were reacted in molar ratio (1:1) with Na[AuCl$_4$] and an excess of KPF$_6$, as in the scheme reported in Figure 47:

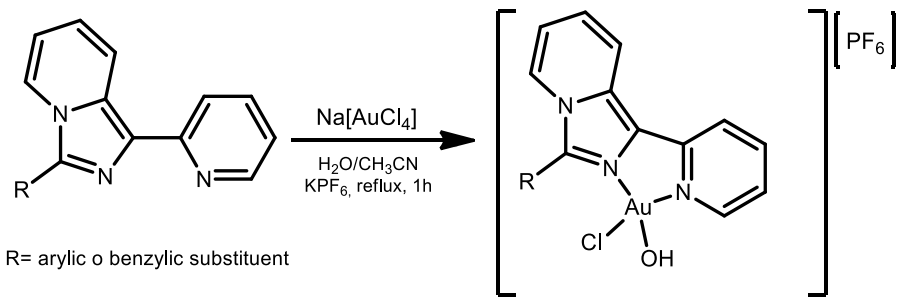


Figure 47. *General scheme for [AuL^n(OH)Cl][PF$_6$]*

No cyclometalate species was obtained, but it was possible to isolate three different compounds, [AuL^n(OH)Cl][PF$_6$], n=1-3**, (38-40)**, in a

single stereoisomeric form, obtained as yellow solids, in a good yields.

Also, in this case, in the complexes just obtained, L^{1-3} acts as a classic chelating N^N ligand, and the spectroscopic investigation confirms the presence in solution of a cationic adducts.

These compounds were characterized in detail in solution by ^{1}H, ^{31}P NMR and $^{13}C\{^{1}H\}$ NMR spectroscopy, mono and two-dimensional, and all the signals were assigned (see **Table 12**).

In the ^{1}H NMR spectra is evident a little shift towards lower field of the proton H6' of the pyridine ring caused by the proximity of an hydroxyl group, and a shift towards higher field of the proton H8, generated by the coordination effect of the metal centre.

The other protons do not show any significant changes, while the signal of the hydroxyl proton is present as a broad singlet, probably for hydrogen interaction, around δ 4.00 ppm.

In addition, the existence of a cationic adduct is confirmed by the presence of anion $[PF_6]$. In fact with ^{31}P NMR and infrared spectra (characteristic band at 840 cm^{-1}) is possible to see the signals attributable at this species. Finally, the elementary analyses are in perfect agreement with the proposed formulation.

In the **Table 12** were reported ^{1}H NMR data for all adducts, **(38-40)**.

Table 12. ^{1}H NMR in acetone-d^6 of $[AuL^n(OH)Cl][PF_6]$

	H6'	H5'	H3'	H8	H4'	H_{ar}	H5	H7	H6	Other
38	8.62	7.54	8.50	8.06	8.40	7.88-7.61	8.23	7.45	7.02	4.45, OH
39	8.48	7.46	8.17	7.84	8.33	7.41-7.38	8.01	7.31	6.91	3.93, OH; 2.16, CH_3ortho
40	8.41	7.45	8.16	7.53	8.33	6.99	8.15	7.40	6.90	4.69, OH; 2.31, CH_3para 1.87, CH_3ortho

The same reaction, just described, was done with the benzylic ligand L^4, with the idea to try to force the C*(sp³)*-H activation and to obtain a cycle with six terms, less tensioned. A mixture of compounds was obtained including the expected cyclometalated species.

In fact, in the ^1H NMR spectrum (see in Figure 48) is possible to observe the characteristic signal for the spacer CH_2, where, with the coordination, its protons became diasterotopic showing the AB spin system.

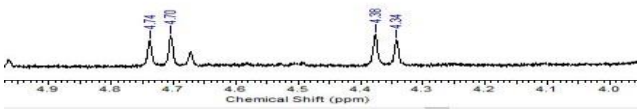


Figure 48. *Diasterotopic protons with AB spin system]*

Having fully characterized the compounds obtained, with the methods described above, it was possible to fine-tune the last two reactions with Au(III).

In the first the cationic adducts, $[AuL^nCl_2][PF_6]$, n=1-3**, (33-35)**, were reacted with Ag_2O in molar ratio (1:1) in acetone to give a corresponding bis(hydroxo) adducts $[AuL^n(OH)_2][PF_6]$, as in the scheme reported in Figure 49:

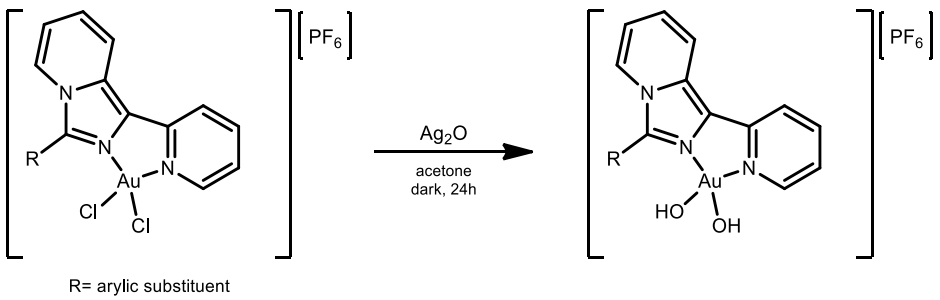


Figure 49. *General scheme for [AuL^n(OH)$_2$][PF$_6$]*

Three news cationic adducts, [AuL^n(OH)$_2$][PF$_6$], (**41-43**), were isolated as red solids in good yields.

These products were characterized in detail in solution by ^{1}H, ^{31}P NMR and ^{13}C{^{1}H} NMR spectroscopy, mono and two-dimensional, and the signals were assigned (see **Table 13**):

The NMR data are in full agreement with the proposed formulation.

In the ^{1}H NMR spectra it is also evident a little shift towards lower field of the proton H6' of the pyridine ring caused by the proximity to a hydroxyl group, and a shift towards higher field of the proton H8, generated by the coordination effect of the metal centre. Other protons do not show any significant changes.

For the hydroxyl protons two distinct singlets are evident. They are obviously different because one is in *trans* to the pyridine ring and the other is in *trans* to the imidazo-pyridine group.

In addition, the existence of a cationic adduct is confirmed by the presence of anion [PF6]. In fact with ^{31}P NMR and infrared spectrum (characteristic band at 840 cm^{-1}) is possible to see the signals attributable at this species

Finally, the elementary analyses are in perfect agreement with the proposed formulation.

In the **Table 13** were reported ^{1}H NMR data for all adducts, **(41-43)**.

Table 13. ^{1}H NMR in acetone-d^6 of $[AuL^n(OH)_2][PF_6]$

	H6'	CH_3 of the arylic substituent in 3 (L^2 and L^3)	Au-OH
41	8.93		2.97, s [OH]; 1.03, s [OH]
42	8.95	2.23, s [3H]	2.99, s [OH]; 1.01, s [OH]
43	8.94	2.44, s [3H], para; 2.07, s [6H], ortho	3.04, s [OH]; 1.24, s [OH]

For the second reaction was selected only the complex $[AuL^3(OH)_2][PF_6]$, **(43)**, with the idea to obtain the corresponding oxo-bridge adduct, similar to those previously reported with a series of 6-alkil-2,2'bipyridines.[42]

Complex $[AuL^3(OH)_2][PF_6]$**, (43),** was quantitatively converted into corresponding oxo-complex, $[\{Au(L^3)(\mu\text{-}O)\}_2][PF_6]_2$, **(44),** by refluxing with anhydrous THF[43], as reported in the scheme in Figure 50:

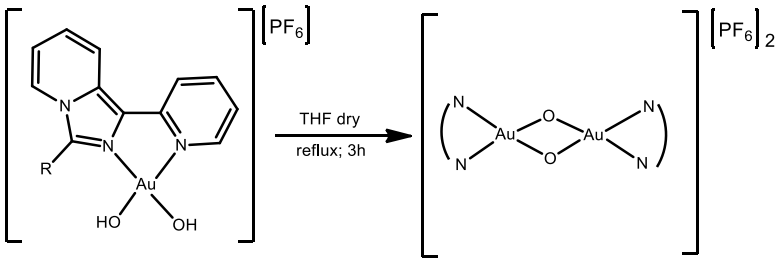


Figure 50. *General scheme for $[\{AuL^3(\mu\text{-}O)\}_2][PF_6]_2$*

[42]M. A. Cinellu, G. Minghetti, M. V. Pinna, S. Stoccoro, A. Zucca, M. Manassero, and M. Sansoni; *J. Chem. Soc*., *Dalton Trans*., **1998**, 1735–1741.

[43] M. A. Cinellu, G. Minghetti, M. V. Pinna, S. Stoccoro, A. Zucca and M. Manassero*, J. Chem. Soc., Dalton Trans.*, **2000,** 1261-1265.

Compound $[\{Au(L^3)(\mu\text{-}O)\}_2][PF_6]_2$**, (44),** was obtained as a red solid in a good yield.

The new species was fully characterized in solution with ^1H NMR.

Surprisingly, only one set of signals is observed suggesting that of the two possible geometrical isomers, *cis* and *trans*, one only is present in solution at room temperature.

Moreover it is possible to observe that the signals attributable a two different hydroxyl group in the hydroxo complexes are disappeared and the number of protons, compared to value obtained from the integral in the ^1H NMR spectrum of the corresponding bis(hydroxo) complex $[AuL^3(OH)_2][PF_6]$, **(43)**, is changed. confirming the formation of a dimeric species.

It is also evident that in general protons do not show any significant changes in their positions in the spectrum. At the end all data including elementary analysis data are in agreement with the proposed formulation.

In Figure 51, it is reported a comparison between the ^1H NMR spectra of complexes **(43)** and **(44)** just discussed:

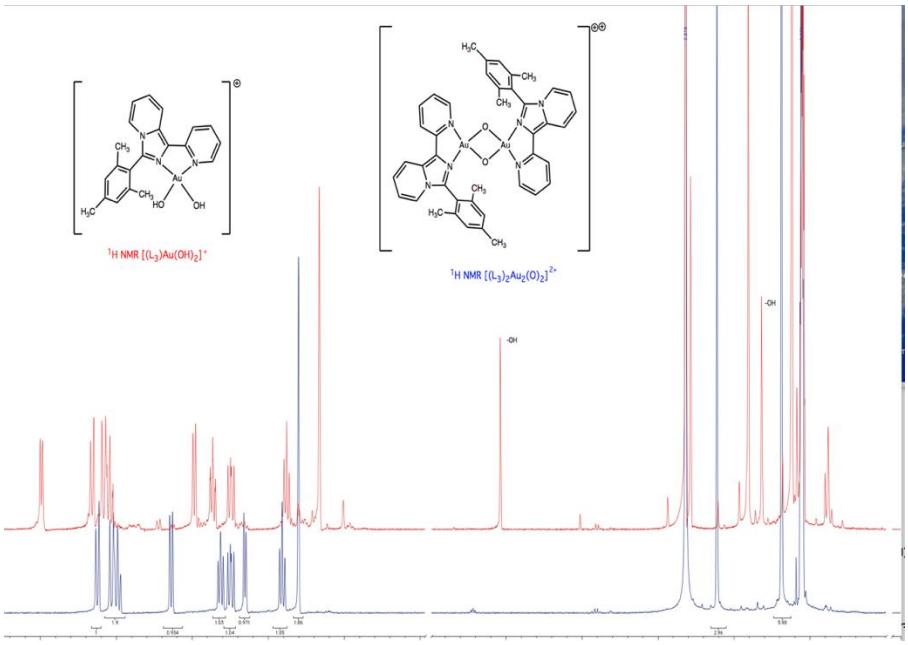


Figure 51. *Comparison between **(43)**, red,and **(44)**, blue, species.*

Synthesis and characterization of Y(III), La(III) and Sm(II) complexes

During this PhD thesis it was also my objective to study the behaviour of 3-substituted 1-(pyridin-2-yl)imidazo[1,5-a]pyridines, in particular L[1,5,6] ligands**,** versus terrae rare ions, Y(III), La(III) and Sm(II).

This part of my PhD project was conducted at the University of Manchester first under the supervision of Dr. D. Mills, and in the University of Leicester, then under the supervision of Dr. F. Ortu.

In Manchester, initially were synthetized starting materials, $Ln(OTf)_3$, using a general procedure[44] reporting in Figure 52:

[44] Shû Kobayashi and Iwao Hachiya., *Eur. J. Inorg. Chem.* **1994**, 59, 3590–3596.

$$Ln_2O_3 \xrightarrow[100°C;\ 2h]{HOTf/H_2O} 2Ln(OTf)_3 + 3H_2O$$

Figure 52. *General procedure for Ln_2O_3*

In this way it was possible to obtain $La(OTf)_3$, and $Y(OTf)_3$, as white powders in good yields (85% and 56% respectively).

These compounds were reacted in a (1:1) molar ratio with ligand L^1, in acetonitrile at room temperature in a Schlenk's tube as in the scheme reported in Figure 53.

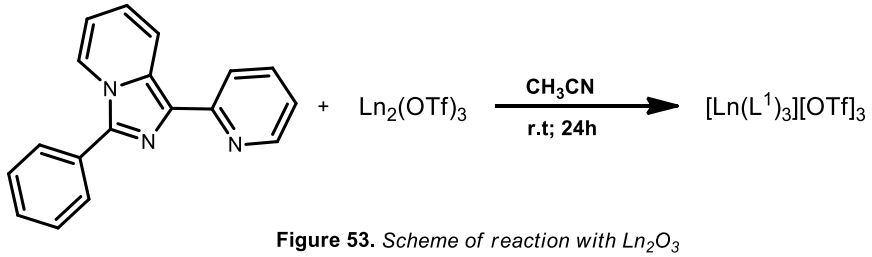


Figure 53. *Scheme of reaction with Ln_2O_3*

These complexes are quite difficult to characterize with normal spectroscopic techniques, such as NMR, but luckily it was possible to obtain a preliminary X-Ray structure for **$[Y(L^1)_3(OTf)_3]$.**

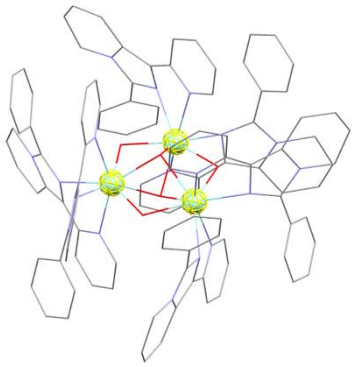
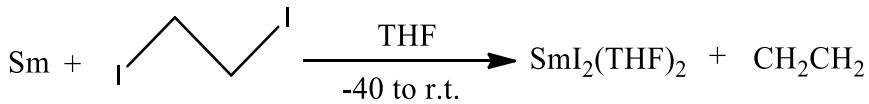


Figure 54. *Preliminary X-Ray structure for* $[Y(L^1)_3(OTf)_3]$

Later, in Leicester, the study of the behaviour of the 3-substituted 1-(pyridin-2-yl)imidazo[1,5-a]pyridines versus terrae rare ions was continued with the synthesis of a new starting material, in particular $SmI_2(THF)_2$.

This compound was synthetized with a facile procedure, see experimental section, by reacting the Sm with the diiodoethane in THF:



Then $SmI_2(THF)_2$ was reacted with L^6, like in the scheme reported in Figure 55:

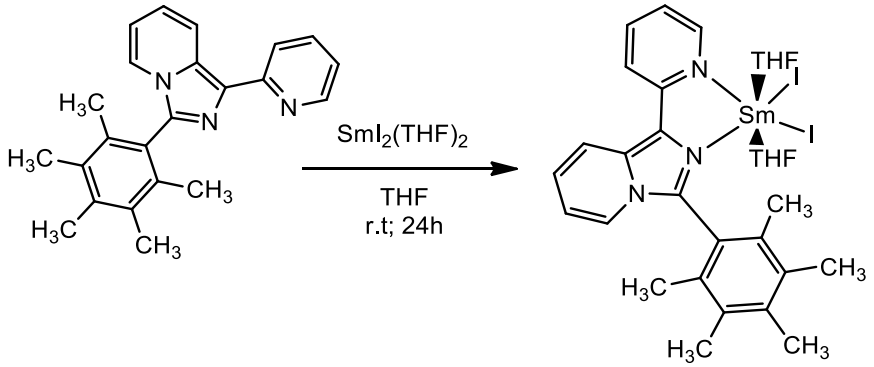


Figure 55. *General scheme for complex of Sm(II)*

The obtained complex is quite difficult to characterize with normal spectroscopic techniques, such as NMR. For this reason, it was necessary to synthesize the same complexes of Sr(II) and Ca(II). In fact, these nucleus are diamagnetic and it's possible to study the corresponding complexes with ^{1}H NMR spectroscopy.

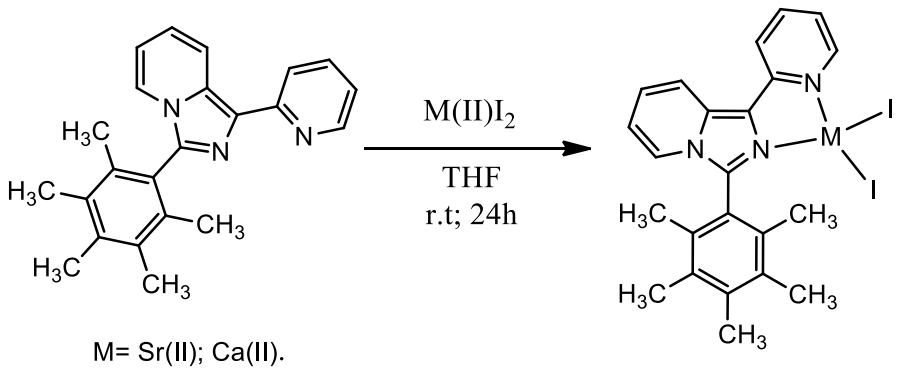


Figure 56. *General scheme for complexes of M(II)*

Unfortunately, for these reactions there are no data to propose because it wasn't possible to characterize the products due to the pandemic Covid 19.

Cyclometalated rollover complexes of Pt(II)

The behaviour of cyclometalated rollover complexes reflects a delicate balance of different contribution from the metal, the ancillary ligands, and the rollover cyclometalated bipyridine. In particular, the nature of the substituent in 6-substituted-2,2'-bipyridines affects not only their behaviour towards C(3)-H bond activation, but also the reactivity of the resulting rollover complexes. All these considerations are also valid for classic cyclometalated complexes; in addition, "rollover" deprotonated ligands have the peculiarity of being no more a spectator in the reactivity of the complex but may act as a "*ligand with multiple personalities*" due to the presence of the uncoordinated nitrogen.

Part of the thesis have been dedicated to the completion of a research regarding a series of Pt(II) cyclometalated rollover complexes with two substituted bipyridines: *6-ethyl-2,2'-bipyridine* (bpy6Et) and *6-methoxy-2,2'-bipyridine* (bpy6OMe) in comparison with previously studied 2,20-bipyridine complexes.

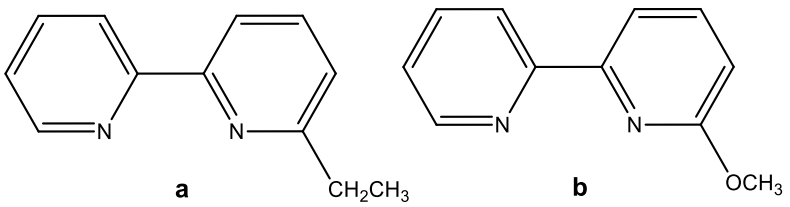


Figure 57. *6-ethyl-2,2'-bipyridine* ***(a)*** *and 6-methoxy-2,2'-bipyridine* ***(b)****.*

The two ligands have similar steric hindrance but different electronic properties. In particular, the new complexes behave differently

towards protonation reactions, differences given by substituents and ancillary ligands, added to the presence of several nucleophilic centers.

As a result, reaction of complex [Pt(bpy6OMe-H)(PPh_3)CH_3)] with [H_3O^+18-crown-6][BF4] results in a retro-rollover reaction whose final product is the cationic adduct [Pt(bpy6OMe)(PPh3)Me)]$^+$. Surprisingly, only the isomer with the *cis*-PPh_3-OMe geometry is formed; in spite of an expected instability due to steric hindrance, Density-Functional theory (DFT) calculations showed that this isomer is the most stable. This result shows that the cone angle is far from being a real “solid cone” and should lead to a different interpretation of well-known concepts concerning steric bulk of ligands, such as cone angle. Proton affinity values of ligands, neutral complexes and their protonated counterparts were analyzed by means of DFT calculations, allowing a comparison of their properties.

The synthesis of the rollover complexes and the results just discussed have been reported in the article: *Pt(II) Derivatives with Rollover-Coordinated 6-substituted 2,2’-bipyridines: Ligands with Multiple Personalities* in Applied Sciences, **2020**, 10, 6665.

Conclusion

In conclusion, with this doctoral project we wanted to study synthesis and characterization of new complexes of transition metal ions, Pd(II), Pt(II), Au(III), and terrae rare, Y(III), La(III), Sm(II), with different N-heterocyclic aromatic ligands. Mainly with the idea to evaluating the behaviour of ligands, characterized by imidazo[1,5a]pyridine skeleton.

The result is that only new adducts have been obtained in which the ligand acts as an N,N chelating to obtain cyclometalated derivatives.

The theoretical study performed on the Pt(II) series suggest that the high angle steric strain of the 5- and 6-member rings formed by the ligands L1-4 as well as the deviation from ideal Pt(II)-N distances could be responsible of the thermodynamics inertia of these complexes toward cyclometallation.

Experimental part

All the solvents were purified and dried according to standard procedures.[45]

Elemental analyses were performed with a Perkin-Elmer elemental analyzer 240B at the Department of Chemistry and Pharmacy of the University of Sassari.

FT-IR spectra were registered with a Jasco FT-IR-480 Plus spectrometer

^{1}H spectra were recorded with a Bruker Avance III 400 spectrometer operating at 400.0 MHz. Chemical shifts are given in ppm relative to internal TMS for ^{1}H, J values are given in Hz. Two dimensional ^{1}H COSY and NOESY spectra were performed by means of standard pulse sequences.

Crystals were examined using an Agilent Supernova diffractometer, equipped with CCD area detector and mirror-monochromated Mo Kα radiation (λ = 0.71073 Å).

[45]Vogel, A.I. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman Scientific and Technical: Harlow, UK, **1989**.

Synthesis of L^1, 3-phenyl-1-(pyridin-2-yl)imidazo[1,5-*a*] pyridine

To a solution of bis(2-pyridyl)ketone (0.9209 g; 5.00 mmol) in acetic acid (30 ml) were added benzaldehyde (1.01 ml; 10 mmol) and ammonium acetate (1.9010 g; 25 mmol). The pale-yellow solution was refluxed under inert atmosphere for 5h. The solution was then put in a mixture of water/ice (250 ml), extracted with dichloromethane, dried with Na_2SO_4, filtered and concentrated to small volume. The product was purified with a chromatographic column using a mixture of ethyl acetate and n-hexane (8:2). The solution was concentrated to a small volume and n-hexane was added to give a yellow precipitate **(L^1)**.

Yield: 0.6647 g (49%).

Selected ^{1}H NMR data in [$CDCl_3$]:

8.70 (d, 1H, **H8**); 8.64 (d, 1H, **H6'**); 8.26 (d,1 H, **H5**); 8.24 (d, 1H, **H3'**); 7.85 (dd, 2H, ***ortho* H**); 7.72 (td, 1H, **H4'**); 7.54 (td, 2H, ***meta* H**); 7.47 (tt,1H, ***para* H**); 7.10 (dd, 1H, **H5'**); 6.92 (dd, 1H, **H7**); 6.65 (td,1H, **H6**).

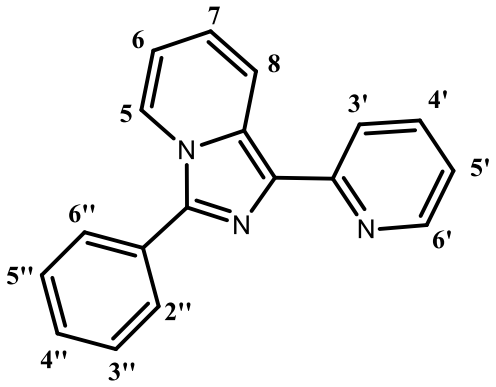
Selected ^{1}H NMR data in [CD_2Cl_2]:

8.71 (d, 1H, **H8**); 8.61 (d,1H,**H6**'); 8.30 (d,1H,**H3'**); 8.21 (d,1H,**H5**); 7.85 (d, 2H, ***ortho* H**); 7.74 (t,1H, **H4'**); 7.58 (t, 2H, **meta H**); 7.49 (t,1H, **para H**); 7.11 (dd,1H, **H5'**); 6.95 (td,1H, **H7**); 6.61 (dd,1H, **H6**).

Selected ^{1}H NMR data in [CD_3COCD_3]:

8.74 (d, 1H, **H8**); 8.62 (d, 1H, **H6'**); 8.50 (d,1 H, **H5**); 8.26 (d, 1H, **H3'**); 7.94 (d, 2H, ***ortho* H**); 7.80 (td, 1H, **H4'**); 7.60 (t, 2H, **meta H**);

7.51 (t,1H, ***para* H**); 7.16 (dd, 1H, **H5'**); 7.04 (dd, 1H, **H7**); 6.84 (t,1H, **H6**).



Molecular Weight: 271.32

Synthesis of L^2, 3-(*o*-tolyl)-1-(pyridin-2-yl)-imidazo[1,5-*a*] pyridine

To a solution of bis(2-pyridyl)ketone (0.9209 g; 5.00 mmol) in acetic acid (30 ml) were added o-tolyl aldehyde (1.20 ml; 10 mmol) and ammonium acetate (1.9003 g; 25 mmol). The pale-yellow solution was refluxed under inert atmosphere for 5h. The solution was put in a mixture of water/ice (250 ml), extracted with dichloromethane, dried with Na_2SO_4, filtered and concentrated to small volume. The product was purified with a chromatographic column using a mixture of ethyl acetate and n-hexane (8:2). The solution was concentrated to a small volume and n-hexane was added to give a yellow precipitate **(L^2)**.

Yield: 0.8560 g (60%).

Selected ^{1}H NMR data in [$CDCl_3$]:

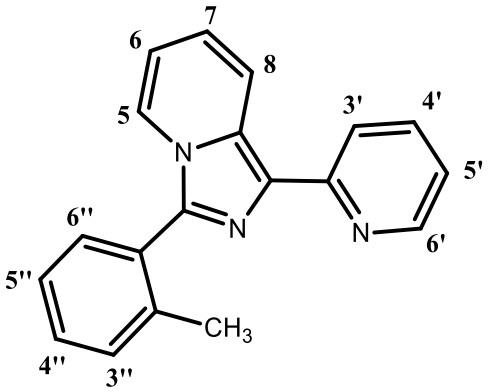
8.71 (d, 1H, **H8**); 8.64 (d,1H, **H6'**); 8.23 (d,1H, **H3'**); 7.70 (t,1H, **H4'**); 7.64 (d, 1H, **H5**); 7.51 (d, 1H, **H6"**); 7.40 (m, 3H, **H5+H4**+**H3"**); 7.09 (t, 1H, **H5'**); 6.93 (dd, 1H, **H7**); 6.60 (t, 1H, **H6**), 2.26 (s, 3H, **CH_3**).

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.71 (d, 1H, **H8**); 8.63 (d,1H, **H6'**); 8.20 (d,1H, **H3'**); 7.73 (t,1H, **H4'**); 7.69 (d, 1H, **H5**); 7.51 (d, 1H, **H6"**); 7.42 (m, 3H, **H5"+H4"**+**H3"**); 7.11 (t, 1H, **H5'**); 6.96 (t, 1H, **H7**); 6.65 (t, 1H, **H6**), 2.27 (s, 3H, **CH_3**).

Selected ^{1}H NMR data in [CD_3COCD_3]:

8.72 (d, 1H, **H8**); 8.62 (d,1H, **H6'**); 8.21 (d, 1H, **H3'**); 7.85 (d, 1H, **H5**); 7.78 (td, 1H, **H4'**); 7.56 (d, 1H, **H6"**); 7.44 (m, 3H, **H5"+H4"**+**H3"**); 7.15 (dd, 1H, **H5'**); 7.03 (dd, 1H, **H7**); 6.78 (t, 1H, **H6**), 2.27 (s, 3H, **CH_3**).



Molecular Weight: 285.34

Synthesis of L^3, 3-mesityl-1-(pyridin-2-yl)imidazo[1,5-*a*] pyridine

To a solution of bis(2-pyridyl)ketone (0.9209 g; 5.00 mmol) in acetic acid (30 ml) were added mesityl aldehyde (1.04 ml; 10 mmol) and ammonium acetate (1.9023 g; 25 mmol). The pale-yellow solution was refluxed in an inert atmosphere for 5h. The solution was put in a mixture of water/ice (250 ml), extracted with dichloromethane, dried with Na_2SO_4, filtered and concentrated to small volume. The product was purified with a chromatographic column using a mixture of ethyl

acetate and n-hexane (8:2). The solution was concentrated to a small volume and n-hexane was added to give a yellow precipitate **(L^3)**.

Yield: 0.9088 g (58%).

Selected ^{1}H NMR data in [$CDCl_3$]:

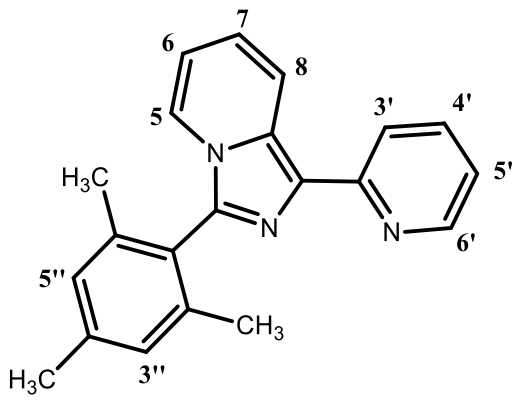
8.94 (d, 1H, **H8**); 8.89 (d, 1H, **H6'**); 8.48 (d, 1H, **H3'**); 7.95 (td, 1H, **H4'**); 7.61 (d, 1H, **H5**); 7.33 (dd, 1H, **H5'**); 7.26 (s, 2H, ***meta* H**); 7.17 (dd, 1H, **H7**); 6.82 (td, 1H, **H6**); 2.62 (s, 3H, ***para* CH_3**); 2.27 (s, 6H, ***ortho* CH_3**).

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.68 (d, 1H, **H8**); 8.62 (d, 1H, **H6**'); 8.20 (d, 1H, **H3'**); 7.72 (t, 1H, **H4'**); 7.36 (d,1H, **H5**); 7.09 (t, 1H, **H5'**); 7.05 (s, 2H, ***meta* H**); 6.93 (t,1H,**H6**); 6.60 (t,1H,**H7**); 2.38 (s,3H, ***para* CH_3**); 1.99 (s,3H, ***ortho* CH_3**).

Selected ^{1}H NMR data in [CD_3COCD_3]:

8.71 (d, 1H, **H8**); 8.62 (d, 1H, **H6'**); 8.20 (d, 1H, **H3'**); 7.77 (td, 1H, **H4'**); 7.51 (d, 1H, **H5**); 7.14 (dd, 1H, **H5'**); 7.08 (s, 2H, ***meta* H**); 7.02 (dd, 1H, **H7**); 6.75 (t, 1H, **H6**); 2.37 (s, 3H, ***para* CH_3**); 1.99 (s, 6H, ***ortho* CH_3**).



Molecular Weight: 313.40

Synthesis of L^4, 3-benzyl-1-(pyridin-2-yl)imidazo[1,5-*a*] pyridine

To a solution of bis(2-pyridyl)ketone (1.3998 g; 7.60 mmol) in methanol (30 ml) were added phenylalanine (1.2554 g; 7.6 mmol) and slowly few drops of acetic acid. The pale yellow solution was refluxed in an inert atmosphere for 12h. The resulting orange solution was concentrated to a small volume and diethyl ether added to give a product which was purified with a chromatographic column using a mixture of ethyl acetate and n-hexane (10:1). The solution was evaporated completely to give **L^4** as a brown oil.

Yield: 1.4963 g (69%).

Selected ^{1}H NMR data in [$CDCl_3$]:

8.62 (d,1H, **H6'**); 8.60 (d,1H, **H8**); 8.17 (d,1H, **H3'**); 7.71 (td,1H, **H4'**); 7.59 (d, 1H, **H5**); 7.24 (m, 5H, **Har**); 7.07 (dd,1H, **H5'**); 6.84 (dd, 1H, **H7**); 6.52 (t, 1H, **H6**); 4.51 (s, 2H, **CH_2**).

Selected ^{1}H NMR data in [CD_2Cl_2]:

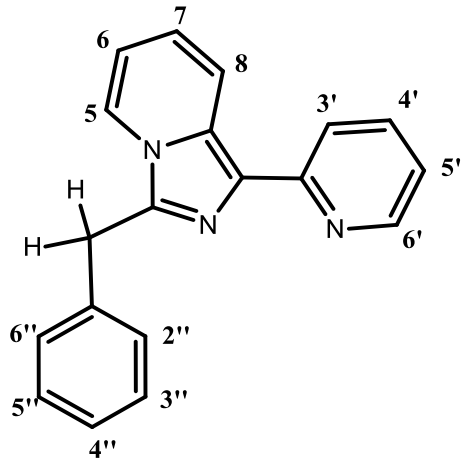
8.62 (d,1H, **H8'**); 8.60 (d,1H, **H6'**); 8.16 (d,1H, **H3'**); 7.73 (t,1H, **H4'**); 7.68 (d, 1H, **H5**); 7.27 (m, 5H, **Har**); 7.10 (t,1H, **H5'**); 6.88 (t, 1H, **H7**); 6.59 (t, 1H, **H6**); 4.49 (s, 2H, **CH_2**).

Selected ^{1}H NMR data in [CD3COCD3]:

8.62 (d,1H, **H8**); 8.58 (d,1H, **H6'**); 8.20 (d,1H, **H3'**); 8.03 (d, 1H, **H5**); 8.02 (t,1H, **H4'**); 7.25 (m, 5H, **Har**); 7.12 (dd,1H, **H5'**); 6.92 (dd, 1H, **H7**); 6.69 (t, 1H, **H6**); 4.52 (s, 2H, **CH_2**).

Selected ^{1}H NMR data in [CD_3SOCD_3]:

8.56 (d,1H, **H6'**); 8.47 (d,1H, **H8**); 8.16 (d,1H, **H5**); 8.05 (d, 1H, **H3'**); 7.78 (t,1H, **H4'**); 7.27 (s, br 5H, **Har**); 7.17 (dd,1H, **H5'**); 6.97 (t, 1H, **H7**); 6.75 (t, 1H, **H6**); 4.48 (s, 2H, **CH_2**).



Molecular Weight: 285.34

Synthesis of L^5, 3-methoxy-1-(pyridin-2-yl)imidazo[1,5-*a*] pyridine

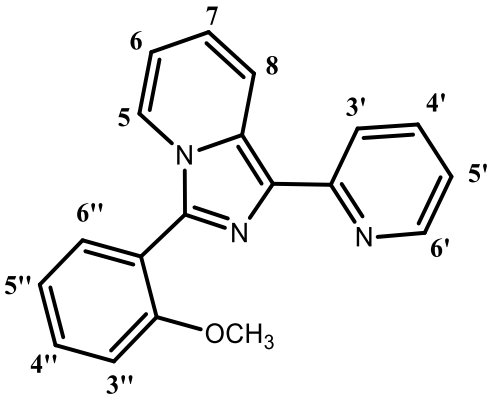
To a solution of bis (2-pyridyl) ketone (0.9209 g; 5.0 mmol) in acetic acid (30 ml) were added 2-methoxybenzaldehyde (1.3615 g; 10 mmol) and ammonium acetate (1.9023 g; 25 mmol). The pale-yellow solution was refluxed in an inert atmosphere for 5h. The solution was put in a mixture of water/ice (250 ml), extracted with dichloro methane, anhydrified with Na_2SO_4, filtered and concentrated.

The product was purified with a chromatographic column using a mixture of ethyl acetate and n-hexane (8:2). The solution was concentred to a small volume and n-hexane was added to give a yellow precipitate **(L^5)**.

Yield: 0.0949 g (63%).

Selected ^{1}H NMR data in [$CDCl_3$]:

8.70 (d,1H,**H8**); 8.62 (d,1H,**H6**'); 8.24 (d,1H,**Har**); 7.69 (m,2H,**H3'+Har**); 7.62 (d,1H,**H5**); 7.50 (t,1H,**H4'**); 7.14 (t,1H,**Har**); 7.07 (m,2H,**Har+H5');** 6.94 (t,1H,**H7**); 6.61 (t,1H,**H6**), 3.81 (s,3H,**OCH_3**).



Molecular Weight: 301.34

Synthesis of L^6, 3-pentamethyl-1-(pyridin-2-yl)imidazo[1,5-*a*] pyridine

To a solution of bis (2-pyridyl) ketone (0.9209 g; 5.0 mmol) in acetic acid (30 ml) were added penta metil benzaldehyde (1.7625 g; 10 mmol) and ammonium acetate (1.907 g; 25 mmol). The pale-yellow solution was refluxed in an inert atmosphere for 5h. The solution was put in a mixture of water/ice (250 ml), extracted with dichloro methane, anhydrified with Na_2SO_4 and filtered.

The solution was concentrated to a small volume and n-hexane was added to give a yellow precipitate **(L^6)**.

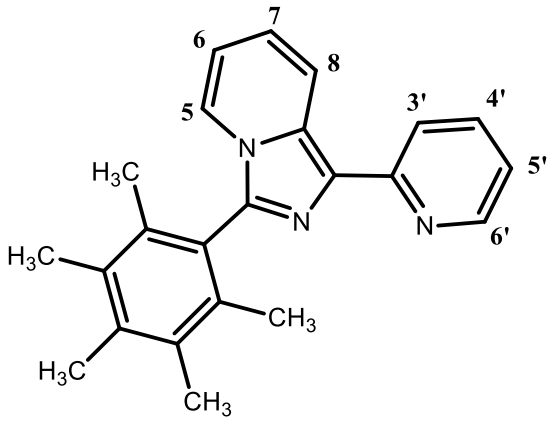
Yield: 1.2804 g (75%).

Selected ^{1}H NMR data in [$CDCl_3$]:

8.70 (d,1H,**H8**); 8.64 (d,1H,**H6**'); 8.25 (d,1H,**H5**); 7.70 (t,1H,**H4'**); 7.34 (d,1H,**H3**'); 7.09 (t,1H,**H5'**); 6.92 (t,1H,**H6**); 6.55 (t,1H,**H7**); 2.33 (s,3H, ***para*** **CH_3**); 2.27 (s,6H, ***meta*** **CH_3**); 1.90 (s,6H, ***orto*** **CH_3**).

Selected ^{1}H NMR data in [CD_3COCD_3]:

8.73 (d,1H,**H8**); 8.63 (d,1H,**H6**'); 8.22 (d,1H,**H5**); 7.79 (t,1H,**H4'**); 7.45 (d,1H,**H3**'); 7.16 (t,1H,**H5'**); 7.02 (t,1H, **H7**); 6.73 (t,1H,**H6**); 2.34 (s,3H, ***para*** **CH_3**); 2.27 (s,6H, ***meta*** **CH_3**); 1.87 (s,6H, ***orto*** **CH_3**)



Molecular Weight: 341.45

Synthesis of L^7, 1-phenyl-3-(pyridin-2-yl)imidazo[1,5-*a*] pyridine

To a solution of 2-benzoylpyridine (0.9160 g; 5 mmol) in toluene (25 ml) were added benzyl ammine (950 µL; 5.5 mmol), iodine (1.5302 g; 6 mmol) and sodium acetate (1.2302 g; 15 mmol). The dark solution was refluxed in an inert atmosphere for 6h, until to disappearance of the ketone. To the solution was added Na_2SO_3 (5%) and the mixture was extracted with dichloro methane and water. The organic fraction was anhydrified with Na_2SO_4 and filtered. The product was purified

through column chromatographic using a mixture of ethyl acetate and petroleum ether (1:3) affording a yellow precipitate **(L^7)**.

Yield: 0.5964 g (44%).

Selected ^{1}H NMR data in [$CDCl_3$]:

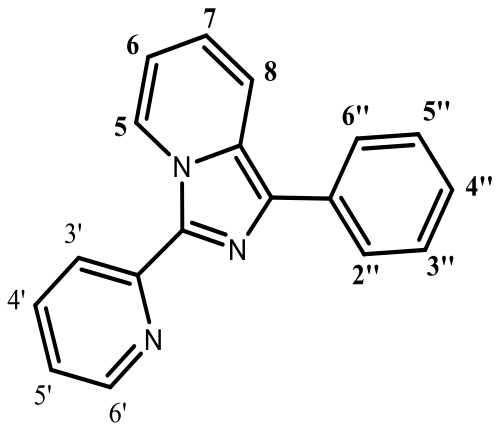
10.04 (d,1H,**H5**); 8.66 (d,1H,**H6**'); 8.50 (d,1H,**H8**); 7.98 (d,2H, ***orto* H**); 7.92 (d,1H,**H3'**); 7.81 (td,1H,**H4'**); 7.50 (t,2H, ***meta* H**); 7.34 (t,1H, ***para* H**); 7.22 (t,1H,**H5**'); 6.95 (t,1H,**H6**); 6.78 (t,1H,**H7**).

Selected ^{1}H NMR data in [CD_3COCD_3]:

10.08 (d,1H,**H5**); 8.695 (d,1H,**H6**'); 8.48 (d,1H,**H8**); 8.04 (m,3H, ***orto* H+H3'**); 7.93 (td,1H,**H4'**); 7.49 (t,2H, ***meta* H**); 7.33 (t,1H, ***para* H+ H5**'); 7.07 (t,1H,**H6**); 6.91 (t,1H,**H7**).

Selected ^{1}H NMR data in [CD_3SOCD_3]:

9.97 (d,1H, **H5**); 8.715 (d,1H, **H6**'); 8.10 (d,1H, **H8**); 8.04 (m,3H, ***orto* H+H3'**); 7.51 (t,2H, **Har**); 7.39 (t,1H, **H4'**); 7.33 (t,1H, **H5**'); 7.11 (t,1H, **H6**); 6.99 (t,1H, **H7**).



Molecular Weight: 271.32

Synthesis of L^8, 3-pentafluoro-1-(pyridin-2-yl)imidazo[1,5-*a*] pyridine

To a solution of bis (2-pyridyl) ketone (0.9209 g; 5 mmol) in acetic acid (30 ml) were added pentafluoro benzaldehyde (0.806 ml; 10 mmol) and ammonium acetate (1.907 g; 25 mmol). The pale-yellow solution was refluxed in an inert atmosphere for 5h. The solution was put in a mixture of water/ice (250 ml), extracted with dichloro methane, anhydrified with Na_2SO_4 and filtered.

The solution was concentrated to a small volume and n-hexane was added to give a pale-yellow precipitate **(L^8)**.

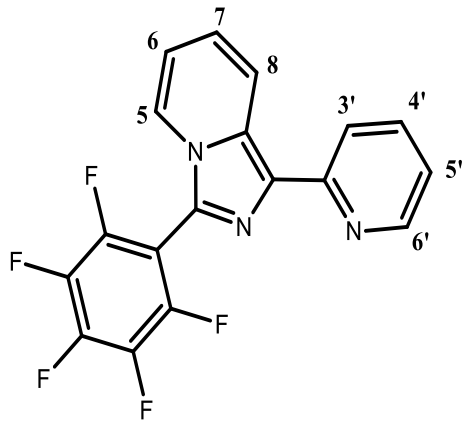
Yield: 1.1102 g (61.5%).

Selected ^{1}H NMR data in [$CDCl_3$]:

8.80 (d,1H, **H8**); 8.655 (d,1H, **H6'**); 8.20 (d,1H, **H5**); 7.75 (t,1H, **H4'**); 7.69 (d,1H, **H3'**); 7.16 (t,1H, **H5'**); 7.07 (t,1H, **H6**); 6.81 (t,1H, **H7**).

Selected ^{19}F NMR data in [$CDCl_3$]:

-137.00 (dd,2F, ***orto* F**); -150.96 (t,1F, ***para* F**); -160.39 (dt,2F, ***meta* F**).



Molecular Weight: 361.27

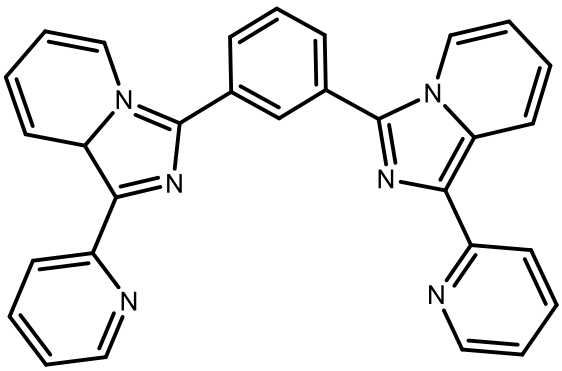
Synthesis of L^1_p, 1,3-bis(1-(pyridin-2-yl)imidazo[1,5-a]pyridin-3-yl) benzene

A mixture consisting of bis (2-pyridyl) ketone (0.6188 mg; 3.36 mmol), terephthalaldehyde (0.1958 mg; 1,46 mmol), and ammonium acetate (1.66 g; 21.85 mmol) in 25 mL of glacial acetic acid was stirred at 118 °C. After 12 h, the reaction mixture was cooled to room temperature and the acetic acid was removed by evaporation under vacuum. The solid was dissolved in an aqueous solution of Na_2CO_3 and the mixture extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4, separated, and the solvent evaporated under vacuum. The formed solid was washed several times with diethyl ether and dried under vacuum obtaining a quantitative yield of the product **(L^1p)** as a yellow powder.

Yield: 0.5855 g (85.61%).

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.74 (d, 2H, **H8**), 8.64 (d, 2H, **H6**'), 8.33 (m, 3H, **H5+H5**), 8.26 (d, 2H, **H4+H6**), 7.95 (d, 2H,**H3'**), 7.73 (m, 3H, **H4'+H2**), 7.11 (m, 2H, **H5**'), 6.96 (m, 2H, **H7**), 6.70 (t, 2H, **H6**).



Molecular Weight: 465.53

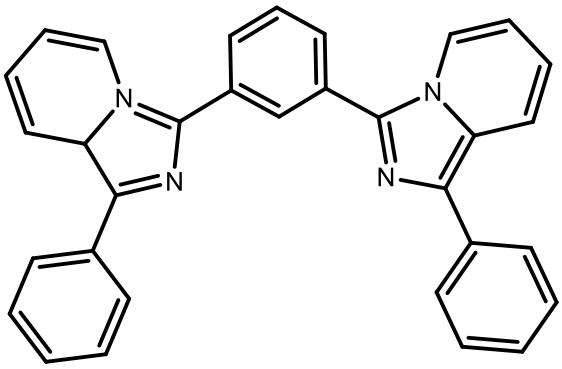
Synthesis of L^2_p, 1,3-bis(1-phenylimidazo[1,5-a] pyridin-3-yl) benzene

A mixture consisting of phenyl(pyridin-2-yl) methanone (0.6155 mg; 3.36 mmol), terephthalaldehyde (0.1958 mg; 1,46 mmol), and ammonium acetate (1.66 g; 21.85 mmol) in 25 mL of glacial acetic acid was stirred at 118 °C. After 12 h, the reaction mixture was cooled to room temperature and the acetic acid was removed by evaporation under vacuum. The solid was dissolved in an aqueous solution of Na_2CO_3 and the mixture extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4, separated, and the solvent evaporated under vacuum. The formed solid was washed several times with diethyl ether and dried under vacuum obtaining a quantitative yield of the product **(L^2p)** as a yellow powder.

Yield: 0.1754 g (26%).

Selected ^{1}H NMR data in [$CDCl_3$]:

8.33 (m, 2H, **H5+H2**), 7.95 (m, 6H, **Ho+H4+H6**), 7.86 (d, 2H, **H8**), 7.72 (t, 1H, **H5'**), 7.48 (t, 4H, **Hm**), 7.31 (t, 2H, **Hp**), 6.83 (m, 2H, **H7**), 6.63 (t, 2H, **H6**).



Molecular Weight: 465.53

Synthesis of [PdL^{1}Cl$_2$], (1).

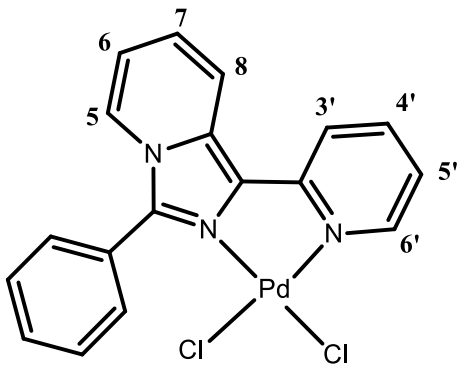
To a solution of **L^1** (0.1193 g; 0.44 mmol) in acetic acid (25 ml) was added $Pd(OAc)_2$ (0.1000 g; 0.44 mmol). The orange solution was refluxed under inert atmosphere for 6h and evaporated to dryness. The crude obtained was solubilized with chloroform (25 ml), treated with LiCl in excess, stirred for 12h at room temperature then filtered. The resulting solution was concentrated to a small volume and diethyl ether added to give a precipitate which was recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as yellow solid **(1)**.

Yield: 0.0947 g (48%). M.p.:>290°C

Found: C 47.85; H 2.80; N 9.25%. Calc. for $C_{18}H_{13}Cl_2N_3Pd$: C, 48.19; H, 2.92; N, 9.37.

Selected ^{1}H NMR data in [CD_2Cl_2]:

9.10 (d, 1H, **H6'**); 7.98 (d, 1H, **H3'**); 7.97 (t, 2H, **H5**); 7.91 (d, 1H, **H8**); 7.85 (t, 1H, **H4'**); 7.65 (m, 5H, **Har**); 7.33 (d, 1H, **H7**); 7.22 (t, 1H, **H5'**); 6.89 (t, 1H, **H6**).



Molecular Weight: 448.64

Synthesis of [PdL^{2}Cl$_2$], (2).

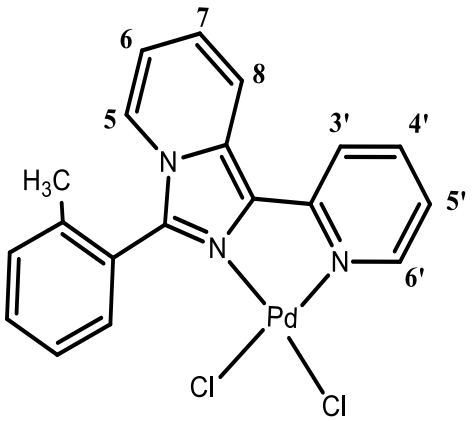
To a solution of **L^2** (0.1259 g; 0.44 mmol) in acetic acid (25 ml) was added $Pd(OAc)_2$ (0.1001 g; 0.44 mmol). The orange solution was refluxed under inert atmosphere for 6h and evaporated to dryness. The crude obtained was solubilized with chloroform (25 ml), treated with LiCl in excess, stirred for 12h at room temperature then filtered. The resulting solution was concentred to a small volume and diethyl ether added to give a precipitate which was recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as yellow solid **(2)**.

Yield: 0.0997 g (49%). M.p.:215°C.

Found: C 49.30; H 2.99; N 8.94%. Calc. for $C_{19}H_{15}Cl_2N_3Pd$: C, 49.32; H, 3.27; N, 9.08.

Selected ^{1}H NMR data in [CD_2Cl_2]:

9.25 (d, 1H, **H6'**); 8.03 (t, 1H, **H4'**); 7.95 (d, 1H, **H8**); 7.85 (d, 1H, **H3'**); 7.55 (m, 2H, **H6"**+**H5**); 7.41 (m, 5H, **H5"+H4"+ H3" +H5'+ H7**); 6.88 (t, 1H, **H6**); 2.21 (s, 3H, **CH_3**).



Molecular Weight: 462.67

Synthesis of [PdL^{3}Cl$_2$], (3).

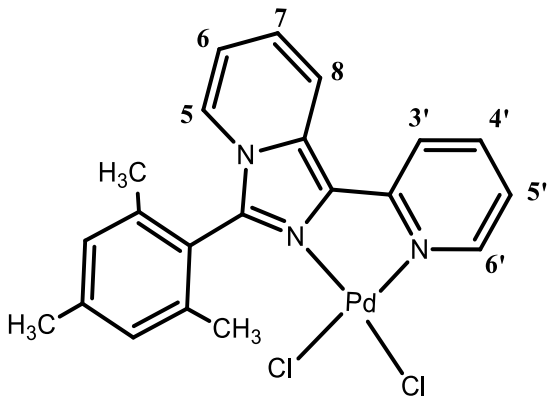
To a solution of **L^3** (0.1391 g; 0.44 mmol) in acetic acid (25 ml) was added $Pd(OAc)_2$ (0.1000 g; 0.44 mmol). The orange solution was refluxed under inert atmosphere for 6h and evaporated to dryness. The crude obtained was solubilized with chloroform (25 ml), treated with LiCl in excess, stirred for 12h at room temperature then filtered. The resulting solution was concentred to a small volume and diethyl ether added to give a precipitate which was recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as yellow solid **(3)**.

Yield: 0.1900 g (88%). M.p.:>290°C

Found: : C 51.04; H 3.50; N 8.46%. %. Calc. for $C_{21}H_{19}Cl_2N_3Pd$: C, 51.40; H, 3.90; N, 8.56.

Selected ^{1}H NMR data in [CD_2Cl_2]:

9.26 (d, 1H, **H6'**); 8.01 (t, 1H, **H4'**); 7.93 (d, 1H, **H8**); 7.84 (d, 1H, **H5**); 7.43 (d, 1H, **H3'**); 7.33 (m, 2H, **H5'+H7**); 7.08 (s, 2H, ***meta* H**); 6.87 (t, 1H, **H^6**); 2.41 (s, 3H, ***para* CH$_3$**); 2.13 (s, 3H, ***ortho* CH$_3$**); 2.03 (s, 3H, ***ortho* CH$_3$**).



Molecular Weight: 490.72

Synthesis of [PdL^{4}Cl$_2$], (4).

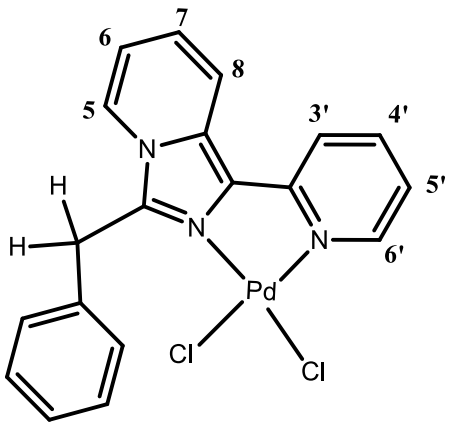
To a solution of **L^4** (0.1251 g; 0.44 mmol) in acetic acid (50 ml) was added $Pd(OAc)_2$ (0.1002 g; 0.44 mmol). The solution was refluxed under inert atmosphere for 6h and evaporated to dryness. The crude obtained was solubilized with chloroform (25 ml), treated with LiCl in excess, stirred for 12h at room temperature then filtered. The resulting solution was concentred to a small volume and diethyl ether added to give a precipitate which was recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as yellow solid **(4)**.

Yield: 0.0631 g (31%). M.p.:225°C

Found: C 49.30; H 2.99; N 8.90 %. Calc. for $C_{19}H_{15}Cl_2N_3Pd$: C, 49.32; H, 3.27; N, 9.08.

Selected ^{1}H NMR data in [CD_2Cl_2]:

9.27 (d, 1H, **H6'**); 7.97 (t, 1H, **H4'**); 7.89 (m, 2H, **H8+H3'**); 7.77 (t, 1H, **H5**); 7.34 (m, 5H, **Har**); 7.27 (m, 2H, **H5'+H7**); 6.88 (t, 1H, **H6**); 4.44 (broad, 2H, **CH_2**).



Molecular Weight: 462.67

Synthesis of [PdL^{5}Cl$_2$], (5).

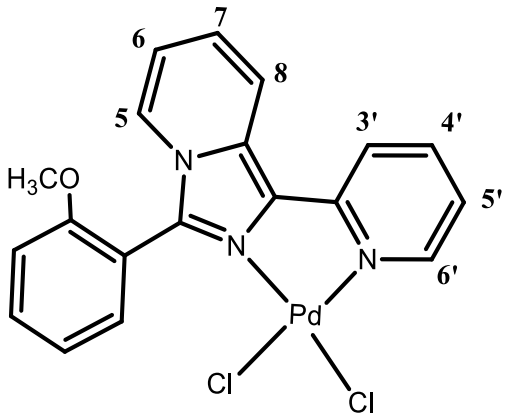
To a solution of **L^5** (0.1511 g; 0.5 mmol) in 10ml of CH_3CN was added [Pd(CH_3CN)$_2$Cl$_2$] (0.1304 g; 0.5 mmol). Temperature was set to 70°C. After 4hours, reactions mixture was cooled down and filtered. The resulting solution was concentred to a small volume and diethyl ether added to give a precipitate which was recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as yellow solid **(5)**.

Yield: 0.1866 g (78%). M.p.: >290°C

Found: C 47.64; H 2.88; N 8.60%. Calc. for $C_{19}H_{15}Cl_2N_3OPd$: C, 47.67; H, 3.16; N, 8.78.

Selected ^{1}H NMR data in [$CDCl_3$]:

9.245 (d,1H,**H6'**); 7.97 (t,1H,**H4'**); 7.86 (d,1H,**H8**); 7.67 (d,1H,**H3'**); 7.59 (t,1H,**H5'**); 7.42 (d,1H,**Har**); 7.31 (t,2H,**Har**); 7.13 (m,2H,**H5+H7**); 7.06 (d,1H,**H^{ar}**); 7.13 (t,1H,**H^6**); 3.86 (s,3H,**OCH$_3$**).



Molecular Weight: 478.67

Synthesis of [PdL^{6}Cl$_2$], (6).

To a solution of **L^6** (0.1506 g; 0.44 mmol) in acetic acid (25 ml) was added Pd(OAc)$_2$ (0.1000 g; 0.44 mmol). The solution was refluxed

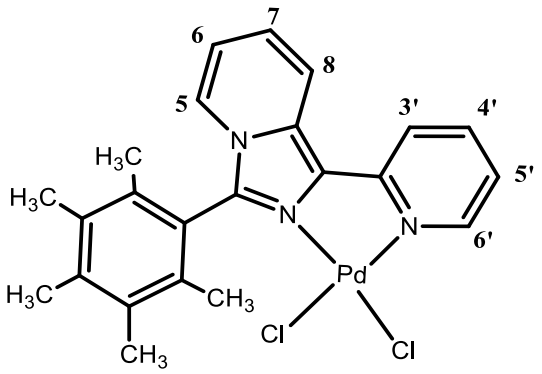
under inert atmosphere for 6h and evaporated to dryness. The crude obtained was solubilized with chloroform (25 ml), treated with LiCl in excess, stirred for 12h at room temperature then filtered. The resulting solution was concentrated to a small volume and diethyl ether was added to give a precipitate which was recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as yellow solid **(6)**.

Yield: 0.2122 g (93%). M.p.: >290°C

Found: C 53.22; H 4.08; N 7.93%. Calc. for $C_{23}H_{23}Cl_2N_3Pd$: C, 53.25; H, 4.47; N, 8.10.

Selected ^{1}H NMR data in [CD_2Cl_2]:

9.23 (d,1H,**H6'**); 7.99 (t,1H,**H4'**); 7.92 (d,1H,**H8**); 7.84 (d,1H,**H3'**); 7.36 (d,1H,**H5**); 7.29 (m,2H,**H5'+H7**); 6.82 (t,1H,**H6**); 2.35 (s,3H, ***para*** **CH_3**); 2.27 (s,6H, ***meta*** **CH_3**); 1.90 (s,6H, ***ortho*** **CH_3**).



Molecular Weight: 518.77

Synthesis of [Pd$L^7$$Cl_2$], (7).

Method A:

To a solution of **L^7** (0.0759 g; 0.28 mmol) in methanol (25 ml) was added Na_2PdCl_4 (0.1000 g; 0.28 mmol). Immediately an orange solid. Precipite The solid was filtered and washed with diethyl ether. The

solid product was dissolved in dichloromethane (25 ml), concentrated to a small volume and diethyl ether was added to give an orange product **(7)**.

Yield: 0.0314 g (25%). M.p.:>290°C

Method b:

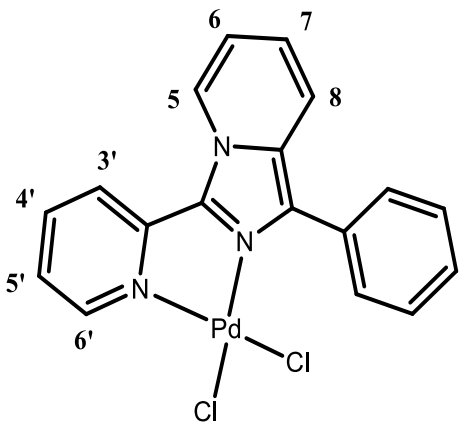
To a solution of **L**^{7} (0.1031 g; 0.38 mmol) in chloroform (25 ml) was added $[PdCl_2(PhCN)_2]$ (0.1010 g; 0.28 mmol). Immediately an orange solid precipitated. The solid was filtered and washed with diethyl ether. The solid product was dissolved in dichloromethane (25 ml), concentrated to a small volume and diethyl ether was added to give an orange product **(7)**.

Yield: 0.1183 g (85%). M.p.: >290°C

Found: C 48.15; H 2.66; N 9.18%. Calc. for $C_{18}H_{13}Cl_2N_3Pd$: C, 48.19; H, 2.92; N, 9.37.

Selected ^{1}H NMR data in [$CDCl_3$]:

9.45 (d,1H,**H6'**); 8.61 (d,1H,**H5**); 8.10 (t,1H,**H4'**); 7.99 (d,1H,**H8**); 7.71 (d,1H,**H3'**); 7.61 (t,1H,**Har**); 7.48 (m,4H,**Har**); 7.36 (t,1H,**H5'**); 7.18 (m,2H,**H6+H7**).



Molecular Weight: 448.64

Synthesis of [Pd(L^1_p)Cl_2], (8).

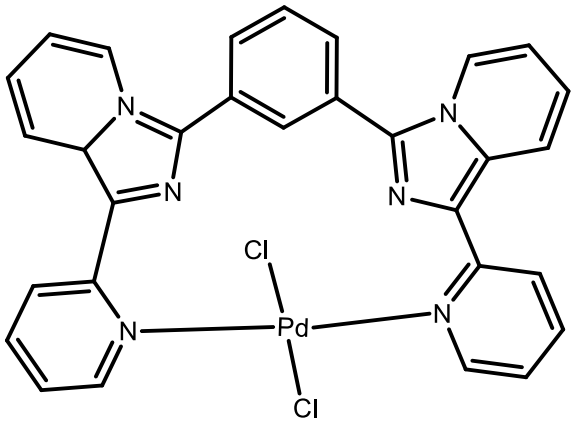
To a solution of ligand **(L^1_p)** (0.1000 g; 0.21 mmol) in acetic acid (30 mL) was added $Na_2[PdCl_4]$ (0.0731 g; 0.21 mmol), and a yellow precipitate immediately appeared. The mixture was heated at 118°C (reflux) for 1 h. After being cooled to room temperature, the yellow precipitate was filtered off and washed with acetic acid, H_2O, diethyl ether and finally dried in vacuum. The analytical sample **(8)** was obtained by recrystallization from dichloromethane/ diethyl ether.

Yield: 0.064 g (46%). M.p.:>290°C

Found: C 59.38; H 3.03; N 13.58%. Calc. for $C_{30}H_{20}ClN_6Pd$: C, 59.42; H, 3.32; N, 13.86.

Selected ^{1}H NMR data in [CD_3SOCD_3]:

8.985 (d, 2H, **H6'**); 8.44 (d, 2H, **H8**); 8.33 (d, 2H, **H3'**); 8.18 (t, 2H, **H4'**); 8.03 (d, 2H, **H5**); 7.88 (s, 1H, **H2**); 7.84 (d, 4H, **H6+H4**); 7.75 (t, 2H, **H5**); 7.47 (m, 4H, **H5+H6**); 7.13 (t, 2H, **H7**).



Molecular Weight: 642,85

Reaction with L^2_p and $Na_2[PdCl_4]$

To a solution of ligand **(L^2_p)** (0.1000 g; 0.21 mmol) in acetic acid (30 mL) was added $Na_2[PdCl_4]$ (0.0732 g; 0.21 mmol), and a yellow precipitate immediately appeared. The mixture was heated at 118°C (reflux) for 1 h. After being cooled to room temperature, the yellow precipitate was filtered off and washed with acetic acid, H_2O, diethyl ether and finally dried in vacuum. The analytical sample wasn't isolated.

Synthesis of $[PdL^1(OAc)_2]$, (1').

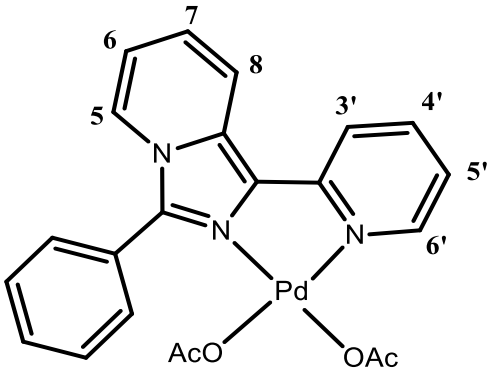
To a solution of **L^1** (0.1193 g; 0.44 mmol) in dichloromethane (25 ml) was added $Pd(OAc)_2$ (0.1000 g; 0.44 mmol). The orange solution was stirred for 12 h at room temperature, then evaporated to a small volume and diethyl ether was added. The yellow precipitate formed was filtered off and recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as a yellow solid **(1')**.

Yield: 0.2050 g (94%). M.p.:176°C

Found: C 52.95; H 3.74; N 8.30%. Calc. for $C_{22}H_{19}N_3O_4Pd$: C, 53.29; H, 3.86; N, 8.47.

Selected ^{1}H NMR data in $[CD_2Cl_2]$:

8.12 (d, 1H, **H6'**); 7.98 (td, 1H, **H4'**); 7.91 (d, 1H, **H8**); 7.85 (d, 1H, **H5**); 7.80 (d, 1H, **H3'**); 7.67-7.60 (m, 5H, **Har**); 7.29 (dd, 1H, **H7**); 7.24 (t, 1H, **H5'**); 6.86 (t, 1H, **H6**); 1.99 (s, 3H, C(O)**CH_3**); 1.13 (s, 3H, C(O)**CH_3**).



Molecular Weight: 495.82

Synthesis of [PdL^2(OAc)$_2$], (2').

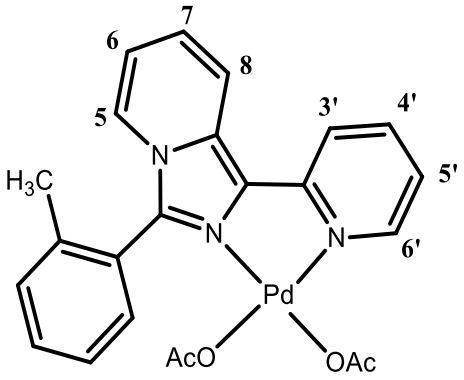
To a solution of **L^2** (0.1259 g; 0.44 mmol) in dichloromethane (25 ml) was added Pd(OAc)$_2$ (0.1002 g; 0.44 mmol). The orange solution was stirred for 12h at room temperature, then evaporated to a small volume and diethyl ether was added. The yellow-green precipitate was filtered off and recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as yellow solid **(2')**.

Yield: 0.0919 g (41%). M.p.:250°C

Found: C 53.90; H 3.95; N 7.99 %. Calc. for $C_{23}H_{21}N_3O_4Pd$: C, 54.18; H, 4.15; N, 8.24.

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.14 (d, 1H, **H6'**); 7.98 (d, 1H, **H4'**); 7.89 (d, 1H, **H8**); 7.79 (d, 1H, **H5**); 7.51 (d, 1H, **H3'**); 7.50-7.40 (m, 4H, **Har**); 7.31 (t, 1H, **H7**); 7.25 (t, 1H, **H5'**); 6.86 (t, 1H, **H6**); 2.26 (s, 3H, ***ortho* CH$_3$**); 1.98 (s, 3H, C(O)**CH$_3$**); 1.11 (s, 3H, C(O)**CH$_3$**).



Molecular Weight: 509.85

Synthesis of [PdL^3(OAc)$_2$], (3').

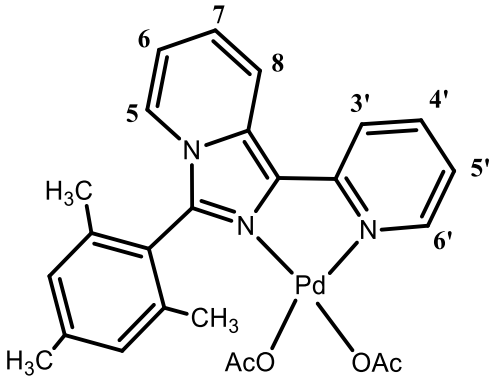
To a solution of **L^3** (0.1383 g; 0.44 mmol) in dichloromethane (25 ml) was added Pd(OAc)$_2$ (0.1001 g; 0.44 mmol). The orange solution was stirred for 12h at room temperature, then evaporated to a small volume and diethyl ether was added. The yellow precipitate formed was filtered off and recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as a yellow solid **(3')**.

Yield: 0.2130 g (90%). M.p.:268°C

Found: C 55.01; H 4.15; N 7.64%. Calc. for $C_{25}H_{25}N_3O_4Pd$: C, 55.82; H, 4.68; N, 7.81.

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.14 (d, 1H, **H6'**); 7.98 (t, 1H, **H4'**); 7.89 (d, 1H, **H8**); 7.77 (d, 1H, **H5**); 7.40 (d, 1H, **H3'**); 7.30 (t, 1H, **H5'**); 7.24 (t, 1H, **H7**); 7.04 (s, 2H, ***meta* H**); 6.85 (t, 1H, **H6**); 2.35 (s, 3H, ***para* CH_3**); 2.09 (s, 6H, ***ortho* CH_3**); 1.98 (s, 3H, C(O)**CH_3**); 1.13 (s, 3H, C(O)**CH_3**).



Molecular Weight: 537.90

Synthesis of [PdL^4(OAc)$_2$], (4').

To a solution of **L^4** (0.1259 g; 0.44 mmol) in dichloromethane (25 ml) was added Pd(OAc)$_2$ (0.1003 g; 0.44 mmol). The orange solution was stirred for 12h at room temperature, then evaporated to a small volume and diethyl ether was added. The yellow precipitate formed was filtered off and recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as a yellow solid **(4')**.

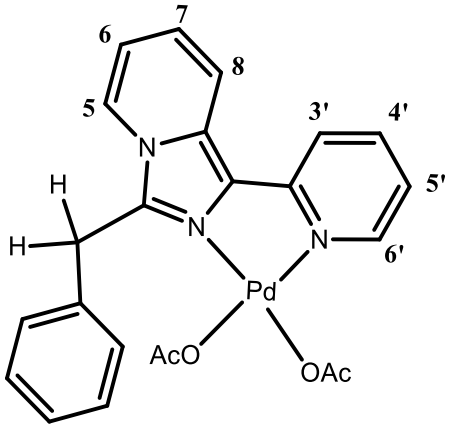
Yield: 0.1435 g (64%). M.p.:160°C

Found: C 53.90; H 3.94; N 8.02%. Calc. for $C_{23}H_{21}N_3O_4Pd$: C, 54.18; H, 4.15; N, 8.24.

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.07 (d, 1H, **H6'**); 7.92 (t, 1H, **H4'**); 7.84 (t, 2H, **H5+H8**); 7.74 (d,1H, **H3'**); 7.35-7.23 (m, 5H, **Har**); 7.16 (m, 2H, **H5'+H7**); 6.77 (t, 1H, **H6**);

4.61 (s, 2H, **CH_2**); 2.10 (s, 3H, , C(O)**CH_3**); 1.73 (s, 3H, , C(O)**CH_3**).



Molecular Weight: 509.85

Synthesis of [PdL^5(OAc)$_2$], (5').

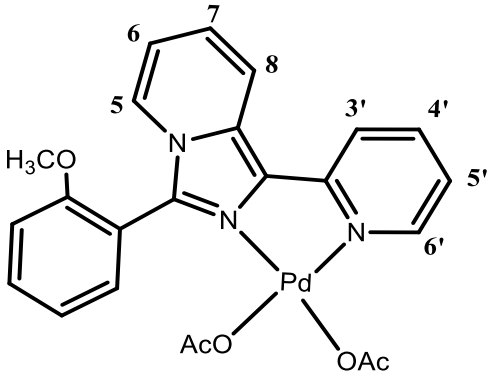
To a solution of **L^5** (0.1326 g; 0.44 mmol) in dichloromethane (25 ml) was added Pd(OAc)$_2$ (0.1002 g; 0.44 mmol). The orange solution was stirred for 12h at room temperature, then evaporated to a small volume and diethyl ether was added. The yellow precipitate formed was filtered off and recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as a yellow solid **(5')**.

Yield: 0.1952 g (83%). M.p.: 240°C

Found: C 52.49; H 3.68; N 7.83%. Calc. for $C_{23}H_{21}N_3O_5Pd$: C, 52.53; H, 4.03; N, 7.99.

Selected ^{1}H NMR data in [$CDCl_3$]:

8.27 (m,2H,**H6'+H8**); 8.09 (t,1H,**H4'**); 7.53 (m,3H,**H3'+H5+Har**); 7.26 (t,1H,**Har**); 7.18 (t,1H,**H5'**); 7.10 (d,1H,**Har**); 6.81 (t,1H,**H7**); 6.72 (t,1H,**H6**); 3.96 (s,3H,**OCH_3**); 2.09 (s,3H, , C(O)**CH_3**); 1.34 (s,3H, , C(O)**CH_3**).



Molecular Weight: 525.85

Synthesis of [PdL^6(OAc)$_2$], (6').

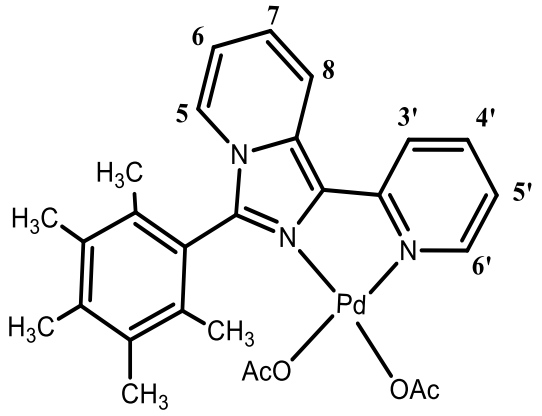
To a solution of **L^6** (0.1524 g; 0.44 mmol) in dichloromethane (25 ml) was added Pd(OAc)$_2$ (0.1000 g; 0.44 mmol). The orange solution was stirred for 12h at room temperature, then evaporated to a small volume and diethyl ether was added. The yellow precipitate formed was filtered off and recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as a yellow solid **(6')**.

Yield: 0.2120 g (85%). M.p: 235°C

Found: C 57,27; H 4.71; N 7.27%. Calc. for $C_{27}H_{29}N_3O_4Pd$: C, 57.30; H, 5.16; N, 7.42.

Selected ^{1}H NMR data in [$CDCl_3$]:

8.15 (d,1H,**H6'**); 7.98 (t,1H,**H4');** 7.90 (d,1H,**H8**); 7.79 (d,1H,**H3'**); 7.375 (d,1H,**H5**); 7.27 (t,1H,**H5'**); 7.15 (t,1H,**H7**); 6.80 (t,1H,**H6**); 2.27 (s,3H,***para*** **CH$_3$**); 2.26 (s,6H, ***meta*** **CH$_3$**); 2.07 (s,3H, , C(O)**CH$_3$**); 1.99 (s,6H,***ortho*** **CH$_3$**); 1.12 (s,3H, , C(O)**CH$_3$**).



Molecular Weight: 565.96

Synthesis of [PdL^7(OAc)$_2$], (7').

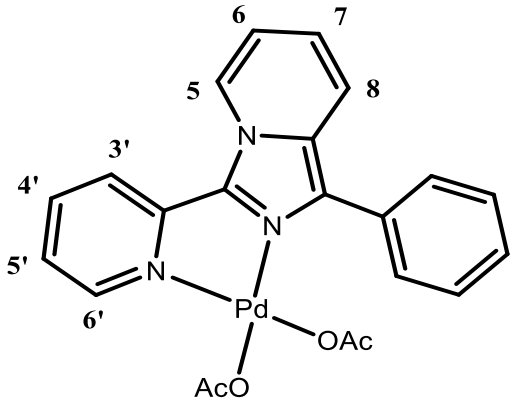
To a solution of **L^7** (0.1193 g; 0.44 mmol) in dichloro methane (25 ml) was added Pd(OAc)$_2$ (0.1000 g; 0.44 mmol). The orange solution was stirred for 12h at room temperature, then evaporated to a small volume and diethyl ether was added. The yellow precipitate formed was filtered off and recrystallized from CH_2Cl_2/Et_2O to give the analytical sample as a yellow solid **(7')**.

Yield: 0.2050 g (94%). M.p.: 210°C

Found: C 53.25; H 3.52; N 8.30%. Calc. for $C_{22}H_{19}N_3O_4Pd$: C, 53.29; H, 3.86; N, 8.47.

Selected ^{1}H NMR data in [$CDCl_3$]:

9.075 (d,1H,**H6'**); 8.38 (d,1H,**H5**); 8.24 (t,1H,**H4'**); 8.13 (d,1H,**H8**); 7.65 (d,2H,**H3'+Har**); 7.52 (m,5H,**H5'+Har**); 7.08 (m,2H,**H6+H7**); 2.13 (s,3H, , C(O)**CH$_3$**); 1.26 (s,3H, , C(O)**CH$_3$**).



Molecular Weight: 495.82

Synthesis of [PtL^{1}Cl$_2$], (9).

Method A:

To a solution of K_2PtCl_4 (0.1005 g; 0.24 mmol) in H_2O (25 ml) were added **L^1** (0.0651 g; 0.24 mmol) were slowly added few drops of HCl (2M). The mixture was heated to reflux under inert atmosphere for 72 h, until the solution became colourless, and then cooled. The yellow precipitate was filtered off, washed with water, ethanol and diethyl ether and finally recrystallized from dichloromethane and diethyl ether to give the analytical sample as a yellow solid **(9)**.

Yield: 0.1225 g (95%).

Method B:

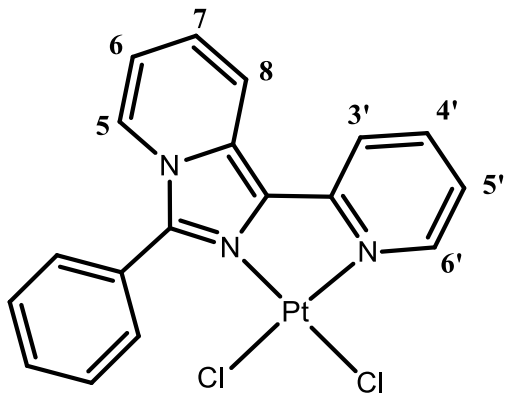
To a solution of K_2PtCl_4 (0.0499 g; 0.12 mmol) in H_2O (25 ml) were added **L^1** (0.0684 g; 0.24 mmol) and slowly few drops of HCl (2M) in a microwave vial. The mixture was stirred to 250 Watt for ten minutes (80°C). The colourless solution was then cooled. The yellow precipitate was filtered off, washed with water, ethanol and diethyl ether and finally recrystallized from dichloromethane and diethyl ether to give the analytical sample as a yellow solid **(9)**.

Yield: 0.0602 g (93%). M.p.:>290°C

Found: C 39.97; H 2.10; N 7.63%. Calc. for $C_{18}H_{13}Cl_2N_3Pt$: C, 40.24; H, 2.44; N, 7.82.

Selected ^{1}H NMR data in [CD_2Cl_2]:

9.51 (d, 1H, 3JPt-H= 36 Hz, **H6'**); 8.05 (t, 1H, **H4'**); 7.95 (d, 1H, **H8**); 7.84 (m, 2H, **H3'+H5**); 7.66 (m, 5H, **Har)**; 7.33 (m, 2H, **H5'+H7**); 6.92 (t, 1H, **H6**).



Molecular Weight: 537.31

Synthesis of [PtL^2Cl_2], (10).

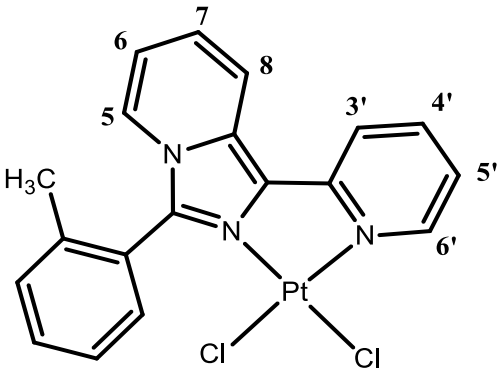
To a solution of K_2PtCl_4 (0.1000 g; 0.24 mmol) in H_2O (25 ml) were added **L^2** (0.0687 g; 0.24 mmol) were slowly added few drops of HCl (2M). The mixture was heated to reflux under inert atmosphere for 72 h, until the solution became colourless, and then cooled. The yellow precipitate was filtered off, washed with water, ethanol and diethyl ether and finally recrystallized from dichloromethane and diethyl ether to give the analytical sample as a yellow solid **(10)**.

Yield: 0.0793 g (60%). M.p.:>290°C

Found: C 41.01; H 2.53; N 7.44%. Calc. for $C_{19}H_{15}Cl_2N_3Pt$: C, 41.39; H, 2.74; N, 7.62.

Selected ^{1}H NMR data in [CD_2Cl_2]:

9.63 (d, 1H, ^{3}JPt-H= 34Hz, **H6'**); 8.07 (t, 1H, **H4'**); 7.96 (d, 1H, **H8**); 7.86 (d, 1H, **H3'**); 7.62-7.28 (m, 7H, **H5+ HAr+H5'+H7**; 6.91 (t, 1H, **H6**); 2.22 (s, 3H, **CH_3**).



Molecular Weight: 551.33

Synthesis of [PtL^3Cl_2], (11).

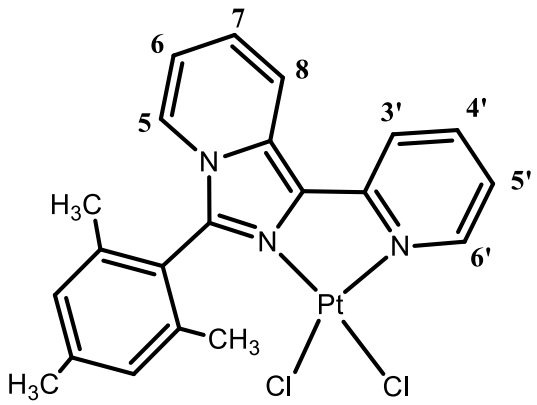
To a solution of K_2PtCl_4 (0.1000 g; 0.24 mmol) in H_2O (25 ml) were added **L^3** (0.0754 g; 0.24 mmol) were slowly added few drops of HCl (2M). The mixture was heated to reflux under inert atmosphere for 72 h, until the solution became colourless, and then cooled. The yellow precipitate was filtered off, washed with water, ethanol and diethyl ether and finally recrystallized from dichloromethane and diethyl ether to give the analytical sample as a yellow solid **(11)**.

Yield: 0.0750 g (54%). M.p.:>290°C

Found: C 43.10; H 2.97; N 7.03%. Calc. for $C_{21}H_{19}Cl_2N_3Pt$: C, 43.53; H, 3.31; N, 7.25.

Selected ^{1}H NMR data in [CD_2Cl_2]:

9.63 (d, 1H, $^{3}J_{Pt-H}$= 37 Hz, **H6'**); 8.07 (t, 1H, **H4'**); 7.97 (d, 1H, **H8**); 7.87 (d, 1H, **H3'**); 7.43 (d, 1H, **H5**); 7.37 (t, H, **H7**); 7.31 (t, H, **H5'**); 7.07 (s, 2H, ***meta*** **H^{Ar}**); 6.91 (t, 1H, **H^{6})**; 2.42 (s, 3H, ***para*** **CH_3**); 2.03 (s, 6H, ***ortho*** **CH_3**).



Molecular Weight: 579.39

Synthesis of [Pt$L^4$$Cl_2$], (12).

To a solution of K_2PtCl_4 (0.1001 g; 0.24 mmol) in H_2O (25 ml) were added **L^4** (0.0687 g; 0.24 mmol) were slowly added few drops of HCl (2M). The mixture was heated to reflux under inert atmosphere for 72 h, until the solution became colourless, and then cooled. The yellow precipitate was filtered off, washed with water, ethanol and diethyl ether and finally recrystallized from dichloromethane and diethyl ether to give the analytical sample as a yellow solid **(12)**.

Yield: 0.0436g (33%). M.p.:>290°C

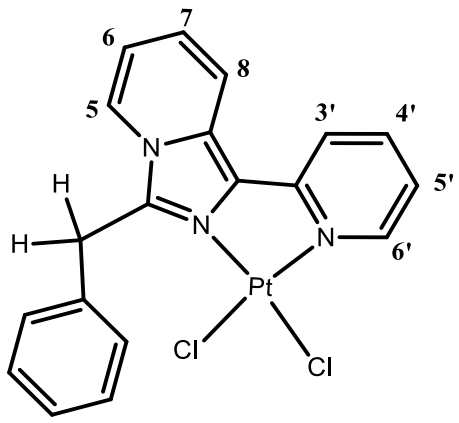
Found: C 40.97; H 2.36; N 7.51%. Calc. for $C_{19}H_{15}Cl_2N_3Pt$: C, 41.39; H, 2.74; N, 7.62.

Selected ^{1}H NMR data in [CD_2Cl_2]:

9.65 (d, 1H, $^3J_{Pt-H}$= 38.0 Hz, **H6'**); 8.02 (t, 1H, **H4'**); 7.90 (t, 2H, **H8+H3'**); 7.79 (d, 1H, **H5**); 7.38-7.21 (m, 7H, **H5'+H7+Har**); 6.91 (t, 1H, **H6**); 5.41 (s, 2H, **CH_2**).

Selected ^{1}H NMR data in [CD_3SOCD_3]:

9.39 (d, br 1H, **H6'**); 8.33 (m, 2H, **H8+H5**); 8.22 (m, 2H, **H3'+H4'**); 7.51- 7.22 (m, 8H, **H5'+H7+Har**); 7.12 (t, 1H, **H6**); 5.41 (s, 2H, **CH_2**).



Molecular Weight: 551.33

Synthesis of [PtL^{5}Cl$_2$], (13).

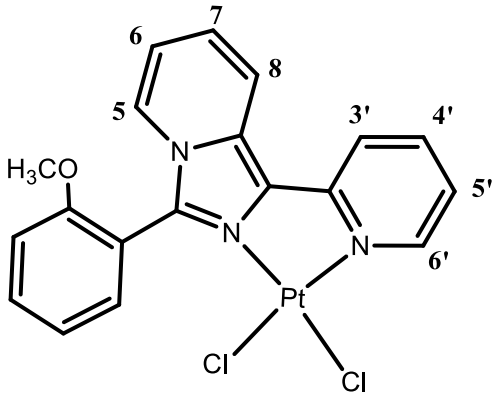
To an aqueous solution of K_2PtCl_4 (0.1000 g; 0.24mmol) and **L^5** (0.0725 g; 0.24mmol) were slowly added few drops of HCl (2M). The mixture was heated to reflux under inert atmosphere for 72 h, until the solution became colourless, and then cooled. The yellow precipitate was filtered off, washed with water, ethanol and diethyl ether and finally recrystallized from dichloromethane and diethyl ether to give the analytical sample as a yellow solid **(13)**.

Yield: 0.1021 g (75%). M.p.: >290°C

Found: C 40.19; H 2.43; N 7.26%. Calc. for $C_{19}H_{15}Cl_2N_3Pt$: C, 40.22; H, 2.66; N, 7.41.

Selected ^{1}H NMR data in [$CDCl_3$]:

9.61 (d,1H,$^3J_{Pt-H}$=38 Hz,**H6'**); 7.90 (m,2H,**H4'+H8**); 7.75 (d,1H,**H3'**); 7.56 (m,2H,**H5+*para* H**); 7.40 (d,1H, ***meta* H**); 7.25 (t,1H, ***meta* H**); 7.09 (m,2H,**H5'+H7**); 7.00 (d,1H, ***ortho* H**); 6.81 (t,1H,**H6**); 3.77 (s,3H,**OCH_3**).



Molecular Weight: 567.33

Synthesis of [PtL^6Cl_2], (14).

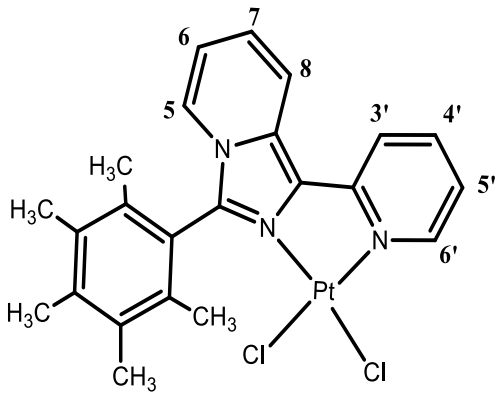
To an aqueous solution of K_2PtCl_4 (0.1000 g; 0.24 mmol) and **L^6** (0.0821 g; 0.24 mmol) were slowly added few drops of HCl (2M). The mixture was heated to reflux under inert atmosphere for 72 h, until the solution became colourless, and then cooled. The yellow precipitate was filtered off, washed with water, ethanol and diethyl ether and finally recrystallized from dichloromethane and diethyl ether to give the analytical sample as a yellow solid **(14)**.

Yield: 0.1195 g (82%). M.p.: >290°C

Found: C 45.45; H 3.49; N 6.78%. Calc. for $C_{23}H_{23}Cl_2N_3Pt$: C, 45.48; H, 3.82; N, 6.92.

Selected ^{1}H NMR data in [CD_2Cl_2]:

9.615 (d,1H,$^3J_{Pt-H}$=38 Hz,**H6'**); 8.05 (t,1H,**H4'**); 7.96 (d,1H,**H8**); 7.86 (d,1H,**H3'**); 7.32 (m,3H,**H5+H5'+H7**); 6.85 (t,1H,**H6**); 2.36 (s,3H, ***para*** **CH_3**); 2.27 (s,6H, ***meta*** **CH_3**); 1.91 (s,6H, ***ortho*** **CH_3**).



Molecular Weight: 607.44

Reaction with L^7 and $[PtCl_2(PhCN)_2]$

To a solution of **L^7** (0.0571 g; 0.21 mmol) in benzene was added under vigorous stirring $[PtCl_2(PhCN)_2]$ (0.1000 g; 0.21 mmol). The yellow solution was heated to reflux under inert atmosphere for overnight, and then cooled. The yellow-orange precipitate formed was filtered off, washed diethyl ether and finally recrystallized from dichloromethane and diethyl ether to give the analytical sample as a yellow-orange solid**.** The desired product isn't obtained.

Synthesis of $[PdL^1(CH_3)Cl]$, (15).

To a solution of **L^1** (0.0976 g; 0.36 mmol) in dichloromethane (25 ml) was added under vigorous stirring $[Pd(COD)(Cl)(CH_3)]$ (0.0970 g; 0.36 mmol). The yellow solution was stirred for 24h at room

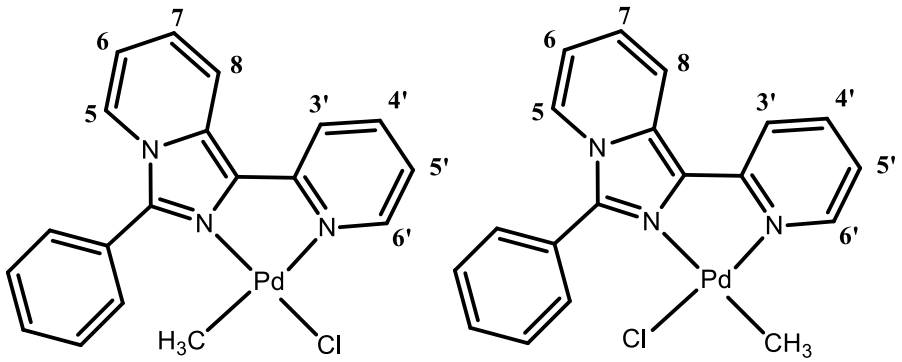
temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a yellow solid **(15)**.

Yield: 0.1341 g (87%).

Found: C 54.02; H 4.01; N 9.73%. Calc. for $C_{19}H_{16}ClN_3Pd$: C, 53.29; H, 3.77; N, 9.81.

Selected ^{1}H NMR data in [$CDCl_3$]:

major stereoisomer: 9.11 (d, 1H, **H6'**); 7.94 (d, 1H, **H8**); 7.86-7.79 (m, 3H, **H3'**+**H4'**+**H5**); 7.64-7.53 (m, 5H, **Har**); 7.24 (td, 1H, **H5'**); 7.18 (dd, 1H, **H7**); 6.78 (t, 1H, **H6**); 0.35 (s, 3H, Pd-**CH_3**); *minor stereoisomer:* 8.51 (d, 1H, **H6**'); 7.71 (m, 5H, **Har**); 6.86 (t, 1H, **H6**); 1.04 (s, 3H, Pd-**CH_3**).



Molecular Weight: 428.22

Synthesis of [PdL^2(CH_3)Cl], (16).

To a solution of **L^2** (0.1030 g; 0.36 mmol) in dichloromethane (25 ml) was added under vigorous stirring [Pd(COD)(Cl)(CH_3)] (0.0975 g; 0.36 mmol). The yellow solution was stirred for 24h at room

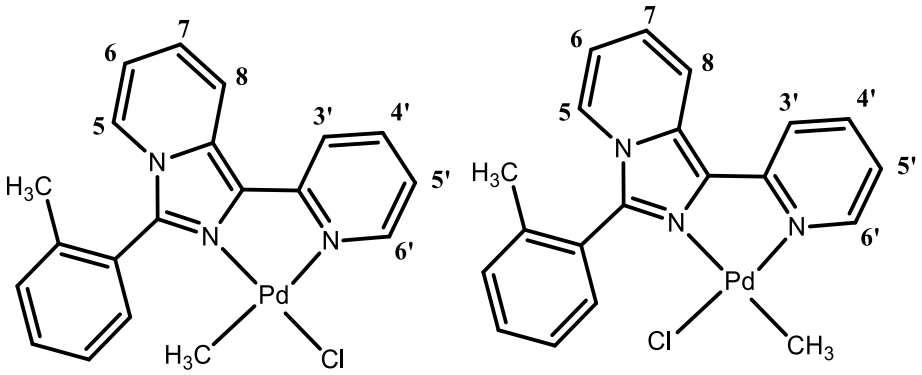
temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a yellow solid **(16)**.

Yield: 0.1353 g (85%).

Found: C 54.95; H 4.61; N 9.27%. Calc. for $C_{20}H_{18}ClN_3Pd$: C, 54.32; H, 4.10; N, 9.50.

Selected ^{1}H NMR data in [$CDCl_3$]:

major stereoisomer: 9.13 (d, 1H, **H6**'); 7.95 (d, 1H, **H8**); 7.85 (m, 2H, **H3'+H4'**); 7.52 (t, 1H, **H5'**); 7.49 (d, 1H, **H5**); 7.41-7.34 (m 3H **Har**); 7.25(7, 1H, **H5'**); 7.19 (dd, 1H, **H7**); 6.78 (t, 1H, **H6**); 2.17 (s, 3H, ***ortho*** **CH_3**); 0.39 (s, 3H, Pd-**CH_3**); 2.15 (s, 1H, ***ortho*** **CH_3**); 0.32 (s, 1H, **CH_3**); *minor stereoisomer*: 8.51 (d, 1H, **H6'**), 2.25 (s, 1H, ***ortho*** **CH_3**); 1.00 (s, 1H, Pd-**CH_3**).



Molecular Weight: 442.25

Synthesis of [PdL^3(CH_3)Cl], (17).

To a solution of **L^3** (0.1131 g; 0.36 mmol) in dichloromethane (25 ml) was added under vigorous stirring [Pd(COD) (Cl)(CH_3)] (0.0974 g; 0.36 mmol). The yellow solution was stirred for 24h at room

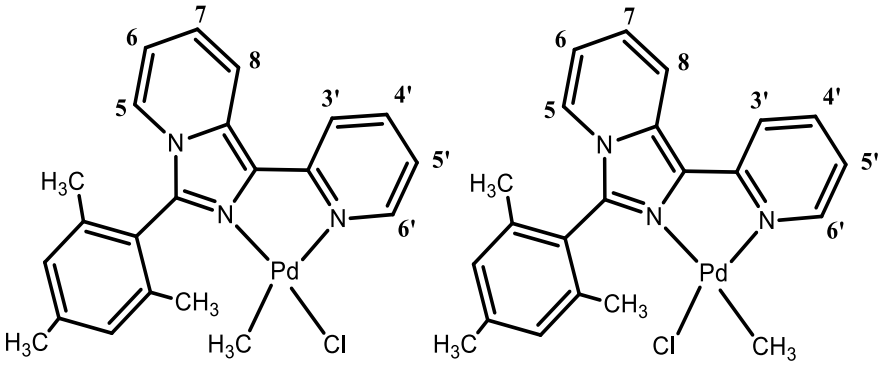
temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a yellow solid **(17)**.

Yield: 0.1286 g (76%).

Found: C 56.99; H 4.97; N 8.70%. Calc. for $C_{22}H_{22}ClN_3Pd$: C, 56.18; H, 4.72; N, 8.93.

Selected ^{1}H NMR data in [$CDCl_3$]:

major stereoisomer: 9.18 (d, 1H, **H6'**); 7.96 (d, 1H, **H8**); 7.88 (m, 2H, **H3'+H4'**); 7.41 (d, 1H, **H5**); 7.30 (t, 1H, **H5'**); 7.22 (t, 1H, **H7**); 7.04 (s, 2H, ***meta* H**); 6.79 (t, 1H, **H6**); 2.41 (s, 3H, ***para* CH_3**); 2.02 (s, 6H, ***ortho* CH_3**); 0.39 (s, 3H, **Pd-CH_3**); *minor stereoisomer*: 8.55 (d, 1H, **H6'**); 6.99 (s, 2H, ***meta* H**); 6.86 (t, 1H, **H6**); 2.38 (s, 3H, ***para* CH_3**); 2.03 (s, 6H, ***ortho* CH_3**); 1.01 (s, 3H, **Pd-CH_3**).



Molecular Weight: 470.30

Synthesis of [PdL^4(CH_3)Cl], (18).

To a solution of **L^4** (0.1255 g; 0.36 mmol) in dichloromethane (25 ml) was added under vigorous stirring [Pd(COD)(Cl)(CH_3)] (0.0971 g; 0.36 mmol). The yellow solution was stirred for 24h at room

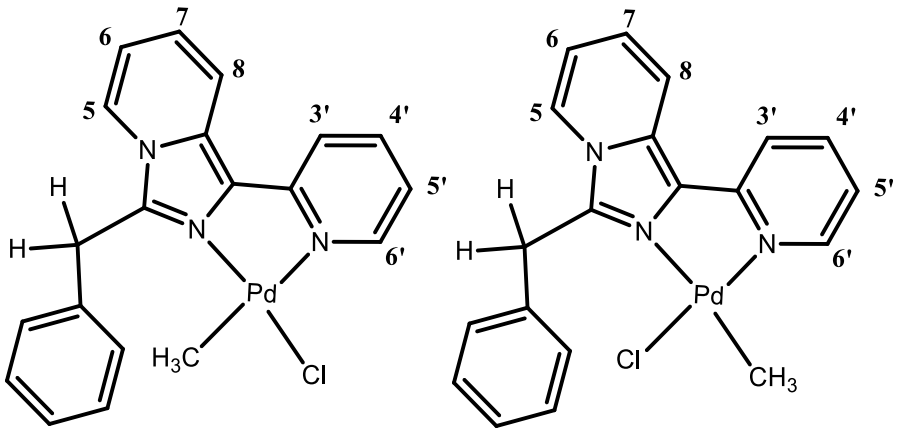
temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a yellow solid **(18)**.

Yield: 0.0429 g (27%).

Found: C 54.95; H 4.69; N 9.29%. Calc. for $C_{20}H_{18}ClN_3Pd$: C, 54.32; H, 4.10; N, 9.50.

Selected ^{1}H NMR data in [$CDCl_3$]:

major stereoisomer: 8.56 (d, 1H, **H$^{6'}$**); 7.89-7.80 (m, 4H, **H^8 H$^{3'}$+H$^{4'}$+H^5**); 7.41 -7.26 (m, 5H, **H^{ar}**); 7.21 (t, 1H, **H^7**); 7.12 (dd, 1H, **H$^{5'}$**); 6.74 (t, 1H, **H^6**); 5.15 (s, 2H, **CH_2**); 1.17 (s, 3H, **Pd-CH_3**); *minor stereoisomer*: 9.23 (d, 1H, **H$^{6'}$**); 6.75 (s, 1H, **H^6**); 5.36 (s, 2H, **CH_2**); 1.26 (s, 3H, **Pd-CH_3**).



Molecular Weight: 442.25

Synthesis of [PdL^5(CH_3)Cl], (19).

To a solution of **L^5** (0.0907 g; 0.3 mmol) in dichloro methane (25 ml) was added [Pd(COD)(Cl)CH_3] (0.0811 g; 0.3 mmol). The yellow

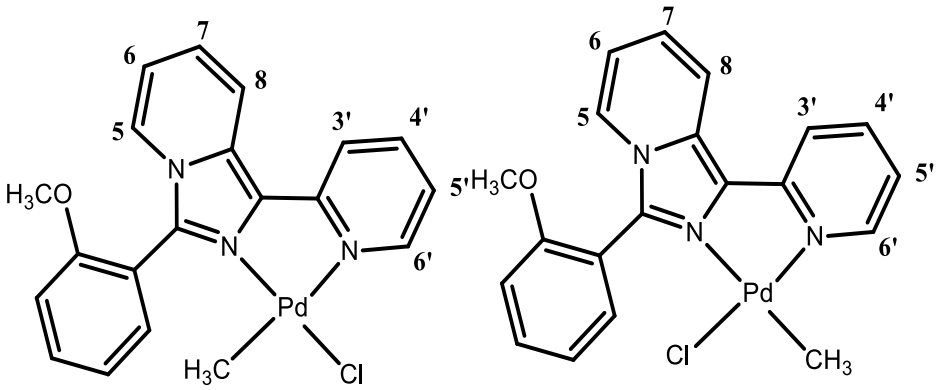
solution was stirred for 24h at room temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a yellow solid **(19)**.

Yield: 0.1182 g (86%).

Found: C 52.39; H 3.62; N 8.98%. Calc. for $C_{20}H_{18}ClN_3Pd$: C, 52.42; H, 3.96; N, 9.17.

Selected ^{1}H NMR data in [$CDCl_3$]:

major stereoisomer: 9.13 (d,1H,**H6'**); 3.81 (s,3H,**CH_3**); 0.38 (s,3H,**Pd-CH_3**) and *minor stereoisomer*: 8.515 (d,1H,**H6'**); 5.30 (s,3H, **OCH_3**); 1.03 (s,3H,**Pd-CH_3**).



Molecular Weight: 458.25

Synthesis of [PdL^6(CH_3)Cl], (20).

To a solution of **L^6** (0.1232 g; 0.36 mmol) in dichloro methane (25 ml) was added [Pd(COD)(Cl)CH_3] (0.0975 g; 0.36 mmol). The yellow solution was stirred for 24h at room temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed

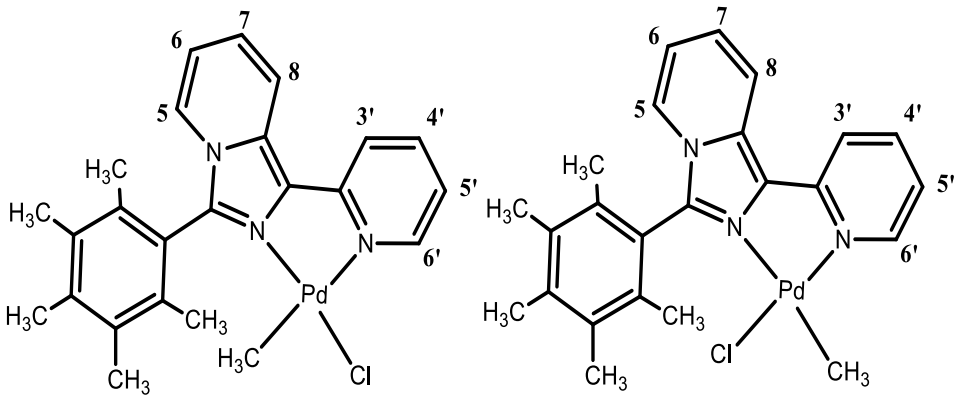
was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a yellow solid. **(20)**

Yield: 0.0950 g (53%).

Found: C 57.81; H 4.80; N 8.26%. Calc. for $C_{24}H_{26}ClN_3Pd$: C, 57.84; H, 5.26; N, 8.43.

Selected ^{1}H NMR data in [CD_2Cl_2]:

major stereoisomer: 9.13 (d,1H,**H6'**); 2.34 (s,3H, ***para*** **CH_3**); 2.26 (s,6H, ***meta*** **CH_3**); 1.90 (s,6H, ***ortho*** CH_3), 0.36 (s,3H,**Pd-CH_3**); *minor stereoisomer*: 8.70 (d,1H,**H6'**); 1.28 (s,3H,**Pd-CH_3**).



Molecular Weight: 498.36

Synthesis of [PtL^1(CH_3)Cl], (21).

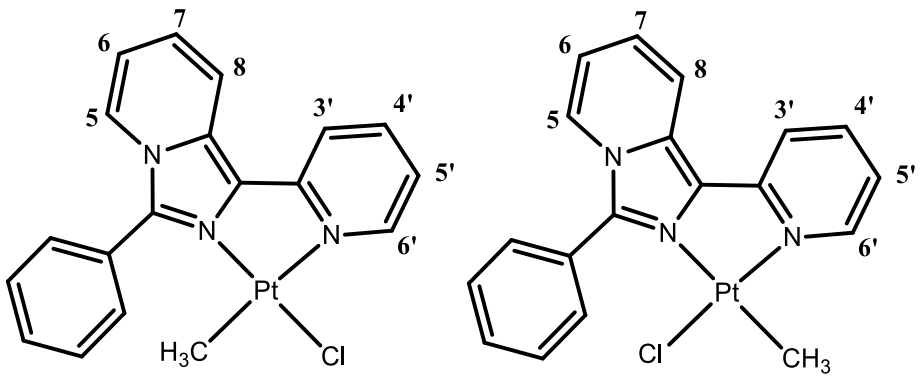
To a solution of **L^1** (0.0379 g; 0.14 mmol) in dichloromethane (25 ml) was added under vigorous stirring [PtCl(CH_3)(DMSO)$_2$] (0.0502 g; 0.14 mmol). The yellow solution was stirred for 72h at room temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a yellow solid **(21)**.

Yield: 0.0528 g (73 %).

Found: C 45.06; H 3.83; N 7.95%. Calc. for $C_{19}H_{16}ClN_3Pt$: C, 44.15; H, 3.12; N, 8.13.

Selected ^{1}H NMR data in [$CDCl_3$]:

major stereoisomer: 9.49 (d, $^3J_{Pt-H}$ too low to be resolved, 1H, **H6'**); 8.00-7.91 (m, 2H, **H8+H4'**); 7.85 (d, 1H, **H5**); 7.75 (d, 1H, **H3'**); 7.65-7.54 (m, 5H, **Har**); 7.30 (t, 1H, **H5'**); 7.22 (dd, 1H, **H7**); 6.82 (t, 1H, **H6**); 0.51 (s, 3H, $^2J_{Pt-H}$= 78.1 Hz, **Pt-CH_3**); *minor stereoisomer:* 8.96 (d, $^3J_{Pt-H}$= 65.5 Hz 1H, **H$^{6'}$**); 1.09 (s, 3H, $^2J_{Pt-H}$= 80.4 Hz, **Pt-CH_3**).



Molecular Weight: 516.89

Synthesis of [PtL^2(CH_3)Cl], (22).

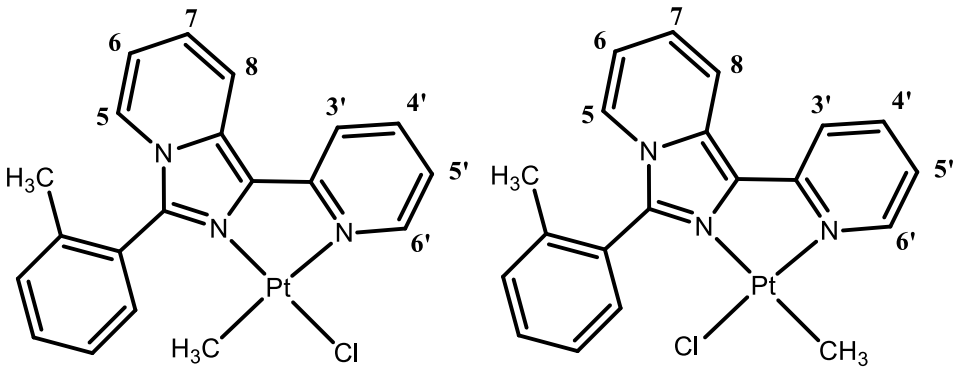
To a solution of **L^2** (0.0400 g; 0.14 mmol) in dichloromethane (25 ml) was added under vigorous stirring [PtCl(CH_3)$(DMSO)_2$] (0.0503 g; 0.14 mmol). The yellow solution was stirred for 72h at room temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a yellow solid **(22)**.

Yield: 0.0661 g (89%).

Found: C 46.21; H 3.87; N 7.68%. Calc. for $C_{20}H_{18}ClN_3Pt$: C, 45.25; H, 3.42; N, 7.91.

Selected ^{1}H NMR data in [$CDCl_3$]:

major stereoisomer: 9.50 (d, $^3J_{Pt-H}$ too low to be resolved, 1H, **H6'**); 7.99-7.92 (m, 2H, **H8+H4'**); 7.87 (d, 1H, **H5**); 7.45 (d, 1H, **H3'**); 7.42-7.34 (m, 4H, **Har**); 7.30 (t, 1H, **H5'**); 7.22 (dd, 1H, **H7**); 6.81 (t, 1H, **H6**); 2.15 (s, 3H, **CH_3**); 0.51 (s, 3H, $^2J_{Pt-H}$= 78.1 Hz, **Pt-CH_3**); *minor stereoisomer:* 8.96 (d, $^3J_{Pt-H}$= 65.5 Hz 1H, **H6**'); 2.23 (s, 3H, **CH_3**); 1.07 (s, 3H, $^2J_{Pt-H}$= 78.8 Hz, **Pt-CH_3**).



Molecular Weight: 530.91

Synthesis of [PtL^3(CH_3)Cl], (23).

To a solution of **L^3** (0.0377 g; 0.12 mmol) in dichloromethane (25 ml) was added under vigorous stirring [PtCl(CH_3)$(DMSO)_2$] (0.0500 g; 0.12 mmol). The yellow solution was stirred for 72h at room temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with

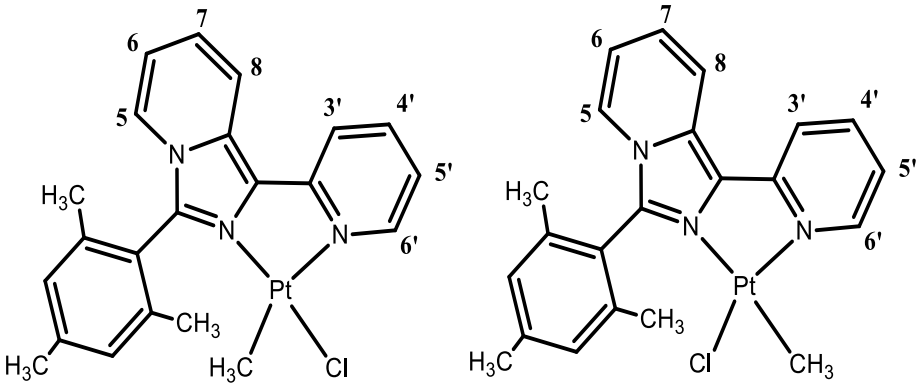
diethyl ether and vacuum pumped to give the analytical sample as a yellow solid **(23)**.

Yield: 0.0603 g (90%).

Found: C 48.16; H 4.29; N 7.31%. Calc. for $C_{22}H_{22}ClN_3Pt$: C, 47.27; H, 3.97; N, 7.52.

Selected ^{1}H NMR data in [CD_2Cl_2]:

major stereoisomer: 9.43 (d,1H, **H6'**); *minor stereoisomer* 8.71 (d, 1H, **H6'**); 8.12-7.89 (m, 6H); 7.50-7.21 (m, 6H); 7.08 (s, 4H, **meta H**); 6.84 (s, 2H, **H6**); 2,41 (*min. st*., s, 6H, **orto CH_3**); 2,20 (*min. st*., s, 3H, **para CH_3**); 2.02 (*Maj. st*., s, 6H, **orto CH_3**); 1.93 (*Maj. st*., s, 3H, **para CH_3**); 1.15 (*min. st*., s, 3H, $^2J_{Pt-H}$= 71.2 Hz, **Pt-CH_3**); 0.53 (*Maj. st*., s, 3H, $^2J_{Pt-H}$=71.4 Hz, **Pt-CH_3**).



Molecular Weight: 558.97

Synthesis of [PtL^4(CH_3)Cl], (24).

To a solution of **L^4** (0.0715 g; 0.25 mmol) in dichloromethane (25 ml) was added under vigorous stirring [PtCl(CH_3)(DMSO)$_2$] (0.0712 g; 0.25 mmol). The yellow solution was stirred for 72h at room temperature then concentrated to small volume and treated with

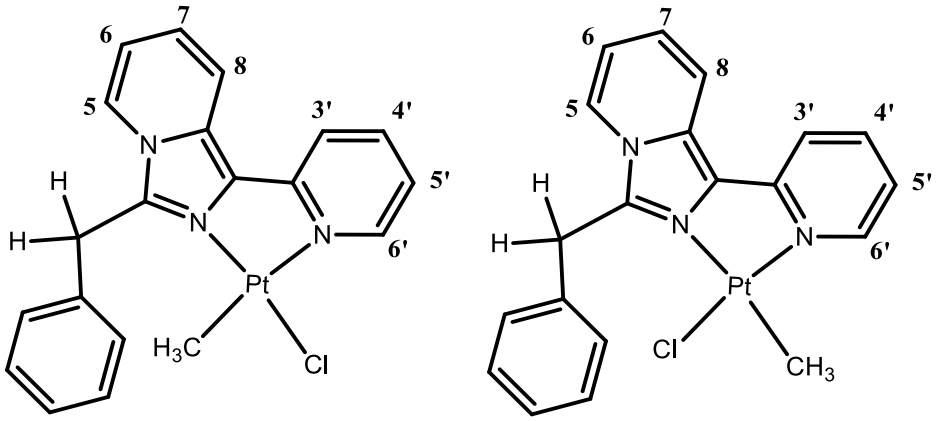
diethyl ether The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a yellow solid **(24)**.

Yield: 0.0305 g (23 %).

Found: C 46.17; H 4.01; N 7.72%. Calc. for $C_{20}H_{18}ClN_3Pt$: C, 45.25; H, 3.42; N, 7.91.

Selected ^{1}H NMR data in [$CDCl_3$]:

9.04 (d, $^3J_{Pt-H}$= 60.0 Hz, 1H, **H6'**); 7.96 t, 1H, **H4'**); 7.90-7.84 (m, 2H, **H8**+**H5**); 7.76 (d, 1H, **H3'**); 7.44-7.24 (m, 5H, **Har**); 7.23-7.13 (m, 1H, **H5'**+**H7**); 6.81 (t, 1H, **H6**); 5.30 (s, 2H, **CH_2**); 1.24 (s, 3H, $^2J_{Pt-H}$= 80.1 Hz, **Pt-CH_3**).



Molecular Weight: 530.91

Synthesis of [PtL^5(CH_3)Cl], (25).

To a solution of **L^5** (0.0665 g; 0.22mmol) in dichloro methane (25 ml) was added under vigorous stirring [PtCl(CH_3)$(DMSO)_2$] (0.0901 g; 0.22mmol). The yellow solution was stirred for 72h at room temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with

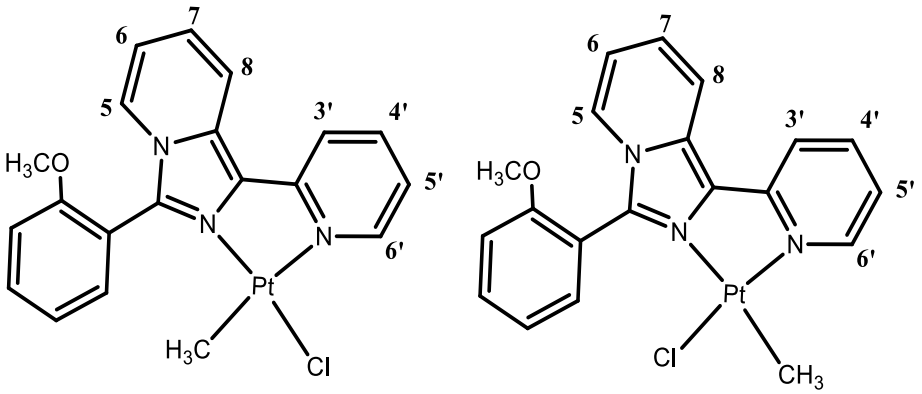
diethyl ether and vacuum pumped to give the analytical sample as a yellow solid **(25).**

Yield: 0.0758 g (63%).

Found: C 42.22; H 3.12; N 7.75%. Calc. for $C_{20}H_{18}ClN_3Pt$: C, 45.25; H, 3.42; N, 7.91

Selected ^{1}H NMR data in [$CDCl_3$]:

majority stereoisomer: 9.535 (d,1H,**H6'**); 3.81 (s,3H,**CH_3**); 0.57 (s,3H,$^2J_{Pt-H}$=80 Hz,**Pt-CH_3**); *minor stereoisomer* 9.005 (d,1H,**H6'**); 2.62 (s,3H,**CH_3**); 1.20 (s,3H,$^2J_{Pt-H}$=78 Hz,**Pt-CH_3**).



Molecular Weight: 546.91

Synthesis of [PtL^6(CH_3)Cl], (26).

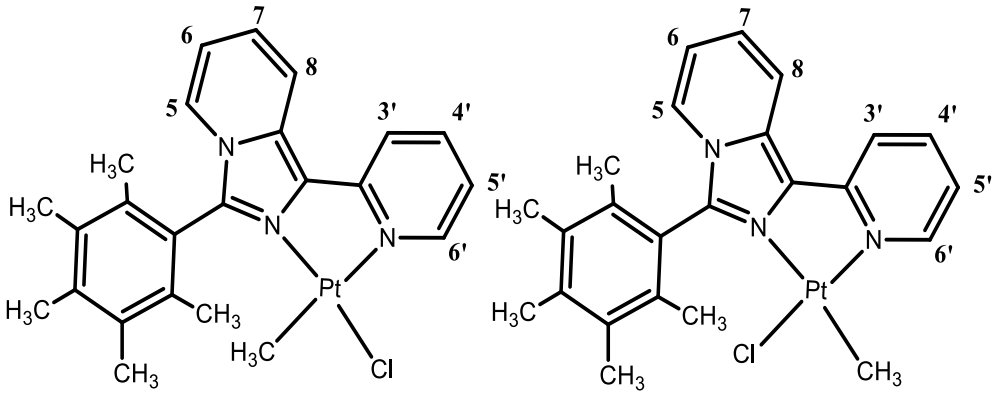
To a solution of **L^6** (0.1005 g; 0.29 mmol) in dichloro methane (25 ml) was added under vigorous stirring [PtCl(CH_3)$(DMSO)_2$] (0.1165 g; 0.29 mmol). The yellow solution was stirred for 72h at room temperature then concentrated to small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a yellow solid **(26).**

Yield: 0.1420 g (83%).

Found: C 49.08; H 4.07; N 7.01%. Calc. for $C_{24}H_{26}ClN_3Pt$: C, 49.11; H, 4.46; N, 7.16.

Selected ^{1}H NMR data in [CD_3COCD_3]:

9.455 (d, 1H, **H6**'); 8.36 (d, 1H, **H8**); 8.27 (d, 1H, **H3'**); 8.16 (t, 1H, **H4'**); 7.525 (d, 1H, **H5**); 7.47 (t, 1H, **H5'**); 7.41 (t, 1H, **H7**); 7.03 (t, 1H, **H6**); 2.35 (s, 3H, **para CH_3**); 2.28 (s, 6H, **orto CH_3**); 1.90 (s, 6H, **meta CH_3**); 0.40 (s, 3H, $J^3_{Pt\text{-}H}$=80Hz, **Pt-CH_3**).



Molecular Weight: 587,02

Synthesis of [PtL^1(CH_3)$_2$], (27).

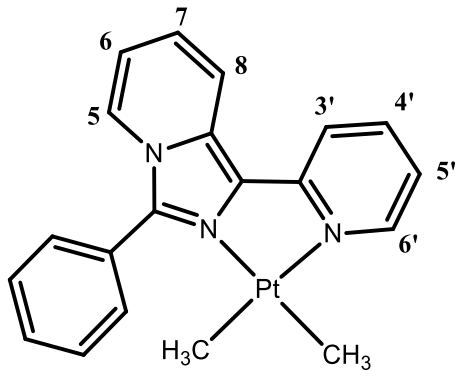
To a solution of **L^1** (0.0732 g; 0.27 mmol) in acetone (25 ml) was added under vigorous stirring [Pt(CH_3)$_2$(DMSO)$_2$] (0.1004 g; 0.27 mmol). The yellow solution was stirred for 24h at room temperature then concentrated to a small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a pale green solid **(27)**.

Yield: 0.0616 g (46 %). M.p.:250°C

Found: C 49.03; H 4.04; N 8.29%. Calc. for $C_{20}H_{19}N_3Pt$: C, 48.38; H, 3.86; N, 8.46.

Selected ^{1}H NMR data in [CD_3COCD_3]:

9.04 (d, 1H, $^3J_{Pt-H}$= 28.1 Hz**, H6'**); 8.29 (d, 1H, **H8**); 8.19 (t, 1H, **H4'**); 8.14 (d, 1H, **H3'**); 8.06 (d, 1H, **H5**); 7.77-7.60 (m, 5H, **Har**); 7.34 (t, 2H, **H5'+H7**); 7.00 (t, 1H, **H6**); 0.76 (s, 3H, $^2J_{Pt-H}$= 90.0 Hz, **Pt-CH_3**); 0.26 (s, 3H,$^2J_{Pt-H}$= 89.4 Hz, **Pt-CH_3**).



Molecular Weight: 496.47

Synthesis of [PtL^2(CH_3)$_2$], (28).

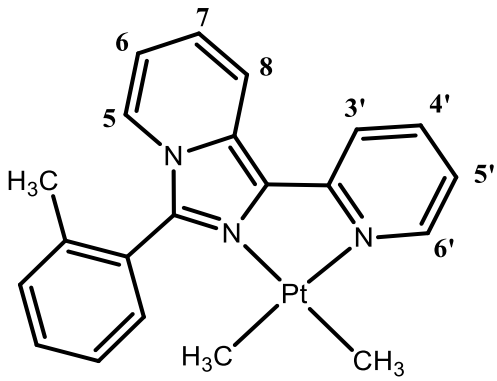
To a solution of **L^2** (0.0667 g; 0.22 mmol) in acetone (25 ml) was added under vigorous stirring [Pt(CH_3)$_2$(DMSO)$_2$] (0.0860 g; 0.22 mmol). The yellow solution was stirred for 24h at room temperature then concentrated to a small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a pale green solid **(28)**.

Yield: 0.085 g (76%). M.p.:269°C

Found: C 50.05; H 4.51; N 8.02%. Calc. for $C_{21}H_{21}N_3Pt$: C, 49.41; H, 4.15; N, 8.23.

Selected ^{1}H NMR data in [CD_3COCD_3]:

9.03 (d, 1H, $^3J_{Pt-H}$= 28.1 Hz**, H6'**); 8.31 (d, 1H, **H8**); 8.20 (t, 1H, **H4'**); 8.14 (d, 1H, **H3'**); 7.74 (d, 1H, **H5**); 7.58-7.32 (m, 4H, **Har**); 7.06-6.98 (m, 2H, **H5'+H7**); 6.78 (t, 1H, **H6**); 2.21 (s, 1H, **CH_3**); 0.75 (s, 3H, $^2J_{Pt-H}$= 88.5 Hz, **Pt-CH_3**); 0.24 (s, 3H,$^2J_{Pt-H}$= 90.6 Hz, **Pt-CH_3**).



Molecular Weight: 510.50

Synthesis of [PtL^3(CH_3)$_2$], (29).

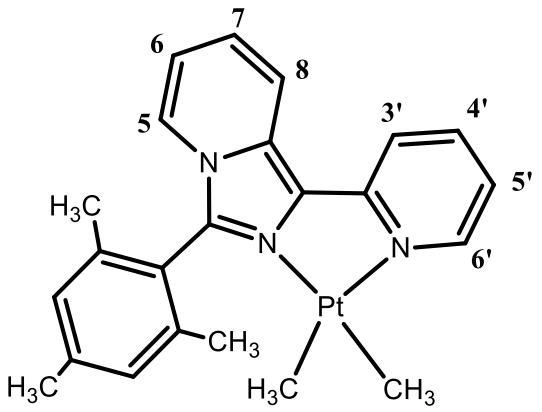
To a solution of **L^3** (0.0626 g; 0.20 mmol) in acetone (25 ml) was added under vigorous stirring [Pt(CH_3)$_2$(DMSO)$_2$] (0.0805 g; 0.20 mmol). The yellow solution was stirred for 24h at room temperature, then concentrated to a small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a pale green solid **(29).**

Yield: 0.0602 g (83%). M.p.:275°C

Found: C 51.97; H 4.89; N 7.61%. Calc. for $C_{23}H_{25}N_3Pt$: C, 51.29; H, 4.68; N, 7.80.

Selected ^{1}H NMR data in [CD_3COCD_3]:

9.03 (d, 1H, $^3J_{Pt-H}$= 28.0 Hz**, H6'**); 8.32 (d, 1H, **H8**); 8.21 (t, 1H, **H4'**); 8.16 (d, 1H, **H3'**); 7.59 (d, 1H, **H5**); 7.37-7.31 (m, 2H, **H5'+ H7**); 7.08 (s, 2H, **Har**); 7.02 (m, 1H, **H6**); 2.38 (s, 3H, **para CH_3**); 2.01 (s, 6H, **ortho CH_3**); 0.77 (s, 3H, $^2J_{Pt-H}$= 88.5 Hz, **Pt-CH_3**); 0.28 (s, 3H,$^2J_{Pt-H}$= 90.6 Hz, **Pt-CH_3**).



Molecular Weight: 538.55

Synthesis of [PtL^4(CH_3)$_2$], (30).

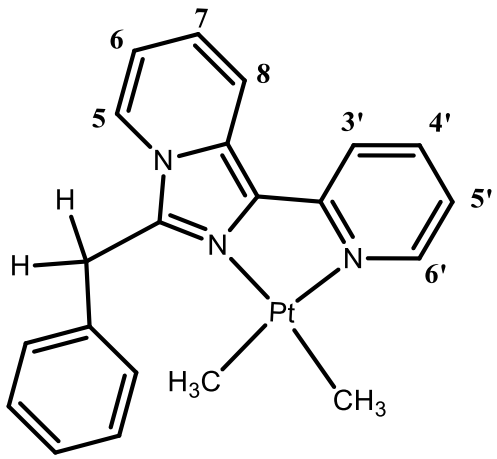
To a solution of **L^4** (0.0372 g; 0.13 mmol) in acetone (25 ml) was added under vigorous stirring [Pt(CH_3)$_2$(DMSO)$_2$] (0.0502 g; 0.13 mmol). The solution was stirred for 72h at room temperature, then concentrated to a small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a pale yellow solid **(30)**.

Yield: 0.0504 g (76%). M.p.:227°C

Found: C 50.51; H 4.62; N 8.03%. Calc. for $C_{21}H_{21}N_3Pt$: C, 49.41; H, 4.15; N, 8.23.

Selected ^{1}H NMR data in [CD_3COCD_3]:

9.04 (d, 1H, $^3J_{Pt-H}$= 28.4 Hz**, H6'**); 8.16 (pt, 2H, **H4'**+**H8**); 8.10 (d, 2H, **H5**+**H3'**); 7.44-7.26 (m, 5H, **Har**); 7.24-7.19 (m, 2H, **H5'+H7**); 6.91 (t, 1H, **H6**); 4.90 (s, 2H, **CH_2**); 1.10 (s, 3H, $^2J_{Pt-H}$= 87.0 Hz, **Pt-CH_3**); 0.91 (s, 3H,$^2J_{Pt-H}$= 87.9 Hz, **Pt-CH_3**).



Molecular Weight: 510.50

Synthesis of [PtL^5(CH_3)$_2$], (31).

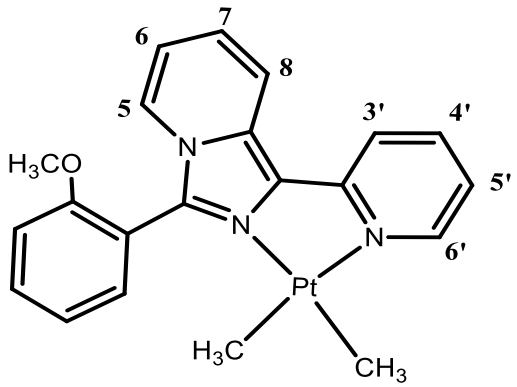
To a solution of **L^5** (0.0634 g; 0.21mmol) in acetone (25 ml) was added under vigorous stirring [Pt(CH_3)$_2$(DMSO)$_2$] (0.0801 g; 0.21mmol). The solution was stirred for 72h at room temperature, then concentrated to a small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a pale yellow solid **(31)**.

Yield: 0.0773 g (70%). M.p.: 222°C

Found: C 49.38; H 3.79; N 8.06%. Calc. for $C_{21}H_{21}N_3Pt$: C, 49.41; H, 4.15; N, 8.23.

Selected ^{1}H NMR data in [CD_3COCD_3]:

9.035 (d,1H,**H6'**); 8.29 (d,1H,**H8**); 8.16 (m,2H,**H3'+H4'**); 7.775 (d,1H,**H5**); 7.63 (t,1H,**Har**); 7.565 (d,1H,**Har**); 7.34 (m,2H,**Har+H5'**); 7.30 (d,1H,**Har**); 7.13 (t,1H,**H7**); 6.99 (t,1H,**H6**); 3.85 (s,3H,**OCH3**); 0.76 (s,3H, $^2J_{Pt-H}$=88Hz, **Pt-CH_3);** 0.30 (s,3H,$^2J_{Pt-H}$=88Hz**, Pt-CH_3**).



Molecular Weight: 526.49

Synthesis of [PtL^6(CH_3)$_2$], (32).

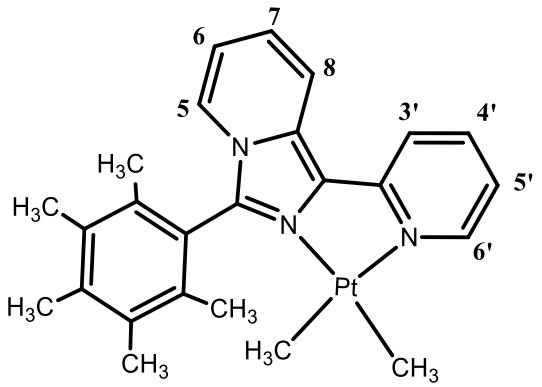
To a solution of **L^6** (0.1027 g; 0.30 mmol) in acetone (25 ml) was added under vigorous stirring [Pt(CH_3)$_2$(DMSO)$_2$] (0.1000 g; 0.30 mmol). The solution was stirred for 72h at room temperature, then concentrated to a small volume and treated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and vacuum pumped to give the analytical sample as a pale yellow solid **(32)**.

Yield: 0.0968 g (57 %). M.p.: 232°C

Found: C 52.96; H 4.74; N 7.27%. Calc. for $C_{25}H_{29}N_3Pt$: C, 52.99; H, 5.16; N, 7.42.

Selected ^{1}H NMR data in [CD_3COCD_3]:

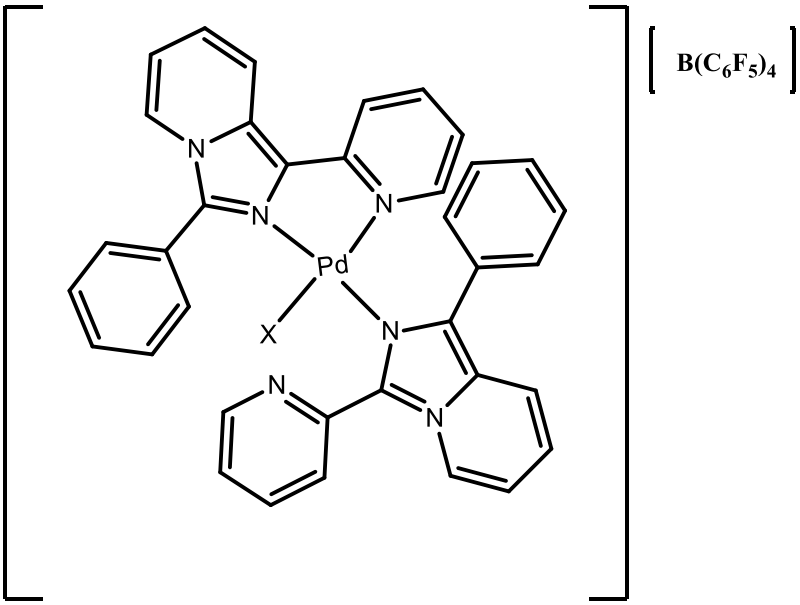
9.04 (d,1H,**H6'**); 8.32 (d,1H,**H8**); 8.22 (d,1H,**H3'**); 8.16 (t,1H,**H4'**); 7.53 (d,1H,**H5**); 7.34 (t,2H,**H5'+H7**); 6.98 (t,1H,**H6**); 2.35 (s,3H, ***para*** **CH_3**); 2.29 (s,6H, ***meta*** **CH_3**); 1.91 (s,6H, ***ortho*** **CH_3**); 0.75 (s,3H,$^2J_{Pt-H}$=88 Hz, **Pt-CH_3**); 0.24 (s,3H, $^2J_{Pt-H}$=92 Hz, **Pt-CH_3**).



Molecular Weight: 526.49

Reaction with [PdL^1(CH_3)Cl] and [($Et_3Si)_2H$][B($C_6F_5)_4$] in NMR tube

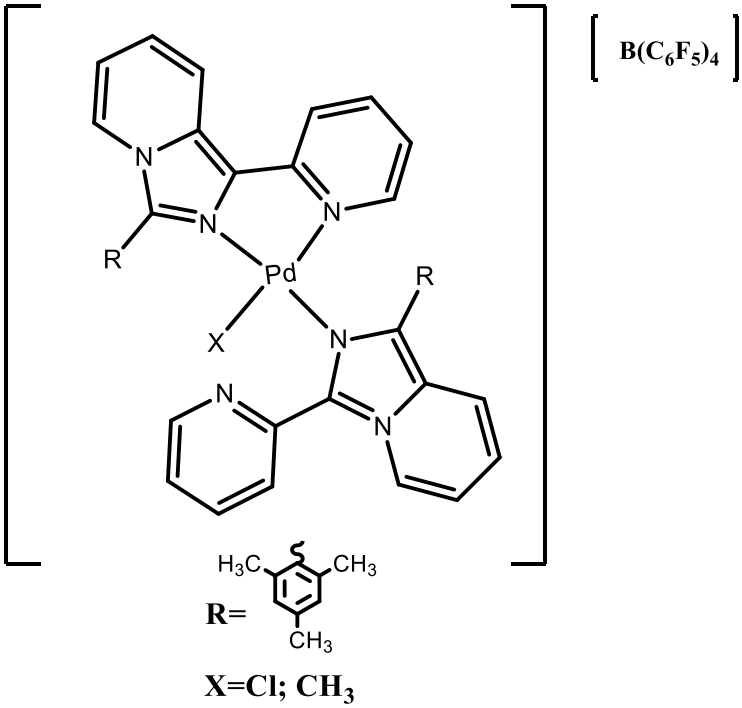
In a glove box under argon atmosphere complex **15** (0.0178 g; 0.039 mmol) was dissolved in deuterated benzene in an NMR tube. To the yellow solution was added [($Et_3Si)_2H$][B($C_6F_5)_4$] (0.0365 g; 0.039 mmol) and immediately the colour of the solution became dark. The NMR tube was left to sonicate for 4hours.



X=Cl; CH_3

Reaction with $[PdL^3(CH_3)Cl]$ and $[(Et_3Si)_2H][B(C_6F_5)_4]$ in NMR tube

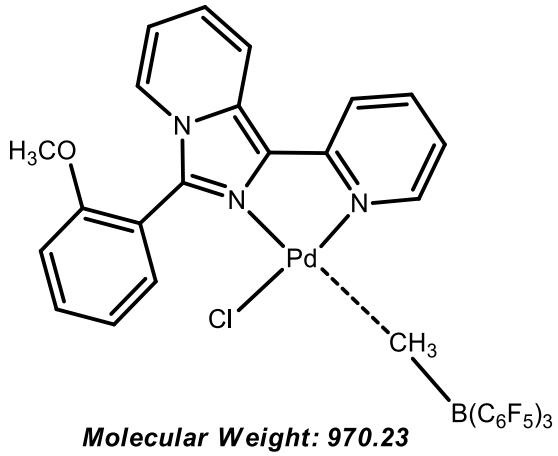
In a glove box under argon atmosphere complex **17** (0.015 g; 0.031 mmol) was dissolved in deuterated benzene in an NMR tube. To the yellow solution was added $[(Et_3Si)_2H][B(C_6F_5)_4]$ (0.029 g; 0.031 mmol) and immediately the colour of the solution became dark. The NMR tube was left to sonicate for 4hours.



Reaction with (PtL^5(CH$_3$)Cl] and B(C$_6$F$_5$)$_3$ in NMR tube

In a glove box under argon atmosphere complex **19** (0.0179 g; 0.032 mmol) was dissolved in deuterated benzene in an NMR tube. To the yellow solution was added B(C$_6$F$_5$)$_3$ (0.0159g; 0.032mmol). The NMR tube was left to sonicate for 1hour to dissolve completely reagents.

For this reaction there are no data to propose because it wasn't possible to characterize the possible product due to the pandemic Covid 19.

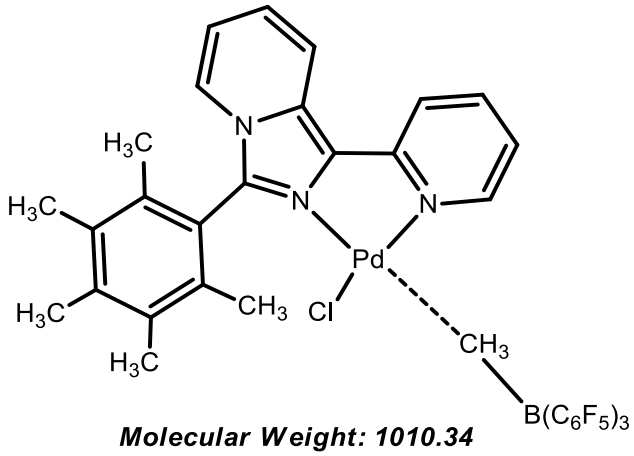


Molecular Weight: 970.23

Reaction with [PtL^6(CH$_3$)Cl] and B(C$_6$F$_5$)$_3$ in NMR tube

In a glove box under argon atmosphere complex **20** (0.0195 g; 0.033 mmol) was dissolved in deuterated benzene in an NMR tube. To the yellow solution was added B(C$_6$F$_5$)$_3$ (0.0159 g; 0.033 mmol). The NMR tube was left to sonicate for 1hour to dissolve completely reagents.

For this reaction there are no data to propose because it wasn't possible to characterize the possible product due to the pandemic Covid 19.



Molecular Weight: 1010.34

Synthesis of $[AuL^1Cl_2][PF_6]$, (33).

To a solution of **L^1** (0.1356 g, 0.5 mmol) in acetonitrile (15ml) was added an aqueous solution of $NaAuCl_4$ (0.2000 g, 0.5 mmol). To the resulting green suspension was added an excess of KPF_6 the mixture was stirred and protected from light for overnight at room temperature, then filtered and washed with small aliquots of ethanol and diethyl ether.

The product was crystallized from acetone/diethyl ether to obtain a pale green solid **(33)**.

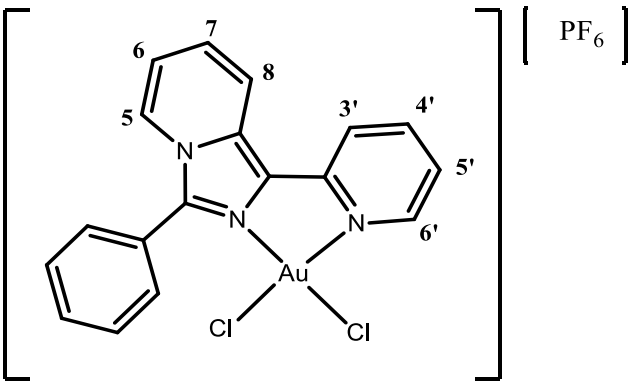
Yield: 0.2498 g (69%). M.p.: 205°C

Found: C 31.58; H 1.75; N 6.01%. Calc. for $C_{18}H_{13}AuCl_2F_6N_3P$: C, 31.60; H, 1.92; N, 6.14.

Selected ^{1}H NMR data in $[CD_3COCD_3]$:

9.42 (d,1H,**H6**'); 8.79 (d,1H,**H3'**); 8.65 (t,1H,**H4'**); 8.29 (d,1H,**H5**); 7.94-7.89 (m,3H,**Har+H8**); 7.83 (t,1H,**H5'**); 7.74-7.69 (m,4H,**H7+Har**); 7.43 (t,1H,**H6**).

IR, $\tilde{\nu}_{max}$/cm^{-1} 840 (PF_6^-).



Molecular Weight: 684.15

Synthesis of $[AuL^2Cl_2][PF_6]$, (34).

To a solution of **L^2** (0.1404 g, 0.5 mmol) in acetonitrile (15ml) was added an aqueous solution of $NaAuCl_4$ (0.2010 g, 0.5 mmol). To the resulting green suspension was added an excess of KPF_6 the mixture was stirred and protected from light for overnight at room temperature, then filtered and washed with small aliquots of ethanol and diethyl ether.

The product was crystallized from acetone/diethyl ether to obtain a pale green solid **(34).**

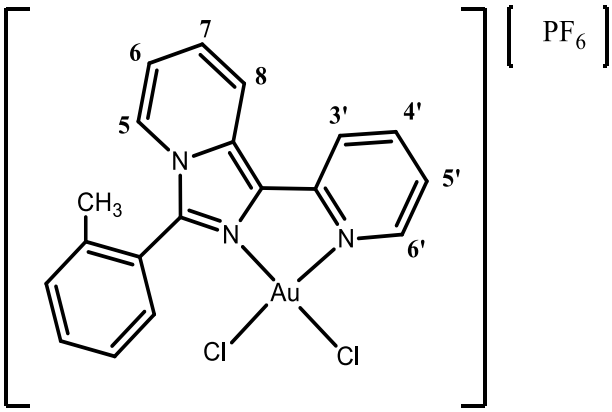
Yield: 0.2657g (75%). M.p.: 215°C

Found: C 32.67; H 1.98; N 5.90%. Calc. for $C_{19}H_{15}AuCl_2F_6N_3P$: C, 32.69; H, 2.17; N, 6.02.

Selected ^{1}H NMR data in $[CD_3COCD_3]$:

9.29 (d,1H,**H6'**); 8.65 (d,1H,**H5**); 8.50 (m,2H,**H3+H4'**); 7.93 (d,1H,**H8**); 7.79 (t,1H,**H5'**); 7.70 (t,1H,**H7**); 7.57-7.54 (m,2H,**Har**); 7.40-7.38 (m,2H,**Har**); 7.30 (t,1H,**H6**); 2.12 (s, 3H, **CH_3**).

IR, $\tilde{\nu}_{max}$/cm^{-1} 840 (PF_6^-).



Molecular Weight: 698.18

Synthesis of $[AuL^3Cl_2][PF_6]$, (35).

To a solution of **L^3** (0.1506 g, 0.5 mmol) in acetonitrile (15ml) was added an aqueous solution of $NaAuCl_4$ (0.2021 g, 0.5 mmol).

To the resulting green suspension was added an excess of KPF_6 the mixture was stirred and protected from light for overnight at room temperature, then filtered and washed with small aliquots of ethanol and diethyl ether.

The product was crystallized from acetone/diethyl ether to obtain a pale green solid **(35)**.

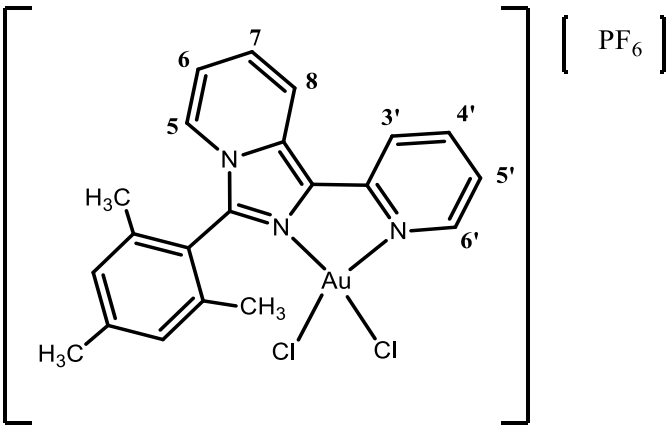
Yield: 0.2246 g (78%). M.p.: 218°C

Found: C 34.70; H 2.41; N 5.67%. Calc. for $C_{21}H_{19}AuCl_2F_6N_3P$: C, 34.73; H, 2.64; N, 5.79.

Selected ^{1}H NMR data in $[CD_3COCD_3]$:

9.44 (d,1H,**H6'**); 8.79 (d,1H,**H5**); 8.64 (m,2H,**H3+H4'**); 8.00 (d,1H,**H8**); 7.93 (t,1H,**H5'**); 7.84 (t,1H,**H7**); 7.47 (t,1H,**H6**); 7.18 (s, 2H, ***meta* H**); 2.43 (s, 3H, ***para* CH_3**); 2.10 (s, 6H, ***ortho* CH_3**).

IR, $\tilde{\nu}_{max}$/cm^{-1} 840 (PF_6^-).



Molecular Weight: 726.23

Synthesis of $[AuL^4Cl_2][PF_6]$, (36).

To a solution of **L^4** (0.1603 g, 0.5 mmol) in acetonitrile (15ml) was added an aqueous solution of $NaAuCl_4$ (0.2015 g, 0.5 mmol). To the resulting green suspension was added an excess of KPF_6 the mixture was stirred and protected from light for overnight at room temperature, then filtered and washed with small aliquots of ethanol and diethyl ether.

The product was crystallized from acetone/diethyl ether to obtain a green solid **(36).**

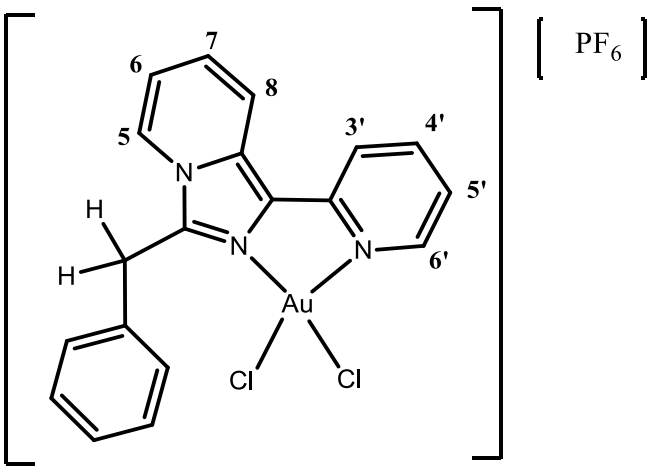
Yield: 0.2289 g (61%). M.p.: 170°C

Found: C 32.67; H 1.98; N 5.90%. Calc. for $C_{19}H_{15}AuCl_2F_6N_3P$: C, 32.69; H, 2.17; N, 6.02.

Selected ^{1}H NMR data in $[CD_3COCD_3]$:

9.49 (d,1H,**H6'**); 8.74 (d,1H,**H3'**); 8.61 (d,2H,**H8+H5**); 7.92 (t,1H,**H4'**); 7.78 (t,1H,**H5'**); 7.41 (m,7H, **Har+H7+H6**); 5.58 (s,2H,**CH_2**).

IR, $\tilde{\nu}_{max}$/cm^{-1} 840 (PF_6^-).



Molecular Weight: 698.18

Synthesis of $[AuL^6Cl_2][PF_6]$, (37).

To a solution of **L^6** (0.0980 g, 0.5 mmol) in acetonitrile (15ml) was added an aqueous solution of $NaAuCl_4$ (0.2010 g, 0.5 mmol To the resulting green suspension was added an excess of KPF_6 the mixture was stirred and protected from light for overnight at room temperature, then filtered and washed with small aliquots of ethanol and diethyl ether.

The product was crystallized from acetone/diethyl ether to obtain a green solid **(37).**

Yield: 0.2691 g (71%). M.p. 230°C

Selected ^{1}H NMR data in [CD_3COCD_3]:

9.42 (d, 1H, **H6'**); 8.79 (d, 1H, **H8**); 8.65 (d, 1H, **H3'**); 8.63 (t, 1H, **H4'**); 7.91 (m, 2H, **H5+H5'**); 7.82 (dd, 1H, **H7**); 7.41 (t, 1H, **H6**); 2.37 (s, 3H, ***para* CH3**); 2.29 (s,6H, ***meta* CH3**) 1.97 (s,6H, ***ortho* CH3**)

IR, $\tilde{\nu}_{max}$/cm^{-1} 840 (PF_6^-).

Synthesis of [AuL^1(OH)Cl][PF_6], (38).

To a solution of **L^1** (0.1342 g, 0.5 mmol) in acetonitrile (15ml) were added an aqueous solution of $NaAuCl_4$ (0.2010 g, 0.5 mmol) and solid KPF_6 (2.7602 g, 15 mmol, in excess). The resulting green suspension was refluxed for 1h, became amber and was evaporated to dryness. The product was crystallized from dichloro methane-diethyl ether to obtain a yellow solid **(38)**.

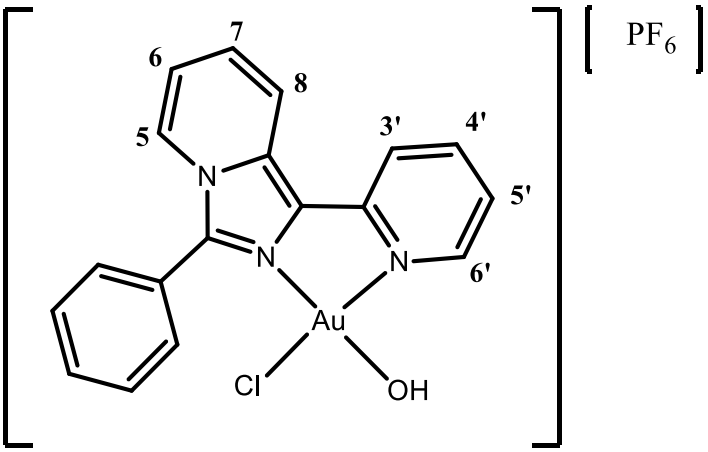
Yield: 0.0798 g (22%). M.p.:168°C

Found: C 32.45; H 1.93; N 6.18%. Calc. for $C_{18}H_{14}AuClF_6N_3OP$: C, 32.48; H, 2.12; N, 6.31.

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.62 (d,1H, **H6'**); 8.50 (d,1H,**H3'**); 8.40 (t,1H,**H4'**); 8.23 (d,1H,**H5**); 8.06 (d,1H,**H8**); 7.88 (d,2H,**Har**); 7.61 (m,3H,**Har**); 7.54 (t,1H,**H5'**); 7.45 (t,1H,**H7**); 7.02 (t,1H,**H6**); 4.45 (wide signal, **OH**).

IR, v~max/cm-1 840 (PF6-).



Molecular Weight: 665.71

Synthesis of [AuL^2(OH)Cl][PF_6], (39).

To a solution of **L^2** (0.1399 g, 0.5 mmol) in acetonitrile (15ml) were added an aqueous solution of $NaAuCl_4$ (0.2060 g, 0.5 mmol) and solid KPF_6 (2.7620 g, 15mmol, in excess). The resulting green suspension was refluxed for 1h, became amber and was evaporated to dryness. The product was crystallized from dichloro methane-diethyl ether to obtain a yellow solid **(39)**.

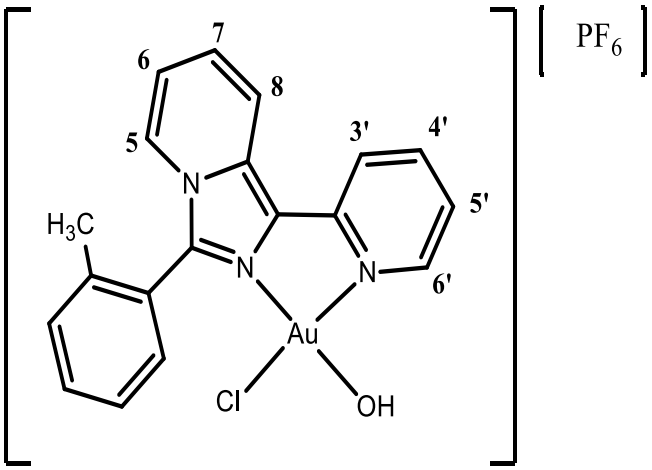
Yield: 0.0889 g (28%). M.p.:173°C

Found: C 33.55; H 2.16; N 6.05%. Calc. for $C_{19}H_{16}AuClF_6N_3OP$: C, 33.57; H, 2.37; N, 6.18.

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.48 (d,1H,**H6'**); 8.33 (t,1H,**H4'**); 8.17 (d,1H,**H3'**); 8.01 (d,1H,**H5**); 7.84 (d,1H,**H8**); 7.46 (t,1H,**H5'**); 7.41-7.38 (m,4H,**Har**); 7.31 (t,1H,**H7**); 6.91 (t,1H,**H6**); 3.93 (wide signal, **OH**) 2.16 (s,3H, ***ortho* CH3**).

IR, v~max/cm-1 840 (PF6-).



Molecular Weight: 679.73

Synthesis of [AuL^3(OH)Cl][PF$_6$], (40).

To a solution of **L^3** (0.1603 g, 0.5 mmol) in acetonitrile (15ml) were added an aqueous solution of $NaAuCl_4$ (0.2020 g, 0.5 mmol) and solid KPF_6 (2.7600 g, 15mmol, in excess). The resulting green suspension was refluxed for 1h, became amber and was evaporated to dryness. The product was crystallized from dichloro methane-diethyl ether to obtain a yellow solid **(40)**.

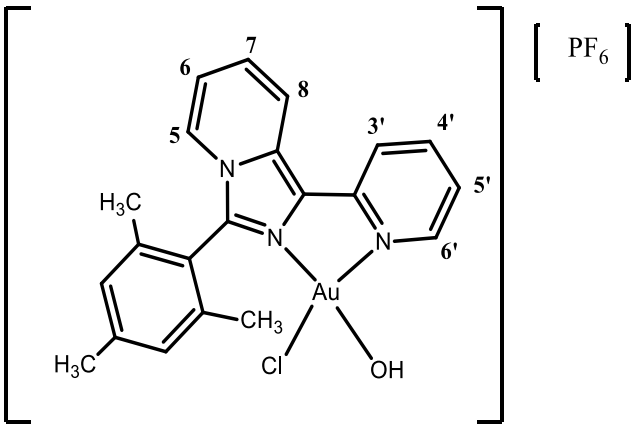
Yield: 0.09 g (25%). M.p.: 175°C

Found: C 35.61; H 2.60; N 5.82%. Calc. for $C_{21}H_{20}AuClF_6N_3OP$: C, 35.64; H, 2.85; N, 5.94.

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.41 (d,1H,**H6'**); 8.33 (t,1H,**H4'**); 8.16 (d,1H,**H3'**); 8.15 (d,1H,**H5**); 7.53 (d,1H,**H8**); 7.45 (t,1H,**H5'**); 7.40 (t,1H,**H7**); 6.99 (s,2H, ***meta* H**); 6.90 (t,1H,**H6**); 4.69 (wide signal, **OH**); 2.31 (s,3H, ***para* CH3**); 1.87 (s,6H, ***ortho* CH3**).

IR, v~max/cm-1 840 (PF6-).



Molecular Weight: 707.79

Reaction with L4 and $NaAuCl_4$

To a solution of **L^4** (0.1589 g, 0.5 mmol) in acetonitrile (15ml) were added an aqueous solution of $NaAuCl_4$ (0.2001 g, 0.5 mmol) and solid KPF_6 (2.7600 g, 15mmol, in excess). The resulting green suspension was refluxed for 1h, became amber and was evaporated to dryness. It was crystallized from dichloro methane-diethyl ether to obtain a mixture of products.

Synthesis of $[AuL^1(OH)_2][PF_6]$, (41).

To a solution of $[AuL^1Cl_2][PF_6]$ (0.0100 g, 0.14 mmol) in acetone (20 ml) was added an aqueous suspension of Ag_2O (0.0301 g, 0.14

mmol). The mixture was stirred and protected from light overnight at room temperature. AgCl was removed by filtration and the solution evaporated to dryness under reduced pressure and the residue was extracted with acetonitrile and filtered throught Celite. The solution was concentrated to a small volume and treated with diethyl ether to give a yellow solid **(41).**

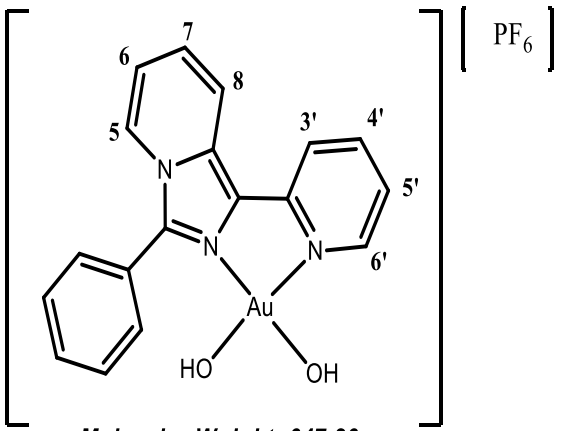
Yield: 0.0623 g (48%). M.p.: 130°C

Found: C 33.37; H 2.13; N 6.36%. Calc. for $C_{18}H_{15}AuF_6N_3O_2P$: C, 33.40; H, 2.34; N, 6.49.

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.93 (d,1H,**H6'**); 8.39 (t,1H,**H4'**); 8.27 (d,1H,**H8**); 8.24 (d,2H,**H3'**+**H5**); 7.72 (t,2H,**H5**'+**Har**); 7.65 (t,2H,**H6**+**H7**); 7.53 (t,4H,**Har**); 2.97 (s,1H,**OH**); 1.03 (s,1H,**OH**).

IR, v~max/cm-1 840 (PF6-).



Molecular Weight: 647.26

Synthesis of [$AuL^2(OH)_2$][PF_6], (42).

To a solution of [AuL^2Cl_2][PF_6] (0.0989 g, 0.14 mmol) in acetone (20 ml) was added an aqueous suspension of Ag_2O (0.0300 g, 0.14

mmol). The mixture was stirred and protected from light overnight at room temperature. AgCl was removed by filtration and the solution evaporated to dryness under reduced pressure and the residue was extracted with acetonitrile and filtered throught Celite. The solution was concentrated to a small volume and treated with diethyl ether to give a yellow solid **(42)**.

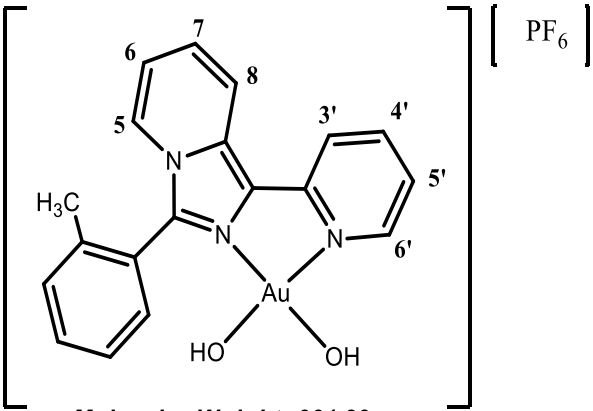
Yield 0.0492 g (54%). M.p.: 143°C

Found: C 34.48; H 2.36; N 6.22%. Calc. for $C_{19}H_{17}AuF_6N_3O_2P$: C, 34.51; H, 2.59; N, 6.35.

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.95 (d,1H,**H6'**); 8.41 (t,1H,**H4'**); 8.29 (d,1H, **H8**); 8.24 (d,1H, **H3'**+**H5**); 7.74 (t,2H, **H5'**+**Har**); 7.66 (t,2H, **H6**+**H7**); 7.55 (m,3H,**Har**); 2.99 (s,1H,**OH**); 2.23 (s,3H,**CH3**); 1.01 (s,1H,**OH**).

IR, v~max/cm-1 840 (PF6-).



Molecular Weight: 661.29

Synthesis of [$AuL^3(OH)_2$][PF_6], (43).

To a solution of [AuL^3Cl_2][PF_6] (0.1400 g, 0.2 mmol) in acetone (20 ml) was added an aqueous suspension of Ag_2O (0.0532 g, 0.2

mmol). The mixture was stirred and protected from light overnight at room temperature. AgCl was removed by filtration and the solution evaporated to dryness under reduced pressure and the residue was extracted with acetonitrile and filtered throught Celite. The solution was concentrated to a small volume and treated with diethyl ether to give a yellow solid **(43)**.

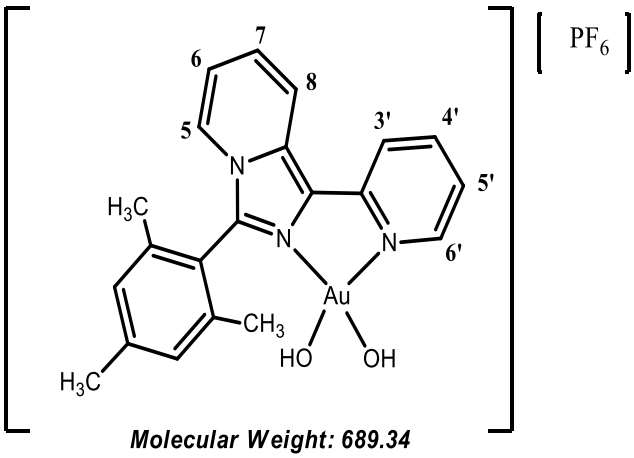
Yield 0.0688 g (51%). M.p.: 170°C

Found: C 36.56; H 2.80; N 5.97%. Calc. for $C_{21}H_{21}AuF_6N_3O_2P$: C, 36.59; H, 3.07; N, 6.10.

Selected ^{1}H NMR data in [CD_2Cl_2]:

8.945 (d,1H,**H6'**); 8.43 (t,1H,**H4'**); 8.32 (d,1H,**H3'**); 8.28 (d,1H,**H8**); 7.66 (m,3H,**H5'+H7+H6**); 7.23 (d,1H,**H5**); 7.19 (s,2H, ***meta* H**); 3.04 (s,1H,**OH**); 2.44 (s,3H, ***para* CH3**); 2.07 (s,6H, ***ortho* CH3**); 1.24 (s,1H,**OH**).

IR, v~max/cm-1 840 (PF6-).



Molecular Weight: 689.34

Synthesis of [{AuL^3(μ-O)}$_2$][PF$_6$]$_2$, (44).

Complex [AuL^3(OH)$_2$][PF$_6$], **(43)**, (0.0485 g, 0.074 mmol) was dissolved in anhydrous THF (20 ml). The yellow solution was

refluxed for 3h and evaporated to dryness under reduced pressure. The residue extracted with acetone, filtered and concentrated to a small volume and treated with diethyl ether to give a yellow precipitate **(44).**

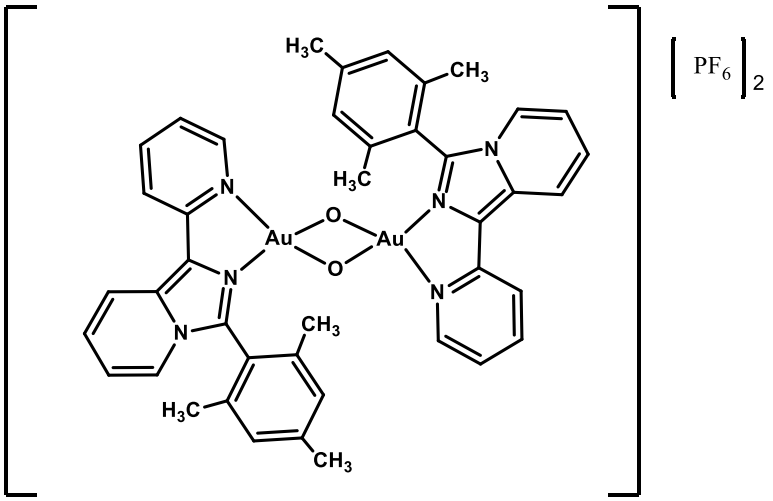
Yield 0.0406 g (40%). M.p.: 210°C

Found: C 42.09; H 2.92; N 6.88%. Calc. for $C_{42}H_{38}Au_2F_6N_6O_2P$: C, 42.12; H, 3.20; N, 7.02.

Selected ^{1}H NMR data in [CD_3COCD_3]:

8.49 (d,1H,**H6'**); 8.37 (m,2H,**H5+H4'**); 8.00 (d,1H,**H8**); 7.68 (t,1H,**H5'**); 7.61 (t,1H,**H6**); 7.52 (d,1H,**H3**); 7.12 (s,2H, ***meta* H**); 2.48 (s,3H, ***para* CH3**); 2.05 (s,6H, ***ortho* CH3**).

IR, v~max/cm-1 840 (PF6-).



Molecular Weight: 1197.69

Synthesis of La(OTf)$_3$

La_2O_3 (9.80 g; 30mmol) was dissolved in a mixture of triflic acid and water (1:1). The colourless solution was refluxed for 2hours and then

it was stirred all night. The white solid was filtered and dryned in a Schlenk flask.

Yield: 15g (85%).

Synthesis of $[La(L^1)_3(OTf)_3]$

$La(OTf)_3$ (0.586 g; 0.1 mmol) and **L^1** (0.081 g; 0.3 mmol) were dissolved in acetonitrile on the Schlenk flask with stir bar. The yellow solution was stirred at room temperature for 24hours. Then it was filtered, concentred and was put away in a freezer.

Yield 0.3516 g (60%).

Synthesis of $Y_2(OTf)_3$

Y_2O_3 (6.77 g; 30 mmol) was dissolved in a mixture of triflic acid and water (1:1). The colourless solution was refluxed for 2hours and then it was stirred all night. The white solid formed was filtered and dryed in a Schlenk flask.

Yield: 8,8 g (56%).

Synthesis of $[Y(L^1)_3(OTf)_3]$

$Y(OTf)_3$ (0.536 g; 0.1 mmol) and **1** (0.083 g; 0.3 mmol) were dissolved in acetonitrile on the Schlenk flask fitted with stir bar. The yellow solution was stirred to room temperature for 24hours. Then it was filtered, concentrated and was put away in a freezer.

Yield 0.3859 g (72%).

Synthesis of $SmI_2(THF)_2$

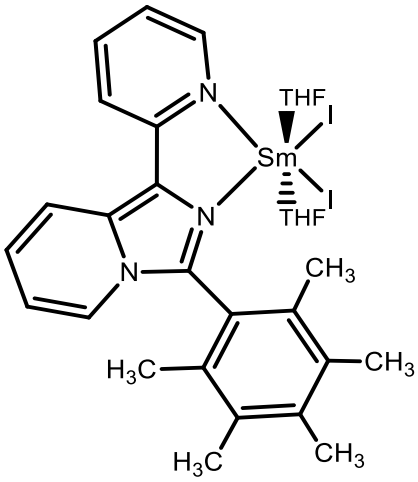
Sm (10g; 66.5mmol) and diiodoethane (17.80g; 63.2mmol) were added to a large Schlenk flask fitted with a stir bar (**Schlenk 1**) under exclusion of light. Foiled and cooled to –40 °C. THF (70 mL) was added. The dark suspension was allowed to warm to –20 °C then removed from cold bath and left to stir open to line overnight. Filtered into another Schlenk flask (**Schlenk 2**). **1** and **2** both stored at –25 °C overnight. Filtered THF from **2** back into **1** and THF added (30mL) to **1**. **2** placed in the freezer (–25 °C). **1** stirred for 2 hours and then allowed to settle for 1 hour. **1** filtered into **2**, then both placed in the freezer overnight. Isolated crystals from **2** (**Crop 1:** 5.482g, 10.4 mmol, 16 %) and supernatant transferred into **1**. **1** stirred until the end of the day then settled overnight. Operation repeated once more, giving a final solid crop.

Yield 26.81g (77%).

Synthesis of $[SmL^6I_2(THF)_2]$

$SmI_2(THF)_2$ (0.3270g;0.0596mmol) and $\mathbf{L^6}$ (0.2043 g; 0.0596 mmol) were added to a large Schlenk flask fitted with stir bar under exclusion of light. Added THF (25ml) and the dark solution was stirred to room temperature overnight. THF was filtered and a yellow solid was placed in the freezer overnight to isolate a crystal.

For this reaction there are no data to propose because it wasn't possible to characterize the possible product due to the pandemic Covid 19.

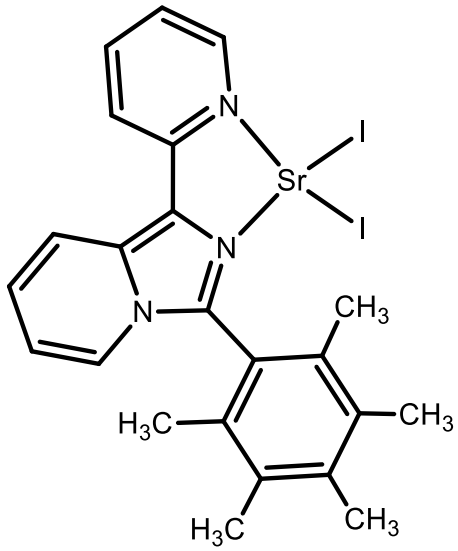


Molecular Weight: 887.81

Synthesis of [SrL^{6}I$_2$]

SrI_2 (0.1987 g; 0.0584mmol) and **L^6** (0.2056 g; 0.0584 mmol) were added to a large Schlenk flask fitted with stir bar. Added THF (20ml) and the pale yellow solution was stirred to room temperature overnight. THF was filtered and a yellow solid was placed in the freezer overnight to isolate a crystal.

For this reaction there are no data to propose because it wasn't possible to characterize the possible product due to the pandemic Covid 19.

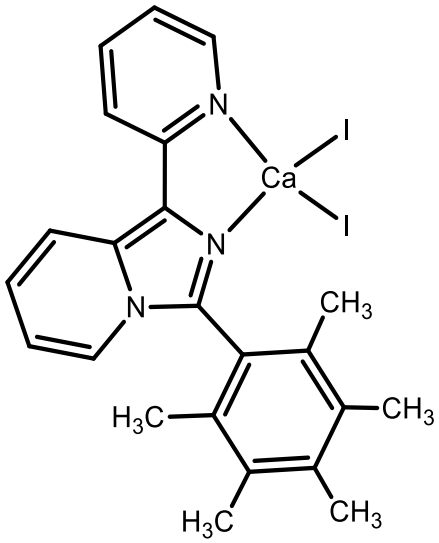


Molecular Weight: 682.88

Synthesis of [CaL^{6}I$_2$]

CaI_2 (0.1780 g; 0.0593 mmol) and **L^6** (0.2032 g; 0.0593 mmol) were added to a large Schlenk flask fitted with stir bar. Added THF (20 ml) and the pale yellow solution was stirred to room temperature overnight. THF was filtered and a yellow solid was placed in the freezer overnight to isolate a crystals.

For this reaction there are no data to propose because it wasn't possible to characterize the possible product due to the pandemic Covid 19.



Molecular Weight: 635.34

RINGRZIAMENTI

Ho deciso di partecipare al concorso per il Dottorato dopo pochi mesi dal conseguimento della Laurea Magistrale in Scienze Chimiche. Inconsapevole di ciò che avrei ricevuto in cambio da questo *viaggio*, ma decisa a mettermi in gioco con determinazione e tanta voglia di imparare.
Ed eccomi qui, finalmente, a scrivere le battute finali di questo capitolo così importante della mia vita, ed a ringraziare tutti quelli che ne hanno fatto parte.

Prima di tutto, vorrei ringraziare il Prof. Sergio Stoccoro per avermi guidato, giorno dopo giorno, nella riuscita di questo mio percorso, specialmente per avermi permesso di lavorare in un ambiente sereno e stimolante. Per avermi insegnato così tanto in questi anni, non solo da un punto di vista scientifico. Per aver sempre creduto in me, e nelle mie capacità, anche quando la prima a non crederci ero io. Le consapevolezze di oggi le devo a lei, e per questo non smetterò mai di ringraziarla. Grazie anche per ogni caffè mattutino, che ci faceva iniziare al meglio la giornata!

Per il suo costante supporto nello sviluppo di questo progetto di ricerca, per aver contribuito alla mia crescita professionale e per avermi dato sempre le giuste chiavi di lettura per risolvere i problemi, che ho dovuto affrontare, ringrazio infinitamente anche il Prof. Antonio Zucca.

Ringrazio anche la Prof.ssa Tina Cinellu per i suoi numerosi consigli e sostegno nello sviluppo del mio progetto di ricerca. Grazie, davvero!

Grazie anche alla Dott.ssa Laura Maiore per ogni consiglio ricevuto, durante le nostre chiacchere. Sono stati fondamentali!

Vorrei ringraziare enormemente anche il Dott. Michele Satta, per avermi insegnato tutti i *trucchi* del mestiere, per aver messo ogni giorno a

disposizione il suo sapere, e per avermi dato sempre ottimi consigli e per aver ascoltato ogni mio sfogo.

Ringrazio anche il Dott. Giuseppe Sciortino per il suo importante contributo, nel conseguire i miei risultati scientifici.

Per aver contribuito alla mia crescita, vorrei ringraziare infinitamente anche il Dott. Fabrizio Ortu. Grazie per ogni singola parola ricevuta, per l'enorme disponibilità, e per avermi fatto sentire sempre a casa. Grazie per avermi dato la possibilità di mettermi in discussione e di confrontarmi. È stata un'esperienza bellissima, che non dimenticherò mai!

Ringrazio anche la Prof.ssa Serenella Medici per ogni sorriso, per ogni chiacchera, e per ogni consiglio ricevuto, durante i suoi passaggi nel *nostro* corridoio.

Per ogni risata ringrazio anche la Dott. Maria Orecchioni. Grazie per aver incrociato ogni volta le dita insieme a me, durante gli esperimenti NMR.

Per avermi sempre aiutato, ma soprattutto per avermi sempre sopportata, vorrei ringraziare il Dott. Salvatore Pintus.

Ringrazio infinitamente la Dott.ssa Francesca Meloni per aver affrontato e superato ogni peripezia di questo percorso insieme a me. Grazie per esserci stata fin dal primo giorno. Grazie per ogni momento condiviso, è stato prezioso. Grazie per avermi dato l'opportunità di capire che non tutti hanno un secondo fine. Grazie per l'amica sincera che sei!

Per la loro costante presenza, e per avermi aiutata a superare anche i momenti più difficili, ringrazio le mie amiche di sempre Claudia e Carla.

Per aver condiviso quotidianamente ogni problematica, ogni mia paura ed ogni mia incertezza, ringrazio Francesco. Grazie per la pazienza che hai avuto, specialmente nell'ultimo periodo. Grazie per avermi sempre

incoraggiata nel raggiungere questo mio traguardo, nonostante avessimo a volte opinioni divergenti. Grazie per avermi insegnato a dare priorità alle cose che effettivamente lo meritano. Grazie semplicemente per esserci stato, e per esserci *sempre.*

Immensa gratitudine va a mia mamma Marta e a mio fratello Luca, a cui è dedicato questo lavoro di Tesi. Senza di voi nulla sarebbe stato possibile!

Sara