A New Cyclometalation Motif: Synthesis, Characterization, Structures, and Reactivity of Pallada- and Platinacycles with a Bidentate {C(sp^2,cyrhetrene),N}$^-$ Ligand

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Abstract

The synthesis, characterization, X-ray crystal structure, and study of the reactivity of the novel cyretrenyl ligand $[\{(\eta^5\text{-}C_5H_4\text{-}2\text{-}C_5H_4N)\}Re(CO)_3$ (**1**) with $Pd(OAc)_2$ or $[MCl_2(DMSO)_2]$ (M = Pd, Pt) are reported. These studies have allowed us to obtain the bis-μ-ligand cyclopalladated complexes $[Pd\{[k^2\text{-}C,N\text{-}(\eta^5\text{-}C_5H_3)\text{-}2(C_5H_4N)]Re(CO)_3\}(\mu\text{-}X)]_2$ (X = OAc (**2a**), Cl (**4a**)) and monomeric pallada- and platinacycles of the general formula $[M\{[k^2\text{-}C,N\text{-}(\eta^5\text{-}C_5H_3)\text{-}2(C_5H_4N)]Re\text{-}(CO)_3\}(X)(L)]$ (M = Pd, L = PPh$_3$, X = OAc (**3a**), Cl (**5a**); M = Pd, L = DMSO, X = Cl (**6a**); M = Pt, X = Cl, L = PPh$_3$ (**5b**), DMSO (**6b**)), where compound 1 acts as a $\{C(sp^2,cyrhetrene),N\}^-$ bidentate ligand. All complexes were characterized by elemental analyses, infrared spectroscopy, and one- and two- dimensional NMR. The X-ray crystal structures of **5a**·$^1/_2$CH$_2$Cl$_2$, **5b**, **6a**·CH$_2$Cl$_2$, and **6b** confirm (a) the existence of the five-membered metallacycle, (b) the $\{C(sp^2,cyrhetrene),N\}^-$ mode of binding of the metallo ligand **1**, and (c) the cis arrangement between the metalated carbon and the neutral L ligands (PPh$_3$ or DMSO) in these products. A comparative study of the structures, spectroscopic properties, and reactivities of the new cyclometalated compounds and those of their analogues with a bidentate $\{C(sp^2,ferrocene),N\}^-$ ligand is also reported.

1. INTRODUCTION

The synthesis of functionalized half-sandwich rhenium complexes derived from $[(\eta^5\text{-}$ $C_5H_5)Re(CO)_3]$ (cyrhetrene) or $[(\eta^5\text{-}C_5H_5)Re(L^1)(L^2)(L^3)]$ (L^1, L^2, L^3 = neutral monodentate ligands) is one of area of organometallic chemistry now experiencing increasing development.[1-5] This is mainly due to (a) their interesting and useful photochemical properties and reactivity,[1,2] (b) their utility in the syntheses of heterodi-, heterotri-, and in general polymetallic organometallic compounds,[1-3] and (c) their potential applications in outstanding catalytic chemical processes, [4] such as hydrogenation of enamines and allylic alkylations.[4] More recently, cyrhetrenyl-hormone compounds have also been described.[5]

On the other hand, cyclopalladated and cycloplatinated complexes derived from N-donor ligands have attracted great interest for a long time.[6-12] Most of the articles published so far have focused on complexes with a $\sigma\{M\text{-}C(sp^2,\text{aryl})\}$ bond or to a lesser extent a $\sigma\{M\text{-}C(sp^3)\}$ bond.[6-10] More recently, parallel studies on cyclometalation of N-donor ferrocenyl ligands (i.e., amines, imines, azo derivatives, oximes, oxazines, and oxazolidines) have provided pallada- and platinacycles with $\{C(sp^2, \text{ferrocene}),N\}^-$ ligands.[8b,c,11,12] Some of these products exhibit outstanding chemical and physical properties, catalytic and/or antitumoral activities,[8b,c] and interesting applications in different fields, including their utility as precursors in organometallic synthesis[12e,13] or even in the design of molecular machines (i.e., pH-based molecular switches).[12c]

Despite these facts and the prochiral nature of the cyrhetrenyl unit in the cyclometalation process,[9f,14] examples of pallada- and platinacycles containing a bidentate $\{C(sp^2,\text{cyrhetrene}),X\}^-$ (X = N, P, S, O) ligand are extremely scarce.[15] Only two types of palladacycles have been described[15] (Figure 1), and in both cases the two donor atoms of the $\{C(sp^2,\text{cyrhetrene}),P\}^-$ unit belong to two different ligands of the rhenium complex. Furthermore, related platinum(II) complexes still remain unknown.

75   In view of these findings and due to our present interest in (a) cyrhetrene

76   derivatives[3,16] and (b) pallada- and platinacycles with bi- or terdentate ligands

77   ({C(sp^2,ferrocene,N)}$^-$ and {C(sp^2, ferrocene),N,X}$^-$, respectively),[12,13c,17] we decided to

78   prepare the novel cyrhetrene derivatives [(η^5-C$_5$H$_4$R)Re(CO)$_3$] with R groups having an

79   additional heteroatom (such as N) with good donor ability and the proper orientation so as

80   to allow the formation of metallacycles with {C(sp^2,cyrhetrene),N}$^-$ ligands.

81   Here, we report our first contribution in this field and in particular (a) the syntheses

82   and characterization of the new cyrhetrene derivative [{(η^5-C$_5$H$_4$)-2-(C$_5$H$_4$N)}Re(CO)$_3$]

83   (**1**), bearing a pyridyl group, (b) a new class of pallada- and platinacycles in which 1 behaves

84   as a {C(sp^2,cyrhetrene),N}$^-$ ligand, and (c) a comparative study of the properties of these

85   new metallacycles and those of their analogues with a {C(sp^2,ferrocene),N}$^-$ ligand.

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2. RESULTS AND DISCUSSION

The Ligand $\{(\eta^5\text{-}C_5H_4)\text{-}2(C_5H_4N)\}Re(CO)_3$ (1). The preparation of this product was carried out in one pot, following a strategy similar to that reported for di-, tri-, and tetraferrocene arenes.[18] The method consisted of the sequence of reactions **A - C** depicted in Scheme 1. In the first step, cyrhetrene was easily converted into its lithium derivative by treatment with n-butyllithium (Scheme 1, step **A**). The subsequent reaction with $ZnCl_2$ produced the Zn(II) derivative (Scheme 1, step **B**), and finally a cross-coupling reaction of the product formed with 2-bromopyridine in the presence of catalytic amounts of $[PdCl_2\text{-}(PPh_3)_2]$ gave, after workup, compound **1** in fairly good yield (88%) (Scheme 1, step **C**).

Elemental analysis of **1** agreed with the proposed formula, and its ESI^+ mass spectrum showed a peak at *m/z* 414, which is consistent with the value expected for the cation $\{[M]+H\}^+$. The IR spectrum exhibited two intense bands at 2023 and 1929 cm^{-1}, which are characteristic of the terminal CO ligands of related rhenium complexes.[16]

The X-ray crystal structure of **1** confirmed the existence of molecules of $[\{(\eta^5\text{-}C_5H_4)\text{-}2(C_5H_4N)\}Re(CO)_3]$ (Figure 2) with the expected three-legged piano-stool structure and the presence of a pyridyl unit attached to the C_5H_4 ring. Average values of the Re–CO (1.908(6) Å) and C–O (1.147(2) Å) bond lengths and the Re-centroid distance (1.961(6) Å) are similar to those reported for $[\{(\eta^5\text{-}C_5H_4)CH_2NH(C_6H_4\text{-}4\text{-}OCH_3)\}\text{-}Re(CO)_3]$ (1.904 Å).[16a]

The C_5H_4N ring is planar and forms an angle of 9.6° with the (C_5H_4) cycle; its bond lengths and angles agree with those reported for complexes containing a 2-substituted pyridyl group.[19]

In the crystal, two proximal molecules of **1** are connected by two weak intermolecular N···H interactions (the distance N···H(2) is 2.739 Å), giving dimers. The assembly of

118   these units through C–H$\cdots$O contacts[20–22] and C–H$\cdots\pi$ intermolecular interactions[20,23]

119   results in a three-dimensional network.[20,23]

120   Compound **1** was also characterized in solution by NMR experiments. The

121   assignment of all signals detected in the ^{1}H and ^{13}C$\{^1$H$\}$ NMR spectra was achieved with

122   the aid of twodimensional $\{^1$H–^{1}H$\}$ NOESY, $\{^1$H–^{13}C$\}$ HSQC and HMBC experiments.

123   The ^{1}H NMR spectrum of 1 in CDCl$_3$ at 298 K exhibited (a) the typical pattern of

124   monosubstituted cyrhetrene derivatives[16] and (b) a group of four signals due to the pyridyl

125   moiety in the same region as those reported by Butler et al.[24] for the ferrocene analogue.

126   The ^{13}C$\{^1$H$\}$ NMR spectrum of **1** showed (a) three signals in the range $80.0 < \delta <$

127   110.0 ppm, the least intense of which (at δ 105.3) corresponds to the ipso carbon (C^1) of the

128   C$_5$H$_4$ ring, (b) a singlet at $\delta \sim$194 (due to the CO ligands), and (c) a group of resonances

129   between 115 and 155 ppm assigned to the carbon-13 nuclei (C^9– C^{13}) of the 2-substituted

130   pyridyl group.

131   **Study of the Reactivity of 1 with Palladium(II) Salts or Complexes**.

132 In a first attempt to evaluate the binding ability of compound **1** toward palladium(II) and to

133   elucidate if the activation of the $\sigma\{$C(sp^2,cyrhetrene)–H$\}$ bond could be induced by

134   palladium(II) salts or complexes, we decided to use one of the most common procedures

135   described for the cyclopalladation of N-donor ligands.[6a,25] This method consists of the

136   reaction between the ligand and Pd(OAc)$_2$ in acetic acid. Treatment of **1** with an equimolar

137   amount of Pd(OAc)$_2$ in refluxing glacial acetic acid for 24 h gave, after workup, a brown

138   solid (hereafter referred to as **2a**) (Scheme 2, step **A**).

139   Elemental analyses of **2a** agreed with those expected for the cyclopalladated complex

140   [Pd$\{[k^2$-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]-Re(CO)$_3\}(\mu$-OAc)]$_2$. In the IR spectrum of **2a**, the

141   separation between the bands due to the asymmetric and symmetric stretchings of the

142   carboxylatomoiety (at 1563 and 1415 cm^{-1}),[26] suggested, according to the

143   bibliography,[25,26] that the OAc-groups behaved as a O,O' bridging ligands. All these

144 findings, as well as the ESI$^+$ mass spectrum of **2a**, agreed with data expected for [Pd{[k^2-

145 C,N-(η^5-C$_5$H$_3$)-2(C$_5$H$_4$N)]Re(CO)$_3$}(μ-OAc)]$_2$, in which **1** adopted a

146 {C(sp^2,cyrhetrene),N} - mode of binding. To the best of our knowledge, palladacycles with

147 this type of bidentate ligand have not been described yet.

148 The ^{1}HNMRspectra of **2a** in acetone-d$_6$ at 298 K showed two sets of superimposed

149 signals (Figure 3), thus suggesting the coexistence of two isomeric species (**2a$_I$** and **2a$_{II}$**) in

150 solution. Variable-temperature NMR experiments revealed that the relative abundance of

151 **2a$_I$** and **2a$_{II}$** did not change substantially on cooling (molar ratios **2a$_I$**: **2a$_{II}$** = 2.50 (at 298

152 K) and 2.56 (at 188 K)).

153 It is well-known that dimeric cyclopalladated complexes with bridging OAc$^-$ groups

154 may exhibit different isomeric forms depending on the relative arrangement of the halves of

155 the molecule (cis or trans).[25-27] Furthermore, the activation of one of the

156 σ{C(sp^2,cyrhetrene)–H} bonds on the ortho sites of **1** induces planar chirality.[9f,14]

157 The {^{1}H–^{1}H} NOESY spectrum of **2a** revealed that **2a$_I$** and **2a$_{II}$** (a) adopted an

158 open-book type structure (Chart 1) and (b) differed in the relative disposition of the two

159 {C(sp^2,cyrhetrene, N)}$^-$ units (trans in **2a$_I$** and cis in **2a$_{II}$**).However, no evidence of the

160 interconversion **2a$_I$** $\overset{\leftarrow}{\rightarrow}$ **2a$_{II}$** was detected.

161 Unfortunately attempts to separate **2a$_I$** and **2a$_{II}$** failed and only a poor-quality crystal

162 was isolated. Despite this, X-ray diffraction studies[28] (Figure 4) confirmed the trans

163 arrangement of the halves of the molecule and the open-book-like structure of the product.

164 This is the most common arrangement of ligands found in palladacycles of the type

165 [Pd(C,N)(μ-OAc)]$_2$.[19,27]

166 When the crystal used for the X-ray studies was dissolved in acetone-d_6, its ^{1}H NMR

167 spectrum was identical with that of the crude product **2a**, indicating the presence of **2a$_I$** and

168 **2a$_{II}$** in solution. It is well-known that the planar chirality of enantio- or diastereomerically

169   pure complexes with $\{C(sp^2,ferrocene),N\}$- ligands and 1,2-disubstituted η^5-C_5H_3 rings

170   remains in solution. [17h,i,29,30] Thus, the formation of **2a$_{II}$** upon dissolution of the single

171   crystal should be related to other factors. Previous studies on related palladacycles have

172   demonstrated that the coexistence of isomers in solution is generally due to a trans $\underset{\rightarrow}{\leftarrow}$ cis

173   isomerization of the dinuclear products. [25,27]

174   Treatment of **2a** with PPh$_3$ (in the molar ratio PPh$_3$:**2a** = 2) produced [Pd$\{[k^2$-C,N-

175   (η^5-C_5H_3)-2-(C_5H_4N)]Re(CO)$_3\}$(OAc)-(PPh$_3$)] (**3a**) (Scheme 2, step **B**). Its $^{31}P\{^1H\}$ NMR

176   showed a singlet at δ 34.7. This chemical shift is indicative of a cis arrangement between the

177   phosphine and the metalated carbon atom (C^2), in good agreement with the so-called

178   *transphobia effect*. [31]

179   When a CH_2Cl_2 solution of **2a** was treated with an excess of NaCl (in H_2O), a brown

180   solid formed. It was identified as the di-μ-chloro derivative [Pd$\{[k^2$-C,N-(η^5-C_5H_3)-2-

181   (C_5H_4N)]Re-(CO)$_3\}$(μ-Cl)]$_2$ (**4a**) (Scheme 2, step C). Compound **4a** is airstable, but it is

182   practically insoluble in the common solvents used for NMR studies. This is the typical

183   behavior of most palladacycles of general formula [Pd$\{(k^2$-$(C,N$-ligand)$\}($\mu$-Cl)]$_2$, and

184   commonly their NMR spectra are registered in the presence of deuteriated pyridine (py-

185   d_5). [25f,32]

186   Addition of a slight excess of py-d$_5$ to a suspension of **4a** in CDCl$_3$ at 298 K produced

187   a pale yellow solution. Its ^1H and $^{31}C\{^1H\}$ NMR spectra suggested the presence of [Pd$\{[k^2$-

188   C, N-(η^5-C_5H_3)-2-(C_5H_4N)]Re(CO)3$\}$Cl(py-d_5)], which arises from the cleavage of the

189   central "Pd(μ-Cl)$_2$Pd" ring and the incorporation of the py-d_5 ligand in a cis arrangement

190   with regard to the metalated carbon.

191   Treatment of a suspension of **4a** in benzene with PPh$_3$ (in the molar ratio

192   phosphine:**4a** = 2; Scheme 2, step **D**) produced, after recrystallization, [Pd$\{[k^2$-C,N-(η^5-

193   C_5H_3)-2-(C_5H_4N)]Re(CO)$_3\}$-Cl(PPh$_3$)] · 1/2CH_2Cl_2 (**5a** · 1/2CH_2Cl_2). Characterization

data (see the Experimental Section) agreed with the proposed formula, and its X-ray crystal structure confirmed the existence of $[Pd\{[k^2\text{-}C,N\text{-}(\eta^5\text{-}C_5H_3)\text{-}2\text{-}(C_5H_4N)]Re(CO)_3\}Cl(PPh_3)]$ (5a) and CH_2Cl_2 molecules in a 2:1 molar ratio. In 5a (Figure 5), the palladium(II) is in a slightly distorted square-planar environment,[33] bound to the N and the C(2) atoms of the cyrhetrenyl moiety. This confirms (a) the $\{C(sp^{2'}cyrhetrene),N\}^-$ mode of binding of 1 in the complex and (b) the existence of a fivemembered metallacycle. This cycle is practically planar and forms angles of 5.2 and of 3.4° with the C_5H_3 unit and the pyridyl ring, respectively.

The two remaining coordination sites are occupied by a chloride (Cl(1)), and the phosphorus of the PPh_3 ligand. Bond lengths and angles around the palladium fall in the range expected for most palladacycles with "$Pd\{(C,N),Cl,P\}$" cores.[17f,g,19,30] The value of the C(2) – Pd – P bond angle (97.84(13)°)} confirms the cis arrangement between the C(2) atom and the neutral ligand, in good agreement with the conclusions reached by NMR and the transphobia effect.[31]

In the crystal, there are two weak C–H· · · Cl intermolecular interactions between the hydrogen atoms of the CH_2Cl_2 and the Cl⁻ ligands of two different units of 5a (distance Cl(1) · · ·H(32A) = 2.634 Å)[34] and C–H· · ·Ocontacts between the pair of oxygen atoms O(2) and O(3) of a molecule at (x, y, z) and two hydrogen atoms (H(11) and H(21)) of vicinal units at (-x, 2 - y, -z) and (1/2 - x, 1/2 - y, 1/2 - z), respectively.

The activation of the $\sigma\{C(sp^2,cyrhetrene)–H\}$ bond was also achieved by reaction of equimolar amounts of 1, $[PdCl_2(DMSO)_2]$ and $NaOAc \cdot 3H_2O$ in refluxing toluene for 12 h (Scheme 2, step E). Characterization data of the yellowish crystalline solid isolated agreed with those expected for $[Pd\{[k^2\text{-}C,N\text{-}(\eta^5\text{-}C_5H_3)\text{-}2\text{-}(C_5H_4N)]Re(CO)_3\}Cl(DMSO) \cdot CH_2Cl_2]$ (6a · CH_2Cl_2). In the heterodimetallic units (6a) (Figure 6) the palladium(II) is bound to the C(2) and N atoms of 1. The difference between the Pd – C(2) bond lengths in 6a (1.979(11) Å) and 5a (1.992(5) Å) does not clearly exceed 3σ, while the variation of the Pd – Nbond length (2.091(3) Å in 6a and 2.131(4) Å in 5a) can be attributed to the different

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trans influences of the neutral ligands (L = PPh$_3$ (in **5a**), DMSO (in **6a**)). The sulfur atom of the DMSO occupies the coordination site adjacent to the Pd – C(2) bond, and a Cl-ligand fullfils the coordination sphere. The Pd – Cl bond length (2.3964(13) Å) is similar to that found in [Pd{[k^2-C,N-(2,4-Me$_2$-C$_6$H$_2$)CH=NNHC(O)C$_6$H$_5$)}Cl(DMSO)].[35]

The relative arrangement of the three rings forming the [5.5.6] tricyclic system is similar to that of **5a** (the mean plane of the C$_5$H$_3$ ring forms angles of 5.2 and 7.9° with those of the metallacycle and the pyridyl unit, respectively).

In the crystal state molecules of **6a** are connected by weak C–H· · ·O interactions[20] between the O(4) and the H(15A) atoms of close units. In addition to that, there are short C–H· · ·Cl contacts between the peripheral atoms of the CH$_2$Cl$_2$ and units of **6a**.[20]

It should be noted that since crystals of **5a** · $^1/_2$ CH$_2$Cl$_2$ and **6a** ·CH$_2$Cl$_2$ are centrosymmetric, they contain a mixture of the two enantiomers S_p and R_p. This is consistent with the absence of any factor inducing chirality in the reaction medium.

^{1}H and ^{13}C{^{1}H} NMR data of **5a** are presented in the Experimental Section. The position of the singlet detected in its ^{31}P{^{1}H} NMR spectrum (at δ 33.9) is similar to that of **3a** (δ 34.7). These signals are shifted upfield in comparison with those of [Pd{C(sp^2,ferrocene),N}(X)(PPh$_3$)] complexes (X = OAc$^-$, Cl$^-$ (37.0 < δ < 39.0))[17f,30,36] but fall in the range reported for palladacycles with terdentate ligands {C(sp^2,ferrocene),N,E}^{q} (q = -1 (for E = N, S, O), -2 (for E = O)).[17b,37]

When the reaction was performed in the absence of NaOAc · 3H$_2$O under identical experimental conditions, the formation of **6a** was also detected but the yield decreased from 78 to 56%. [Pd{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re(CO)$_3$}Cl-(DMSO)] (**6a**) could be easily transformed into **5a** by treatment with PPh$_3$ in benzene at 298 K (Scheme 2, step **F**). Compound **5a** was also obtained from ligand **1** through three consecutive reactions (**A**, **C**, and **D** in Scheme 2, path I). However, the procedure summarized in steps **E** and **F** of Scheme 2 (path II) allows the isolation of **5a** (a) in shorter reaction periods, (b) with greater yields (global yields 70% (path II) versus 32% (path I)), and (c) in a cheaper way. Thus, the use of

248   *cis*-[PdCl$_2$(DMSO)$_2$] as metalating agent followed by treatment with PPh$_3$ appears to be the

249   most convenient method for the preparation of **5a**.

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251   **Study the Reactivity of 1 with Platinum(II) Salts or Complexes**. In

252   view of the increasing interest in platinacycles [8a-c,10d,12a,12c,17h,17i,37a] and the lack of

253   compounds with "Pt{C(sp^2,cyrhetrene),N}" cores, we also studied the reactivity of 1 toward

254   platinum(II). For comparison purposes, we decided to follow the same methodology as for

255   the synthesis of **6a** (Scheme 2, step **E**), but using cis-[PtCl$_2$(DMSO)$_2$] as starting material.

256   The final product isolated under identical experimental conditions was identified (see below)

257   as [Pt{[k^2-*C,N*-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re(CO)$_3$}Cl(DMSO)] (**6b**). Further treatment of **6b**

258   with an equimolar amount of PPh$_3$ in benzene produced [Pt{[k^2-*C,N*-(η^5-C$_5$H$_3$)-2-

259   (C$_5$H$_4$N)]Re(CO)$_3$}Cl(PPh$_3$)] (**5b**) (Scheme 2, step **F**).

260   The crystal structures of **5b** and **6b** confirmed the existence of the heterodimetallic

261   molecules of [Pt{[k^2-*C,N*-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re(CO)$_3$}Cl(L)] with L= DMSO (in **6b**)

262   or PPh$_3$ (in **5b**) (Figures 7 and 8, respectively). In compounds **6b** and **5b**, the Pt(II) atom is

263   in a slightly distorted square-planar environment[38] and the distribution of ligands is identical

264   with those of their palladium(II) analogues (**6a** and **5a**, respectively).

265   The Pt–C bonds of **5b** (1.969(5) Å) and **6b** (1.985(6) Å) are a bit shorter than those

266   of [Pt{[k^2-*C,N*-(η^5-C$_5$H$_3$)-C(Me)d   N(C$_6$H$_4$-4-Br)]Fe(η^5-C$_5$H$_5$)}Cl(PPh$_3$)][39] and

267   platinacycles [Pt{C(sp^2,ferrocene),N(sp^2,imine)}Cl(DMSO)] (in the range 1.98–2.05

268   Å),[17h,i,40] but the Pt–Cl distance does not vary significantly from the values

269   reported.[17h,i,19,39,40]

270   The pyridyl ring is planar and nearly coplanar with the 1,2-disubstituted η^5-C$_5$H$_3$.

271   cycle as reflected in the values of the torsion angles N–C(9)–C(1)–C(2) (5.08° (in **5b**) and

272   2.36° (in **6b**)).

273   In the crystals of **5b** two molecules are assembled by weak C–H · · · Cl interactions

274   forming dimers, which are connected by intermolecular C(23) –H(23) · · · O(2) and C(22)

275   –H(22) · · · π interactions, while in **6b** there is a $R_2^{\ 2}(8)$ hydrogen bond structural motif[41]

276   between the O(4) and H(14C) atoms of two DMSO ligands.

277   On the other hand, it is well-known that an upfield shift in ^{195}Pt NMR is related to a

278   strong donor interaction.[12a,c,17i,42,43] Thus, the differences detected in the ^{195}Pt chemical

279   shifts of **5b** (δ–4062 (d, $^1J_{\text{P–Pt}}$=4098Hz)) and **6b** (δ–3664) and those of their analogues

280   [Pt{C(sp^2,ferrocene),N}Cl(L)] (with L = PPh$_3$ (–4150 > δ > –4300). DMSO (–3800 > δ >

281   –3900))[12a,c,17i] can be used as a measure of the different donor abilities of these two types

282   of bidentate ligands {C(sp^2,cyrhetrene),N}$^-$ and {C(sp^2,ferrocene), N}$^-$ in the metallacycles.

283   Further treatment of [M{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]-Re(CO)$_3$}Cl(PPh$_3$)] (M =

284   Pd (**5a**), Pt (**5b**)) with PPh$_3$ in CH$_2$Cl$_2$ or CDCl$_3$ at 298 K did not produce the opening of

285   the metallacycle and the incorporation of a second PPh$_3$ molecule in the coordination sphere

286   of the M(II) atom. This behavior, also observed for their analogues containing

287   ferrocenylimines as chelating ligands, suggested that the M–N bond exhibits low lability.

288   It should be noted that when [Pd{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re(CO)$_3$}(μ-Cl)]$_2$

289   (**4a**) was treated with MeO$_2$CC≡CCO$_2$Me (in molar ratios alkyne:**4a** = 2, 4) inCH$_2$Cl$_2$ or

290   CHCl$_3$ under reflux for 72 h, evidence of the insertion of this alkyne in the

291   σ{Pd–C(sp^2,cyrhetrene)} bond was not detected by ^{1}H NMR spectra of the crude material.

292   This indicated that **4a** is less reactive than its analogues with {C(sp^2,ferrocene),N}$^-$ ligands.

293   Furthermore, attempts to achieve platinum(IV) complexes by treatment of **6b** with an excess

294   of CH$_3$I in refluxing acetone failed, thus showing that in **6b** the Pt(II) center is not prone to

295   undergo the oxidative addition process.

296   **Electronic Spectroscopy.** It is well-known that some squareplanar platinum(II)

297   complexes are photoluminescent, with emissive states usually arising from intraligand $\pi\rightarrow\pi$

298   (IL), metal-toligand charge transfer (MLCT), or even ligand-to-ligand charge transfer

299   (LL'CT).[44] In view of these facts, we also studied the effect produced by the cyclometalation

300   on the spectroscopic properties of the new ligand.

301   Absorption spectra of CH_2Cl_2 solutions of the free ligand (1) and complexes [M{[k^2-

302   C,N-(η^5-C_5H_3)-2-(C_5H_4N)]Re(CO)$_3$}-Cl(L)] (M = Pd, Pt and L = PPh$_3$ (**5a** and **6a**,

303   respectively) or DMSO (**5b** and **6b**)) were also measured at 298 K (Figure 9 and Table 1).

304   The UV–vis spectra of **5a,b** and **6a,b** (Table 1 and Figure 9) showed a band in the range 300

305   nm < λ_3 < 400 nm with extinction coefficients between 2.5 X 10^3 and 3.0 X 10^3 M^{-1} cm^{-1}

306   (Table 1). This absorption was not present in the spectrum of the free ligand, and its position

307   was dependent on the nature of the M(II) ion, the neutral L ligand (PPh$_3$ or DMSO), and the

308   polarity of the solvent (Table 1). This absorption was assigned as a metal-to-ligand charge

309   transfer (MLCT) transition from the 4d or 5d orbitals (forM= Pd(II), Pt(II), respectively) to

310   a π orbital of the ligand.

311   For platinacycles **5b** and **6b**, two additional bands in the same region as **1** were also

312   observed in the spectra, but for **5a** and **5b**, the band at λ_2 ~255 nm was poorly defined.

313   These absorptions are due to metal-perturbed intraligand charge transfer transitions

314   (MPILCT) ($\pi \rightarrow \pi^*$).

315   Due to the increasing interest on the photooptical properties of metallacycles, we also

316   studied the potential emissive properties of the free ligand and compounds **5a,b** and **6a,b**.

317   The results obtained (Table 1) revealed that **1** is not luminescent in CH_2Cl_2 solution at 298

318   K. In contrast with these results, for **5a,b** and **6a,b** the excitation at the corresponding λ_3

319   produced a weak emission at λ_{max} (in the range 350 ≤ λ_{max} ≤ 400 nm, Table 1 and Figure

320   10). Comparison of data (Table 1) shows that when Pd(II) in **5a** (or **6a**) is replaced by Pt(II)

321   in **5b** (or **6b**), the emission shifts to the lower energy region. This variation is greater than

322   that produced by the neutral ligand (DMSO in **5b** (or **6b**) or PPh$_3$ in **5a** (or **6a**)). It should

323   be noted that for the four complexes the excitation spectra at this low-energy band (λ_{max})

324   resemble their corresponding absorption spectra, thus suggesting that the emissive states

325   come from the same absorbing species.

326

3. CONCLUSION

The new cyrhetrenyl-pyridine ligand $[\{(\eta^5\text{-}C_5H_4)\text{-}2\text{-}(C_5H_4N)\}\text{-}Re(CO)_3]$ (**1**) and the first examples of pallada- (**2a–6a**) and platinacycles (**5b** and **6b**), with a $\{C(sp^2,\text{cyrhetrene}),N\}^-$ ligand have been prepared and characterized. The crystal structures of **5a** · ½ CH_2Cl_2, **6a** $3CH_2Cl_2$, **5b**, and **6b** confirmed (a) the mode of binding of **1** in the complexes, (b) a cis arrangement between the metalated carbon and the neutral ligand (PPh_3 (in **5a** and **5b**) or DMSO (in **6a** and **6b**)), and (c) the existence of weak C–H···O (in **6b**) and C–H···Cl (in the remaining cases) intermolecular interactions.

We have also proved that (a) compounds $[M\{[k^2\text{-}C,N\text{-}(\eta^5\text{-}C_5H_3)\text{-}2\text{-}(C_5H_4N)]Re(CO)_3\}Cl(L)]$ (L = PPh_3 (**5a,b**), DMSO (**6a,b**)) are not prone to undergo the cleavage of the M–N bond, (b) the $\sigma\{Pd\text{–}C(sp^2,\text{cyrhetrene})\}$ bond of $[Pd\{[k^2\text{-}C,N\text{-}(\eta^5\text{-}C_5H_3)\text{-}2\text{-}(C_5H_4N)]Re(CO)_3\}(\mu\text{-}Cl)]_2$ (**4a**) is less reactive than the $\sigma\{Pd\text{–}C(sp^2,\text{ferrocene})\}$ bond of complexes arising from the metalation of the ferrocene, and (c) complex **6b** is reluctant to oxidize in the presence of MeI.

Furthermore, the UV–vis spectra of **5a,b** and **6a,b** in CH_2Cl_2 at 298 K showed a metal-to-ligand charge transfer (MLCT) band in the range $300 \leq \lambda_3 \leq 400$ nmand excitation at this wavelength (λ_3) produced a weak emission. Despite the fact that these emissive properties are not spectacular, the complexes presented here are attractive in view of their potential utility in a variety of fields. For instance, they are valuable precursors to achieve related metallacycles with improved photooptical properties or reactivity (i.e., by (a) incorporation of ligands such as –CCR or acetylacetonate (that prevent the deactivation of the lowest emitting exciting state[44]) or (b) substitution of one (or more) of the CO ligands of the "Re(CO)$_3$" moiety, respectively). In addition, they also appear to be excellent candidates for studying not only their catalytic or antitumoral activities but also their interaction with DNA.[4] Thus, the results presented here constitute the first step of further work centered on these fields. Studies on these areas are currently underway.

4. EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under nitrogen using standard Schlenk techniques. All solvents except benzene were purified and dried by conventional methods and distilled under nitrogen prior to use.[45] The complexes $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$, $[PdCl_2(PPh_3)_2]$, and $[MCl_2(DMSO)_2]$ (M = Pd, Pt) were prepared by the published procedures,[46] while the remaining reagents were obtained from Aldrich and used as received. *Caution!* Some of the preparations described here required the use of benzene which should be handled with care.

IR spectra were recorded on a Perkin-Elmer FT-1605 spectrophotometer using KBr pellets (for solid samples) or NaCl disks (for solution studies). Elemental analyses (C, H, N, and S) were carried out at the Serveis Cientifico-Técnics (Universitat de Barcelona).Mass spectra (ESI$^+$) were registered at the Servei de Espectrometría de Masses (Universitat de Barcelona) with a LC/MSD-TOF Agilent Technologies instrument. Routine ^{1}H NMR spectra and ^{13}C$\{^1$H$\}$ NMR spectra were obtained with a Mercury-400 instrument. High-resolution ^{1}H NMR spectra and the two-dimensional ($\{^1$H $-$ ^{1}H$\}$-NOESY and -COSY, $\{^1$H $-$ ^{13}C$\}$- heteronuclear single quantum coherence (HSQC), and heteronuclear multiple bond coherence (HMBC)) NMR experiments were recorded with either a Varian VRX-500 or a Bruker Advance-DMX 500 instrument at 20 °C. The latter instrument was also used for the variable temperature NMR studies in the range 188 – 298 K. ^{31}P$\{^1$H$\}$ NMR spectra of **5a,b** were obtained with a Varian 300 MHz instrument at 298 K, and the ^{195}Pt$\{^1$H$\}$ NMR spectra of **5b** and **6b** were measured under identical conditions with a Bruker 250-DXR instrument. The references used were P(OMe)$_3$ ($\delta(^{31}$P) 140.17) and H$_2$PtCl$_6$ ($\delta(^{195}$Pt) 0.0), respectively. In all cases the NMR studies were performed in CDCl$_3$ (99.8%) using SiMe$_4$ as internal reference, except for **2a**, for which the solvent was acetone-d$_6$. The chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz.[47] UV – vis spectra of CH$_2$Cl$_2$ solutions of the free ligand **1** and complexes **5a,b** and **6a,b** were recorded at 298 K with a Cary 100 scan 388 Varian UV spectrometer, and their emission and excitation spectra were obtained on a Horiba Jobin – Yvon SPEX Nanolog-TM spectrofluorimeter at 298 K.

Preparation of the Compounds. *[{(η^5-C$_5$H$_4$)-2-(C$_5$H$_4$N)}Re-(CO)$_3$] (**1**).* A

200 mg amount of [(η^5-C$_5$H$_5$)Re(CO)$_3$] (6.0 x 10^{-4} mol) was dissolved in THF (15 mL).

The solution was cooled to 175 K, and then 0.63 mL (9.6 x 10^{-4} mol) of a 1.6 M solution of

butyllithium in hexane was added. The mixture was stirred at 175 K for 1.5 h. After this

period ZnCl$_2$ (82 mg, 6.9 x 10^{-4} mol) was added, and the reaction mixture was warmed to

room temperature and then kept stirring for 1.5 h. Afterward [PdCl$_2$(PPh$_3$)$_2$] (21 mg, 3.0 x

10^{-5} mol) suspended in THF (2 mL) and a solution of 2-bromopyridine (57 μL, 6.0 x 10^{-5}

mol) in THF (2 mL) were added. The mixture was stirred for 1.5 h at room temperature and

then poured into water (15 mL), and the residue was extracted with CH$_2$Cl2. The extracts

were dried over Na$_2$SO$_4$, filtered through Celite, and evaporated under reduced pressure.

The oily residue that formed was chromatographed over silica gel. Elution with a

hexane/CH$_2$Cl$_2$ (4/1) mixture produced a band that was collected and concentrated to ca. 3

mL, giving 1 as a white solid. This product was later recrystallized by slow diffusion of

hexane into a CH$_2$Cl$_2$ solution of 1 at −10 °C (yield 217 mg, 3.8 x 10^{-4} mol, 88%). Anal.

Calcd for C$_{13}$H$_8$-NO$_3$Re: C, 37.86; H, 1.96; N, 3.40. Found: C, 37.9; H, 2.1; N, 3.2. MS

(ESI$^+$) *m/z*: 414 [M + H]$^+$. IR: 2023 (s) and 1929 (vs) cm^{-1}, v(CO). ^{1}HNMR: 5.41 (t, 2H,

$^3J_{H-H}$ = 2.3, H^3 and H^4); 6.06 (t, 2H, $^3J_{H-H}$ = 2.3, H^2 and H^5); 7.15 (m, 1H, H^{12}); 7.32 (d,

1H, $^3J_{H-H}$ = 8.3, H^{10}); 7.62 (dt, 1H, $^3J_{H-H}$ = 8.0, $^4J_{H-H}$ = 1.5, H^{11}); 8.51 (d, 1H, $^3J_{H-H}$ =

4.8, H^{13}). ^{13}C{^{1}H} NMR: 83.4 (C^2 and C^5); 84.7 (C^3 and C^4); 105.3 (C^1); 119.4 (C^{12});

122.9 (C^{10}); 136.7 (C^{11}); 149.6 (C^9); 151.2 (C^{13}); 193.7 (C^6, C^7, and C^8).

*[Pd{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re(CO)$_3$}(μ-OAc)]2 (**2**).* To a solution of **1** (100

mg, 2.4 x 10^{-4} mol) in glacial acetic acid (15 mL) was added Pd(OAc)2 (54 mg, 2.4x 10^{-4}

mol), and the mixture was refluxed for 24 h. After this period, the brown-black solution was

concentrated under vacuum, the residue was extracted with CH$_2$Cl$_2$, and the solution was

filtered through Celite. Then the filtrate was concentrated under reduced pressure to ca. 3

mL. Addition of diethyl ether (15 mL) gave a brown solid, which was collected by filtration,

washed with two (10 mL) portions of diethyl ether, and dried. Afterward this solid was

recrystallized by slow diffusion of hexane into a CH_2Cl_2 solution of 2 at −10 °C (yield 86 mg, 1.5 x 10^{-4} mol, 62%). Anal. Calcd for $C_{30}H_{20}N_2O_{10}Pd_2\text{-}Re_2$: C, 31.23; H, 1.75; N, 2.43. Found: C, 30.9; H, 1; N, 2.6. MS (ESI$^+$) *m/z*: 1143.8 $\{[M - CO] + H_2O\}^+$; 1084.8 $\{[M - CO - OAc] + H_2O\}^+$. IR: 2011(s) and 1921 (vs), $v(CO)$; 1563 (m) and 1413 (m) cm^{-1}, $v(-COO)$. Two isomers (**2aI** and **2aII**) coexisted in acetone-*d6* in the molar ratios **2aI:2aII** = 1.00:0.40 (at 298 K) and 1.00:0.39 (at 188 K). ^{1}HNMR for **2aI**: 2.83 (s, 6H, 2OAc); 4.92 (dd, 2H,$^3J_{H-H}$ = 2.5, $^4J_{H-H}$ = 1.0, 2H^3); 5.18 (t, 2H, $^3J_{H-H}$ = 2.5, 2H4); 5.83 (dd, 2H, $^3J_{H-H}$ = 3.0, $^4J_{H-H}$ =1.0, 2H^5); 7.20 (td, 2H, $^3J_{H-H}$ =7.0, $^4J_{H-H}$ =1.5, 2H^{12}); 7.42 (dd, 2H, $^3J_{H-H}$ = 8.0, $^4J_{H-H}$ = 0.5, 2H^{10}); 7.88 (dt, 2H, $^3J_{H-H}$ = 8.0, $^4J_{H-H}$ = 1.5, 2H^{11}); 8.22 (ddd, 2H, $^3J_{H-H}$ = 5.5, $^4J_{H-H}$ = 1.5, $^5J_{H-H}$ = 1.0, 2H^{13}). ^{1}H NMR for 2aII: 2.05 (s, 3H, OAc); 2.12 (s, 3H, OAc); 5.10 (dd, 2H, $^3J_{H-H}$ = 2.5, $^4J_{H-H}$ = 1.0, 2H^3); 5.39 (t, 2H, $^3J_{H-H}$ = 2.5, 2H^4); 6.06 (dd, 2H, $^3J_{H-H}$=2.7, $^4J_{H-H}$=1.2, 2H^5); 6.98 (td,2H, $^3J_{H-H}$=6.6, $^4J_{H-H}$=1.3, 2H^{12}); 7.36 (ddd, 2H, $^3J_{H-H}$ = 8.0, $^4J_{H-H}$ = 1.0, $^5J_{H-H}$ = 0.5, 2H^{10}); 7.72 (td, 2H, $^3J_{H-H}$ = 7.7, $^4J_{H-H}$ = 1.5, 2H^{11}); 8.01 (ddd, 2H, $^3J_{H-H}$ = 5.5, $^4J_{H-H}$ = 1.5, $^5J_{H-H}$ = 0.5, 2H^{13}). $^{13}C\{^1H\}$ NMR data for **2aI**: 24.3 (MeCOO); 83.1 (C^5); 84.2 (C^3); 85.1 (C^4); 118.0 (C^{12}); 122.4 (C^{10}); 139.2 (C^{11}) 152.3 (C^9); 151.9 (C^{13}); 184.2 (COO$^-$); 196.4 (C^6, C^7, and C^8). The signals due to the quaternary carbon atoms C^1 and C^2 could not be detected in the $^{13}C\{^1H\}$NMR spectrum. $^{13}C\{^1H\}$ NMR data for **2aII**: 23.2 (MeCOO); 82.8 (C^5); 83.8 (C^3); 85.3 (C^4); 118.8 (C^{12}); 122.4 (C^{10}); 140.8(C^{11}) 152.0 (C^{13}, partially masked by the signal due to the C^{13} atom of **2aII**); 183.3 – OO$^-$); 196.2 (C^6, C^7, and C^8).

[Pd{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re(CO)$_3$}(OAc)(PPh$_3$)] (3a). This compound was prepared in solution on an NMR scale and characterized by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. Compound **2a** (13 mg, 1.1 x 10^{-5} mol) was introduced into an NMR tube, and

then 0.4 mL of $CDCl_3$ was added. The resulting suspension was treated with a solution

containing triphenylphosphine (6.0 mg, 2.3 x 10^{-5} mol) and 0.3 mL of $CDCl_3$. The solution

was shaken vigorously at 298 K for 3 min. This produced the complete dissolution of **2a**,

giving a pale brown solution. ^1H NMR: 1.46 (br, 3H, OAc); 4.04 (d, 1H, $^3J_{H-H}$ = 2.5, H^3);

4.87 (t, 1H, $^3J_{H-H}$ = 2.7, H^4); 5.83 (d, 1H, $^3J_{H-H}$ = 3.0, H^5); 7.16 (td, 1H, $^3J_{H-H}$ = 7.2,

$^4J_{H-H}$ = 1.5, H^{12}); 7.30 (d, 1H, $^3J_{H-H}$ = 7.8, H^{10}); 7.46 (m, 6H, aromatic protons of PPh3);

7.74 (dd, 1H, $^3J_{H-H}$ = 7.8, $^4J_{H-H}$ = 1.5, H^{11}); 7.80 (m, 9H, aromatic protons of PPh3); 8.43

(br, 1H, H^{13}). $^{31}P\{^1H\}$ NMR: 34.7.

[Pd{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re(CO)$_3$}(μ-Cl)}]$_2$ · CH$_2$Cl$_2$ (4a). A solution

of **2** (100 mg, 9.0 x 10^{-5} mol) in CH_2Cl_2 (10 mL) was added to a saturated solution of NaCl

in water (10 mL), and the mixture was stirred overnight at room temperature. The brown

solid formed was collected by filtration, washed with two (10 mL) portions of H_2O and then

with CH_2Cl_2 (2 x 10 mL), and dried under vacuum (yield 67 mg, 5.6 x 10^{-5} mol, 65%).

Anal. Calcd for $C_{26}H_{14}Cl_2N_2O_6Pd_2Re_2$ · CH_2Cl_2: C, 27.22; H, 1.35; N, 2.35. Found: C,

27.25; H, 1.4; N, 2.5. MS (ESI$^+$) *m/z*: 1049.74 {[M] – 2CO}$^+$; 1152.83 {[M – Cl] $^+$

2CH$_3$CN}$^+$. IR: 2019 (s) and 1917 (vs) cm^{-1}, v(CO). ^1H NMR (in presence of py- d_5,

selected data): 4.43 (dd, 1H, $^3J_{H-H}$ = 2.4, $^4J_{H-H}$ = 1.2, H^3); 5.25 (t, 1H, $^3J_{H-H}$ = 2.8, H^4);

5.78 (dd, 1H, $^3J_{H-H}$ = 2.8, $^4J_{H-H}$ = 1.2, H^5); 7.14 (td, 1H, $^3J_{H-H}$ = 6.0, $^4J_{H-H}$ = 1.6, H^{12});

7.27 (m, 1H, H^{10}); 7.77 (td, 1H, $^3J_{H-H}$ = 7.6, $^4J_{H-H}$ = 1.6, H^{11}); 9.33 (br, 1H, H^{13}).

$^{13}C\{^1H\}$ NMR (in the presence of py-d_5, selected data): 81.9 (C^4); 83.7 (C^3); 86.2 (C^5);

108.8 (C^1); 109.6 (C^2); 118.9 (C^{10}); 123.2 (C^{12}); 124.4 (C^{11}); 151.0 (C^9); 153.9 (C^{13});

195.7 (C^6, C^7 and C^8).

[Pd{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re(CO)$_3$}(PPh$_3$)Cl]   ·   ½CH$_2$Cl$_2$ (5a ·

½CH$_2$Cl$_2$). This compound was obtained using two alternative procedures that differ in the

nature of the starting material: the di-μ-chloro complex [Pd{[k^2-C,N-(η^5-C$_5$H$_3$)-2-

458 (C$_5$H$_4$N)]Re(CO)$_3$}(μ-Cl)]$_2$ · CH$_2$Cl$_2$ (**4a** · CH$_2$Cl$_2$) (method a) and [Pd{[k^2-*C,N*-(η^5-

459 C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re-(CO)$_3$}(DMSO)Cl] · CH$_2$Cl$_2$ (**6a** · CH$_2$Cl$_2$) (method b).

460 *Method a*. To a suspension of **4a** · CH$_2$Cl$_2$ (50 mg, 4.2 x 10^{-5} mol) in benzene (10

461 mL) was added triphenylphosphine (24 mg, 9.1 x 10^{-5} mol). The reaction mixture was stirred

462 at room temperature overnight and then concentrated to dryness, and the residue that formed

463 was treated with the minimum amount of CH$_2$Cl$_2$. Addition of hexane produced the

464 precipitation of **5a** · ½CH$_2$Cl$_2$ as a pale yellow solid that was collected and dried. This

465 product was recrystallized in a hexane/CH$_2$Cl$_2$ (1/3) mixture at −10 °C (yield 27.8 mg, 3.2

466 x 10^{-5} mol, 38.6%).

467 *Method b*. Triphenylphosphine (21 mg, 8 x 10^{-5} mol) was added to a solution of 6a

468 3CH$_2$Cl$_2$ (50 mg, 7.0 x 10^{-5} mol) in benzene (10 mL). The reaction mixture was stirred at

469 room temperature overnight and then concentrated under vacuum. The residue was dissolved

470 in the minimum amount of CH$_2$Cl$_2$. Addition of hexane produced the precipitation of a pale

471 yellow solid, which was collected, dried, and recrystallized as described in method a (yield

472 53.2 mg, 7.4 x 10^{-4} mol, 89%).

473 Characterization data for **5a** · ½ CH$_2$Cl$_2$ are as follows. Anal. Calcd for

474 C$_{31}$H$_{22}$ClNO$_3$PPdRe · ½ CH$_2$Cl$_2$: C, 44.09; H, 2.70; N, 1.63. Found: C, 44.1; H, 2.7; N,

475 1.6. MS (ESI$^+$) *m/z*: 779.99 [M − Cl]$^+$; 821 {[M − Cl] + CH$_3$CN}$^+$. IR: 2014 (s) and 1920

476 (vs) cm^{-1}, ν(CO). ^{1}H NMR: 3.42 (dd, 1H, $^3J_{H-H}$ = 2.5, $^4J_{H-H}$ = 1.0, H^3); 4.95 (td, 1H,

477 $^3J_{H-H}$ = 3.0, $^4J_{H-H}$ = 1.0, 1H, H^4); 5.85 (dd, 1H, $^3J_{H-H}$ = 3.0, $^4J_{H-H}$ = 1.5, H^5); 7.19 (m,

478 1H, H^{12}); 7.27 (dd, 1H, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 0.5, H^{10}); 7.43 (m, 9H, aromatic protons of

479 PPh$_3$); 7.74 (td, 1H, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.0, H^{11}); 7.81 (m, 6H, aromatic protons of

480 PPh$_3$); 9.40 (br, 1H, H^{13}). ^{13}C{^{1}H} NMR: 83.7 (C^4); 85.6 (C^5); 89.6 (C^3); 108.5 (C^1); 109.5

481 (C^2), 118.0 (C^{10}); 122.9 (C^{12}); 132.2 (C^{11}); 151.4 (C^{13}); 159.4 (C^9); 195.8 (C^6, C^7, and

C[8]); four additional doublets centered at 129.5, 131.1, 132.2, 136.3 (due to the four types of carbon-13 nuclei of the PPh3 ligand). $^{31}P\{^1H\}$ NMR: 33.9.

[M{[k^2-C,N-(η^5-C5H3)-2-(C5H4N)]Re(CO)3}(DMSO)Cl] · nCH2Cl2 (M = Pd and n = 1, 6a; M = Pt and n = 0, 6b). A 2.4 x 10^{-4} mol amount of the corresponding [MCl2(DMSO)2] complex (with M = Pd (80.2 mg), Pt (101 mg)), ligand 1 (100 mg), and a 2-fold excess of NaOAc · 3H2O (68.0 mg, 5.0 x 10^{-4} mol) were suspended in 20 mL of toluene. The resulting mixture was refluxed for 12 h; afterward, it was concentrated under reduced pressure to ca. 3 mL and the addition of diethyl ether (20 mL) followed by vigorous stirring at room temperature produced the precipitation of complexes **6a** · CH2Cl2 and **6b** (as yellowish microcrystalline products), which were later collected and dried under vacuum (yields 119 mg (1.65 x 10^{-4} mol), 68% for **6a** · CH2Cl2 and 141 mg (1.97 x 10^{-4} mol), 81% for **6b**). Characterization data for **6a** · CH2Cl2 are as follows. Anal. Calcd for C15H13ClNO4PdReS · CH2Cl2: C, 28.44; H, 2.39; N, 2.22; S, 5.08. Found: C, 28.39; H, 2.35; N, 2.2; S, 5.0. MS (ESI$^+$) m/z: 637.97 {[M − Cl] + CH3CN}$^+$; 545.88 [M − 3CO]$^+$. IR: 2014 (s) and 1920 (vs) cm^{-1}, v(CO), ^1H NMR: 3.52 (s, 3H, Me-(DMSO)); 3.54 (s, 3H, Me(DMSO)); 5.40 (t, 1H, $^3J_{H-H}$ = 2.8, H^4); 5.75 (dd, 1H, $^3J_{H-H}$ = 2.8, $^4J_{H-H}$ = 1.2, H^3); 5.79 (dd, 1H, $^3J_{H-H}$ = 2.8; $^4J_{H-H}$ = 1.2, H^5); 7.22 (td, 1H, $^3J_{H-H}$ = 7.2; $^4J_{H-H}$ = 1.2; H^{12}); 7.35 (d, 1H, $^3J_{H-H}$ = 7.6, H^{10}); 7.84 (td, 1H, $^3J_{H-H}$ = 7.6; $^4J_{H-H}$ = 1.2; H^{11}); 9.17 (d, 1H, $^3J_{H-H}$ = 5.6, H^{13}). $^{13}C\{^1H\}$ NMR: 47.2 (Me(DMSO)); 47.4 (Me(DMSO)); 83.8 (C^4); 86.3 (C^5); 86.9 (C^3); 117.7 (C^{10}); 121.8 (C^{12}); 140.75 (C^{11}); 150.2 (C^{13}); 153.1 (C^9); 196.1 (C^6; C^7, and C^8). Characterization data for **6b** are as follows. Anal. Calcd for C15H13ClNO4PtReS: C, 25.02; H, 1.82; N, 1.95; S, 4.45. Found: C,25.1; H, 1.7, N, 1.9; S, 4.4. MS (ESI$^+$) *m/z*: 725.00 {[M − Cl + CH3CN}$^+$; 683.97 [M − Cl]$^+$. IR: 2015 (s) and 1922 (vs) cm^{-1}, v(CO). ^1H NMR: 3.59 (s, 3H, $^3J_{Pt-H}$ = 21.0, DMSO); 3.61 (s, 3H, $^3J_{Pt-H}$ = 21.5, DMSO); 5.45 (t, 1H, $^3J_{H-H}$ = 3.0, H^3); 5.68 (dd, 1H, $^3J_{H-H}$ = 2.5, $^4J_{H-H}$ = 1.5, H^4); 5.71 (dd, 1H, $^3J_{H-H}$ = 2.5, $^4J_{H-H}$ = 1.5, H^5); 7.26 (td, 1H, $^3J_{H-H}$ = 6.5; $^4J_{H-H}$ = 1.5, H^{12}); 7.36

508 (dm, 1H, $^3J_{H-H}$=8.0,H^{10}); 7.84 (td, 1H, $^3J_{H-H}$=7.5, $^4J_{H-H}$=1.5,H^{11}); 9.40 (ddd, 1H,

509 $^3J_{H-H}$ = 5.75, $^4J_{H-H}$ = 1.5, $^5J_{H-H}$ = 1, H^{13}). $^{13}C\{^1H\}$ NMR: 47.7 ($^2J_{Pt-C}$ = 52.9,

510 Me(DMSO)); 47.9 ($^2J_{C-Pt}$ = 54.2, Me(DMSO)); 81.6 ($^3J_{C-Pt}$ = 44.2, C^4); 86.5 ($^3J_{C-Pt}$ =

511 79.13, C^5); 88.1 ($^2J_{C-Pt}$ = 43.8, C^3); 100.2 (C^1); 109.9 (C^2); 118.8 (C^{10}); 122.9 (C^{12}); 141.9

512 (C^{11}); 151.4 (C^{13}); 161.1 (C^9); 196.2 (C^6, C^7, and C^8). $^{195}Pt\{^1H\}$ NMR: –3664.

513 *[Pt{[k^2-C,N-{(η^5-C$_5$H$_3$)-2(C$_5$H$_4$N)Re(CO)$_3$}(PPh$_3$)Cl]* **(5b)**. This complex was

514 isolated as a pale yellow solid following the procedure described in method b for **5a** · ½

515 CH$_2$Cl$_2$, but with **6b** (60 mg, 8.3x10^{-5} mol) and PPh$_3$ (26 mg, 1.0 x 10^{-4} mol) as starting

516 materials (yield 64 mg, 3.4 x 10^{-5} mol, 85%). Anal. Cal cd for C$_{31}$H$_{22}$ClNO$_3$PPtRe: C,

517 41.18; H, 2.45; N, 1.55. Found: C, 41.4; H, 2.5; N, 1.4. MS (ESI$^+$) *m/z*: 868.05 [M – Cl]$^+$;

518 909.08 {[M – Cl] + CH$_3$CN}$^+$. IR: 2014 (s) and 1920 (vs) cm^{-1}, v(CO). 1H NMR: 3.41 (dd,

519 $^3J_{H-H}$ = 4.8, $^4J_{H-H}$ = 0.8, 1H, H^3); 4.95 (t, $^3J_{H-H}$ = 2.4, 1H,H^4); 5.83 (dd, $^3J_{H-H}$ = 2.5,

520 $^4J_{H-H}$ = 1, 1H, H^5); 7.22 (m, 1H, H^{12}); 7.35 (dd, $^3J_{H-H}$ = 6.4, $^4J_{H-H}$ = 0.4, 1H, H^{10}); 7.43

521 (m, 1H, H^{11}); 7.45–7.84 (m, 15H, aromatic protons of PPh$_3$); 9.68 (t, $^3J_{H-H}$ = 4.5, 1H,H^{13}).

522 $^{13}C\{^1H\}$ NMR: 84.4 ($^3J_{C-Pt}$ = 44.7, C4); 85.1 ($^3J_{C-Pt}$ = 36.1, C^5); 88.5 ($^2J_{C-Pt}$ = 108.2,

523 C^3); 100.4 (C^1); 108.0 (C^2); 118.0 (C^{10}); 122.7 (C^{12}); 140.8 (C^{11}); 150.2 (C^{13}); 160.3 (C^9);

524 196.1 (C^6, C^7 andC^8); four additional doublets at 129.3, 131.1, 132.2, 136.3 due to the PPh$_3$

525 ligand. $^{195}Pt\{^1H\}$ NMR: –4062 (d, $^1J_{P-Pt}$ = 4098). $^{31}P\{^1H\}$ NMR: 12.2 ($^1J_{Pt-P}$ = 4103).

526 **Crystallography**. A prismatic crystal (sizes in Table 2) of **1**, **5a** · ½ CH$_2$Cl$_2$, **5b**,

527 **6a** · CH$_2$Cl$_2$, or **6b** was selected and mounted on a Bruker-Siemens Smart CCD

528 diffractometer (equipped with a normal focus, 2.4 kW sealed-tube X-ray source Mo Kα

529 radiation and operating at 50 kV and 20 mA) for **1** and **5a** · ½ CH$_2$Cl$_2$, on a MAR345

530 diffractometer for **5b** and **6a** · CH$_2$Cl$_2$, or on a Enraf- Nonius CAD4 four-circle

531 diffractometer with an image plate detector for **6b**. In the last two cases, intensities were

532 collected with graphite-monochromated Mo Kα radiation. For **6b**, three reflections were

533   measured every 2 h as orientation and intensity control; significant intensity decay was not

534   observed. Lorentz–polarization and absorption corrections were made.

535   These structures were solved by direct methods using the SHELXS computer

536   program[48] and refined by full-matrix least-squares methods with the SHELX97 computer

537   program[49] using 2455 (for **1**), 5321 (for **5a** · ½ CH_2Cl_2), 12 832 (for **5b**), 9992 (for **6a** ·

538   CH_2Cl_2), or 5068 (for **6b**) reflections (very negative intensities were not assumed). The

539   function minimized was $\Sigma w||Fo|^2-|Fc|^2|^2$, where $w = [\sigma^2(I) + (0.0289P)^2 + 1.3732P]^{-1}$ (for

540   **1**), $w = [\sigma^2(I) + (0.0289P)^2 + 24.3025P]^{-1}$ (for **5a** · ½ CH_2Cl_2), $w = [\sigma^2(I) +$

541    $(0.0951P)^2+0.6924P]^{-1}$ (for **5b** · CH_2Cl_2), $w = [\sigma^2(I) + (0.0563P)^2 + 0.1984P]^{-1}$ (for **6a** ·

542   CH_2Cl_2), and $w= [\sigma^2(I) + (0.0400P)^2]^{-1}$ (for **6b**). $P = (|Fo|^2 + 2|Fc|^2)/3$; f, f ', and f " were

543   taken from the bibliography.[50] In all cases, H atoms were computed and refined, using a

544   riding model, with an isotropic temperature factor equal to 1.2 times the equivalent

545   temperature factor of the atom which to which it is linked. The final R indices and other

546   relevant parameters concerning the resolution of the crystal structures of these compounds

547   are presented in Table 2.

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695   (28) For illustrative purposes, we include the best results obtained for all the crystals of **2a**
696   tested: empirical formula $C_{15}H_7NO_5O_8PdRe$, T = 298 K, crystal system monoclinic,
697   a = 16.034(4) Å, b = 17.082(5) Å, c = 14.781(4) Å, $\alpha = \gamma = 90°$ and $\beta = 121.580(3)°$,
698   V = 3448.9(16) Å3, space group C2/c, crystal dimensions 0.20 x 0.20 x 0.20 mm; no.
699   of reflections 9764 (collected) and 2904 (unique), number of parameters 185; R indices
700   for I > 2σ(*I*) R1 = 0.1673 and wR2 = 0.3082 and for all data R1 = 0.2043 and wR2 =
701   0.3249; completeness to θ = 95.6%.

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759 **Table 1 Absorption and Emission Properties of the Free Ligand [{(η^5-C$_5$H$_4$-2-**

760 **C$_5$H$_4$N)}Re(CO)$_3$] (1) and the Monomeric Pallada- and Platinacycles [M{[k^2-C,N-(η^5-**

761 **C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re(CO)$_3$}Cl(L)] (M = Pd, Pt and L = PPh$_3$, DMSO) in CH$_2$Cl$_2$**

762 **Solution (at 298 K)[a]**

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| compd | M | L | absorption spectroscopic data[b] | | | emission data |
			λ_1 (log ε_1)	λ_2 (log ε_2)	λ_3 (log ε_3)	λ_{max}
1			229 (3.3)	274 (3.1)		none
			230 (3.6)	*269[b]*		
5a	Pd	PPh$_3$	228 (3.7)	245[c]	316 (2.9)	367
			227 (3.5)	*d*	*308 (2.7)*	*e*
5b	Pt	PPh$_3$	230 (3.5)	262 (2.9)	342 (2.5)	394
			231 (3.4)	*255 (2.8)*	*330 (2.2)*	*e*
6a	Pd	DMSO	229 (3.5)	258[c]	326 (2.9)	354
			229 (3.3)	*d*	*312 (2.7)*	*e*
6b	Pt	DMSO	230 (3.1)	263 (2.9)	365 (2.3)	386
			228 (3.0)	*257 (2.6)*	*353 (2.7)*	*e*

[a] Wavelengths λ_i (i = 1−3) and λ_{max} are given in nm and extinction coefficient ε_i in M^{-1} cm^{-1}. [b] For comparison purposes, absorption spectroscopic data in acetone at 298 K are presented in italics. [c] Shoulder. [d] This band was partially overlapped by that at higher energies (λ_1), and its resolution did not allow us to determine accurately the position of the maximum. [e] Not studied in acetone.

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Table 2. Crystal Data and Details of the Refinement of the Crystal Structures of the

Free Ligand [{(η^5-C5H4)-2(C5H4N)}Re-(CO)3}] (1) and the Cyclometalated

Compounds 5a · ½ CH2Cl2, 5b, 6a 3CH2Cl2, and 6b

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	1	5a · $^1/_2$CH$_2$Cl$_2$	5b	6a·CH$_2$Cl$_2$	6b
empirical formula	C$_{13}$H$_8$NO$_3$Re	C$_{31}$H$_{22}$NO$_3$PPdClRe· $^1/_2$CH$_2$Cl$_2$	C$_{31}$H$_{22}$NO$_3$PPtRe	C$_{15}$H$_{13}$NO$_3$PdReS·CH$_2$Cl$_2$	C$_{151}$H$_{13}$NO$_3$PtReS
formula wt	412.40	857.98	904.21	716.30	720.06
T/K	293(2)	293(2)	293(2)	195(2)	293(2)
cryst size/mm	0.40 × 0.40 × 0.30	0.50 × 0.50 × 0.30	0.20 × 0.10 × 0.10	0.20 × 0.10 × 0.08	0.20 × 0.10 × 0.10
λ/Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	Cc	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	11.0260(6)	37.933(3)	9.282(4)	9.806(4)	9.776(3)
b/Å	8,3465(4)	9.1354(7)	10.126(4)	10.001(2)	17.657(6)
c/Å	13.8932(7)	19.5917(16)	16.423(4)	11.644(4)	10.232(8)
α/deg	90.0	90.0	107.84(2)	100.81(2)	90.0
β/deg	107.5920(10)	116.8010(10)	92.51(2)	103.05(2)	99.46(16)
γ/deg	90.0	90.0	104.11(3)	101.79(2)	90.0
Volume/Å^3	1218.78(11)	6059.9(8)	1417.6(8)	1055.8(6)	1742.2(16)
Z	4	8	2	2	4
D_{calcd}/Mg m^{-3}	2.248	1.881	2.118	2.253	2.745
μ/mm^{-1}	9.968	4.848	9.378	7.079	15.255
$F(000)$	768	3304	848	676	1312
no. of collected rflns	9403	22 909	12 832	9992	5068
no. of unique rflns, R(int)	2715, 0.0341	6629, 0.0304	7040, 0.0748	5225, 0.0391	5068, 0.0000
no. of params	164	367	328	224	217
R indices (all data)	R1 = 0.0399, wR2 = 0.0690	R1 = 0.0561, wR2 = 0.0748	R1 = 0.0518, wR2 = 0.1390	R1 = 0.0327, wR2 = 0.0870	R = 0.0645, wR2 = 0.0767
R indices ($I > 2\sigma(I)$)	R1 = 0.0319, wR2 = 0.0663	R1 = 0.0366, wR2 = 0.0701	R1= 0.0502, wR2 = 0.1371	R1 = 0.0327, wR2 = 0.0864	R1 = 0.0333, wR2 = 0.0701

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Figures Captions

Figure 1. Mono- and dinuclear palladacycles derived from half-sandwich rhenium complexes described previously (X = Cl, Br, I and L = neutral ligand such as PR$_3$).[15]

Figure 2. ORTEP diagram of [{(η^5-C$_5$H$_4$)-2(C$_5$H$_4$N)}Re(CO)$_3$] (**1**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and bond angles (in deg): Re(1) – G* , 1.969; C(1) – C(9), 1.453(8); C(2) – C(1), 1.422(7); C(2) – C(1) – C(9), 125.7(5); C(5) – C(1) – C(9), 128.0(5); N(1) – C(9) – C(1), 116.3(5); C(3) – C(2) – C(1), 109.3(5); C(2) – C(1) – C(5), 105.9(5).

Scheme 1^a. ^{a} Legend: (i) in THF, n-butyllithium at -78 °C for 1.5 h; (ii) ZnCl$_2$ for 1.5 h; (iii) [PdCl$_2$(PPh$_3$)$_2$] and 2-bromopyridine for 1.5 h.

Scheme 2^a. ^{a} Legend: (i) Pd(OAc)$_2$ in HOAc, reflux for 24 h; (ii) PPh$_3$ in CDCl$_3$ for 3 min; (iii) NaCl in CH$_2$Cl$_2$/H$_2$O for 12 h; (iv) PPh$_3$ in benzene for 12 h; (v) [MCl$_2$(DMSO)$_2$] (M= Pd(II), Pt(II)), in toluene, reflux for 12 h.

Figure 3. ^{1}H NMR spectrum (500 MHz) of [Pd{[k^2-C,N-(η^5-C$_5$H$_3$)-2(C$_5$H$_4$N)]Re(CO)$_3$}(μ-OAc)]$_2$ (**2a**) in acetone-d6 at 298 K, showing the two sets of superimposed signals ascribed to the two isomers **2a1** and **2aII**, together with an expansion of the region 6.8 < δ < 8.3 ppm. Labeling of the peaks refers to the numbers assigned to the protons in Scheme 2, and the labels in italics correspond to the minor isomer present in solution (**2aII**).

Figure 4. Molecular structure of the trans isomer (**2aI**) of [Pd{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re(CO)$_3$}(μ-OAc)]2 (**2a**).

Figure 5. ORTEP diagram of [Pd{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]-Re(CO)$_3$}Cl(PPh$_3$)] · ½ CH$_2$Cl$_2$ (**5a** · ½ CH$_2$Cl$_2$). The solvate molecule and hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Pd(1) – C(2), 1.992(5); Pd(1) – N(1), 2.131(4); Pd(1) – P(1),2.254(13); Pd(1) – Cl(1), 2.371(13); C-(1) – C(9), 1.444(7); N(1) – Pd – Cl(1), 91,61(11); C(2) – Pd(1) – N-(1), 81,59(17); C(2) – Pd(1) – P(1), 97.84(13); Cl(1) – Pd(1) – P(1), 88.97(5); C(2) – C(1) – C(9) 119.8(4); C(5) – C(1) – C(9), 131.0(5); N(1) – C(9) – C(1), 113.1(4).

Figure 6. ORTEP diagram of [Pd{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]-Re(CO)$_3$}Cl(DMSO)] (**6a**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Pd – C(2), 1.979(3); Pd – N, 2.091(3); Pd – S, 2.2283(12); Pd – Cl, 2.3964(13); C(1) – C(9), 1.455(5);C(2) – Pd – N, 80.93(14);N – Pd – Cl, 95.21(10); C(2) – Pd – S, 94.63(11); Cl – Pd – S, 90.12(5); C(1) – C(2) – C(3), 107.0(7); C(2) – C(1) – C(9), 118.3(3); C(1) – C(9) – N, 112.0(5).

Figure 7. ORTEP diagram of [Pt{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re-(CO)$_3$}Cl(DMSO)] (**6b**). Hydrogen atoms are omitted for clarity. Selected bond lengths (inÅ) and angles (in

808　deg): Pt – C(2), 1.995(6); Pt – N, 2.102(5); Pt – S, 2.203(2); Pt – Cl(1), 2.386(2); C(1) –
809　C(9), 1.476(10); C(2) – Pt – N, 80.6(2); N – Pt – Cl(1), 93.91(16); C(2) – Pt – S, 95.01(19);
810　Cl(1) – Pt – S, 90.40(8); 105.5(5); C(2) – C(1) – C(9), 116.6(5); C(11) – C(9) – N, 113.2(5).

811　**Figure 8.** ORTEP diagram of [Pt{[k^2-C,N-(η^5-C$_5$H$_3$)-2-(C$_5$H$_4$N)]Re-(CO)$_3$}Cl(PPh$_3$)]
812　(**5b**). Hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in
813　deg): Pt – C(2), 1.969(5); Pt – N, 2.127(4); Pt – P, 2.2295(15); Pt – Cl, 2.3814(16); C(1) –
814　C(9), 1.437(7); C(2) – Pt – N, 80.48(18); N – Pt – Cl, 92.42(13); Cl – Pt – P, 86.85(6); C(2)
815　– Pt – P, 100.20(4); C(2) – C(1) –C (9), 116.9(5); C(5) –C (1) –C (9), 134.2(5); C(1) –C(9)
816　– N, 114.7(5).

817　**Figure 9.** UV–visible spectra of the free ligand (1) and the mononuclear cyclometalated
818　complexes **5a** and **6a** in CH$_2$Cl$_2$ at 298 K.

819　**Figure 10.** Emission spectra of compounds **5a,b** and **6a**,b in CH$_2$Cl$_2$ at 298 K.

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821   **Figure 1**

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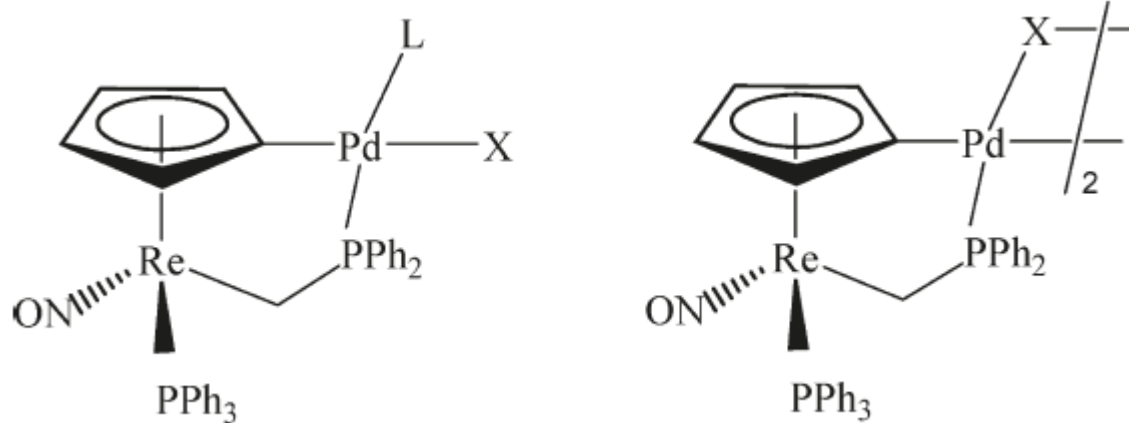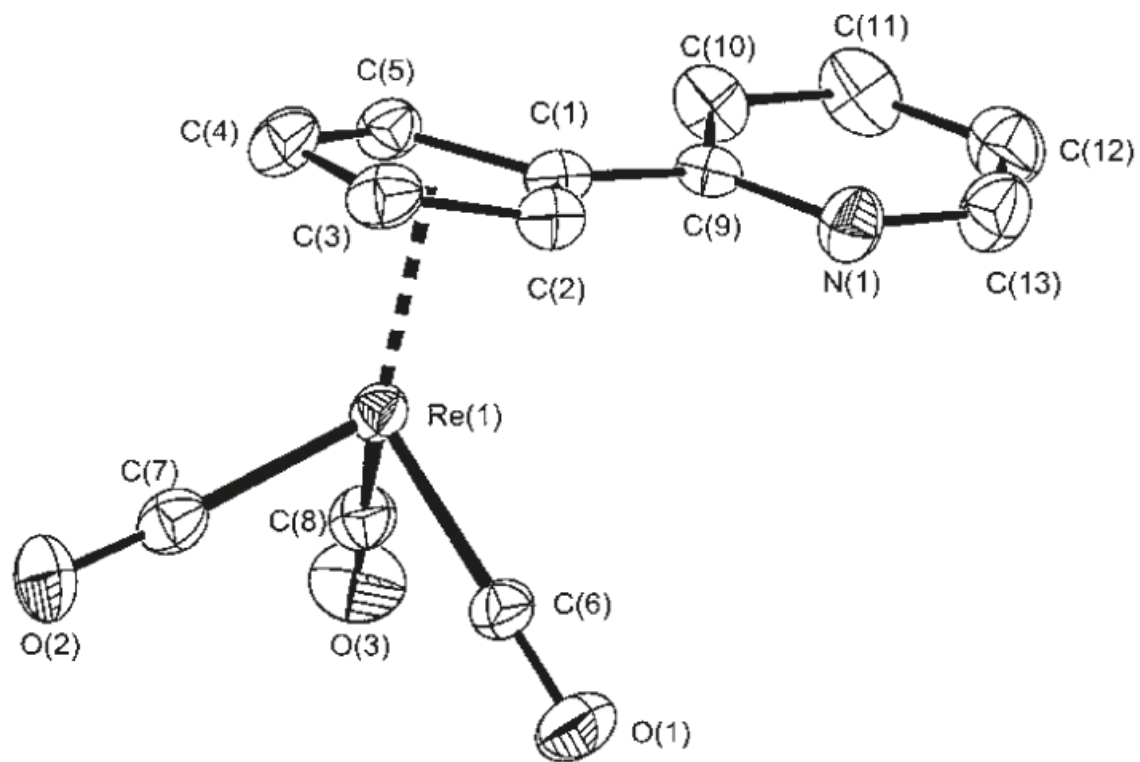
Figure 2

832 **Scheme 1**[a]

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838   **Scheme 2**[a]

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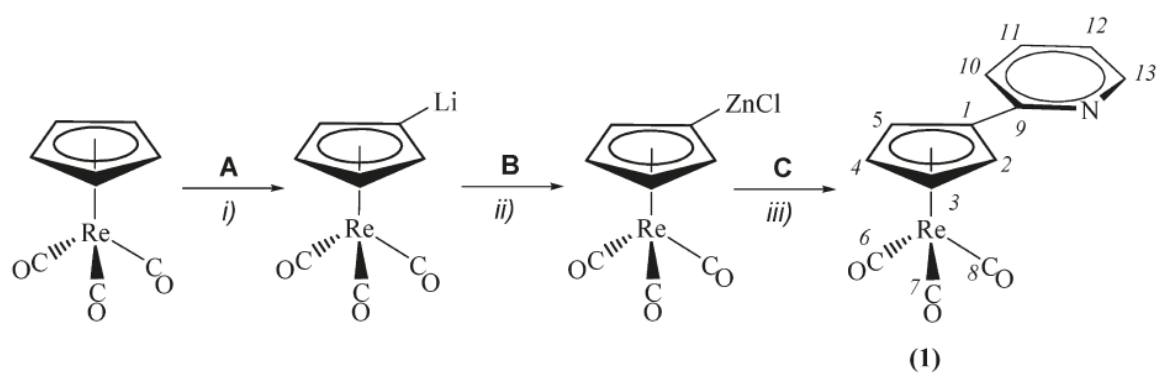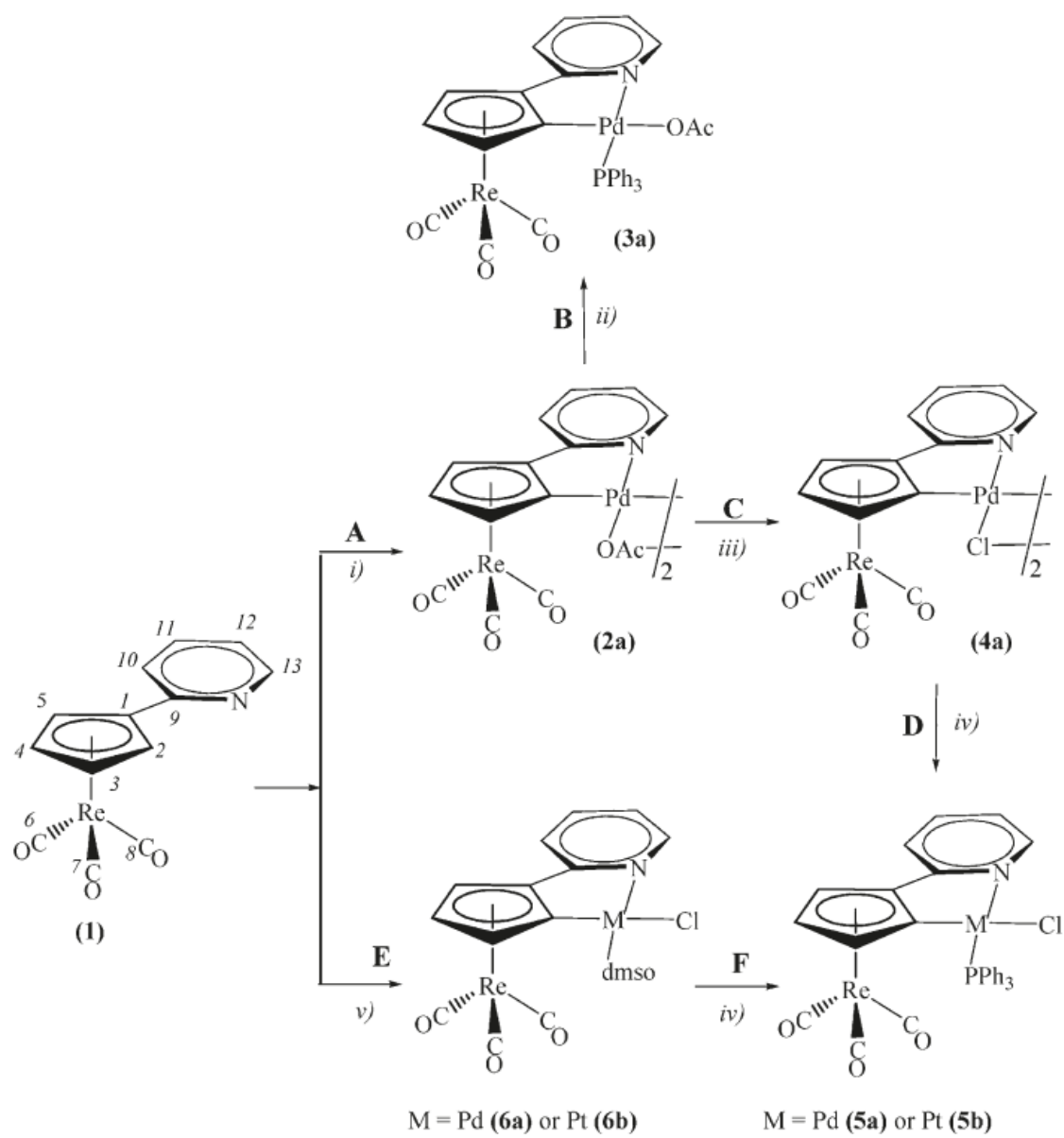
844   **Chart 1**

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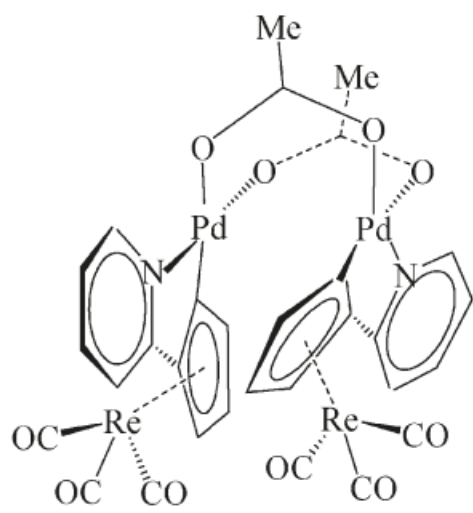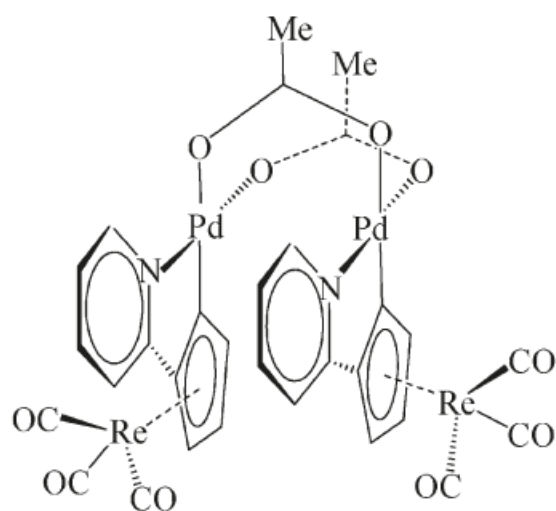
trans (2aI)   *cis* (2aII)

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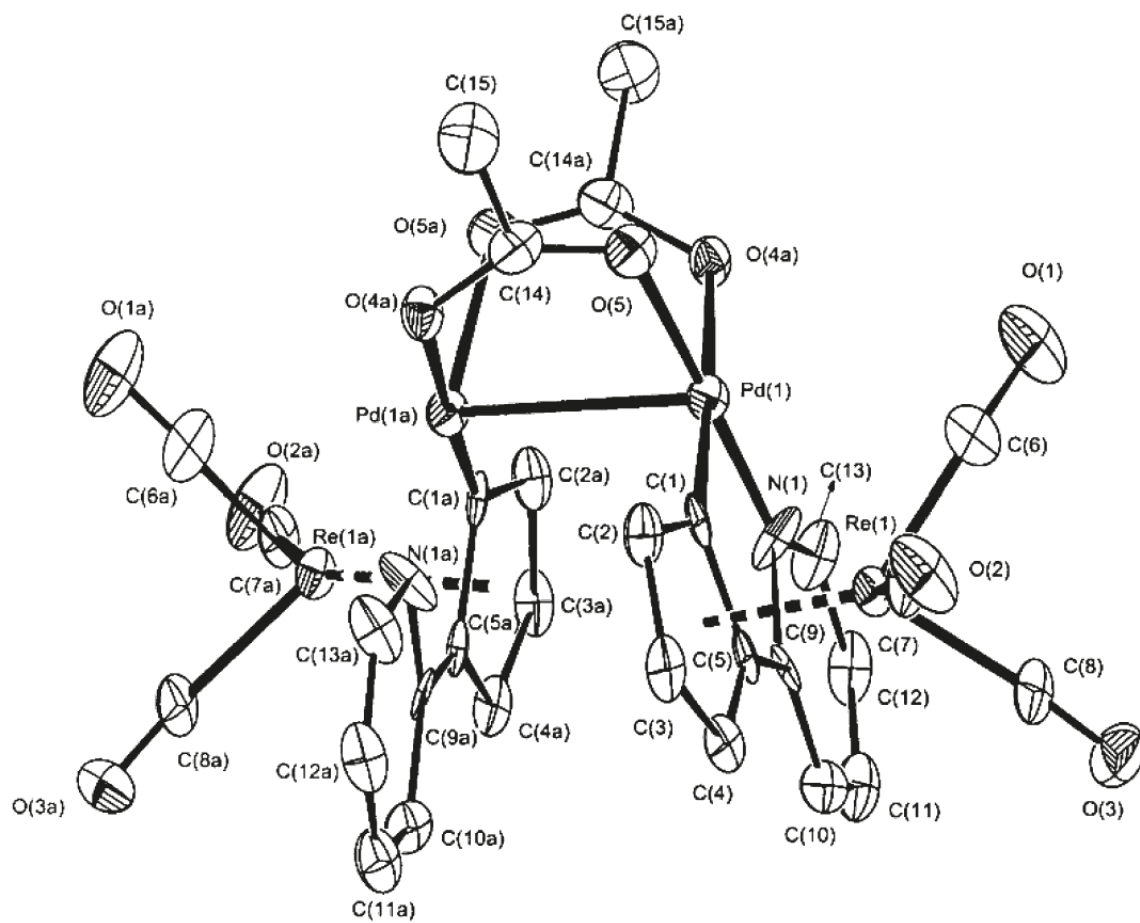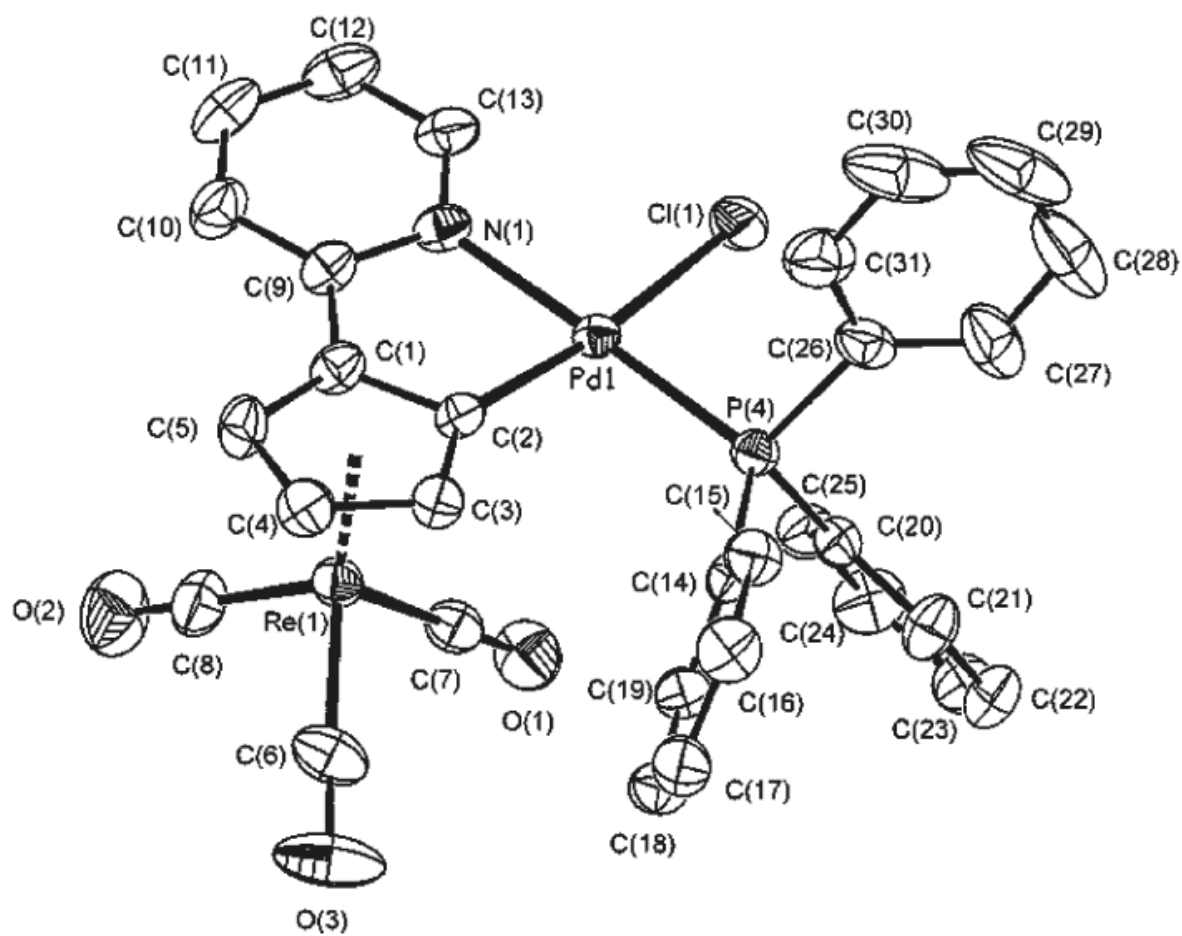849

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Figure 4

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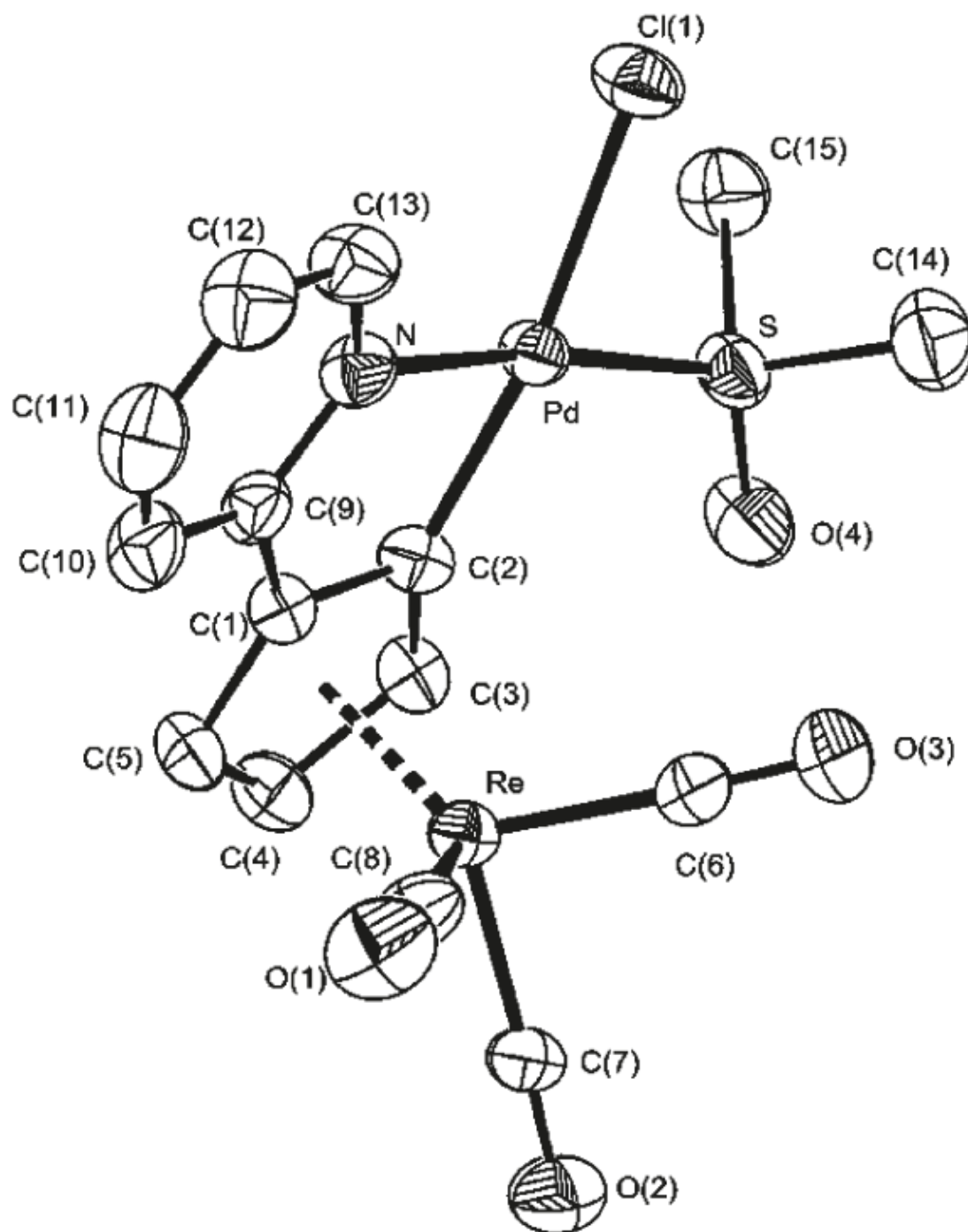855

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Figure 5

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Figure 6

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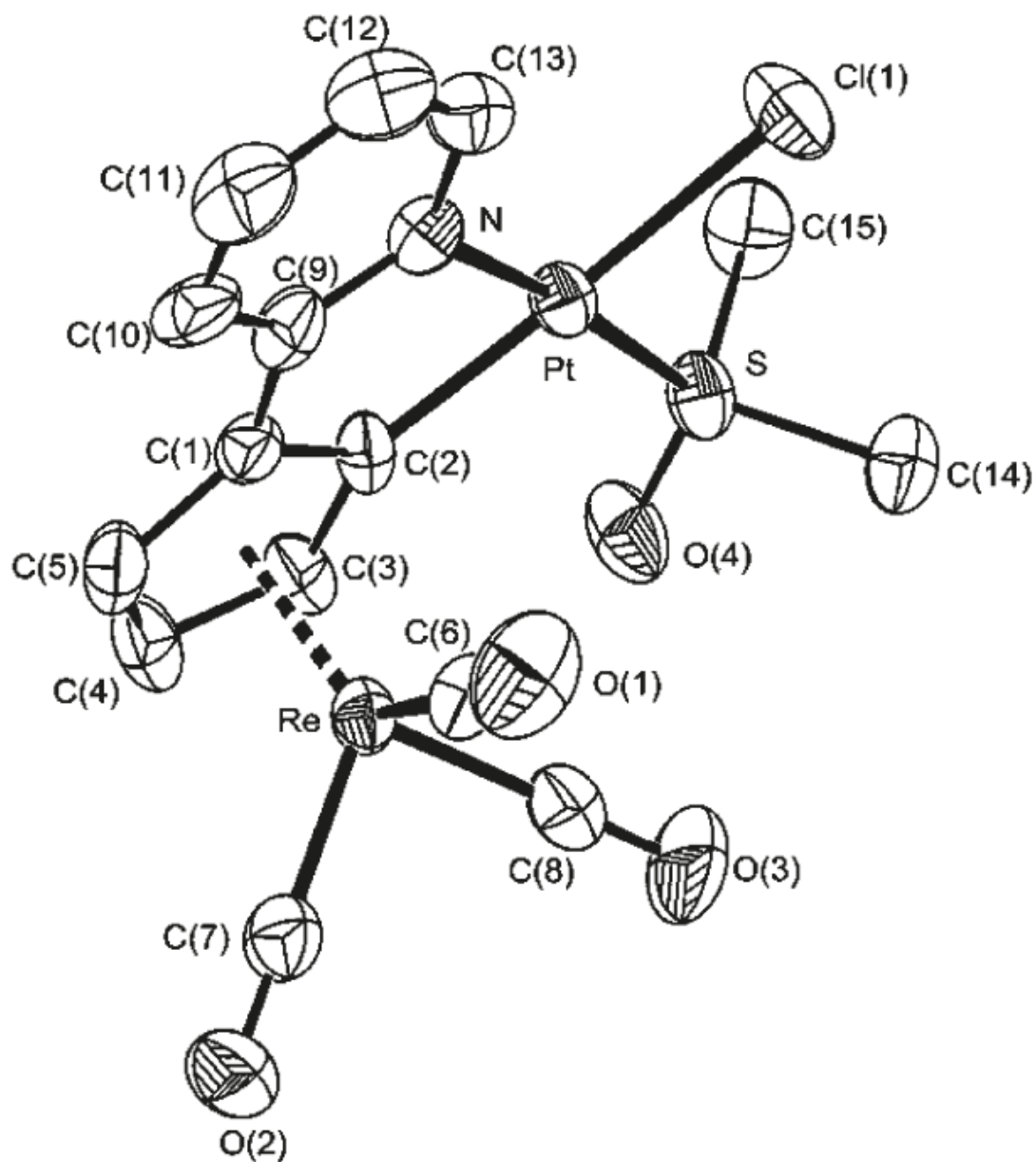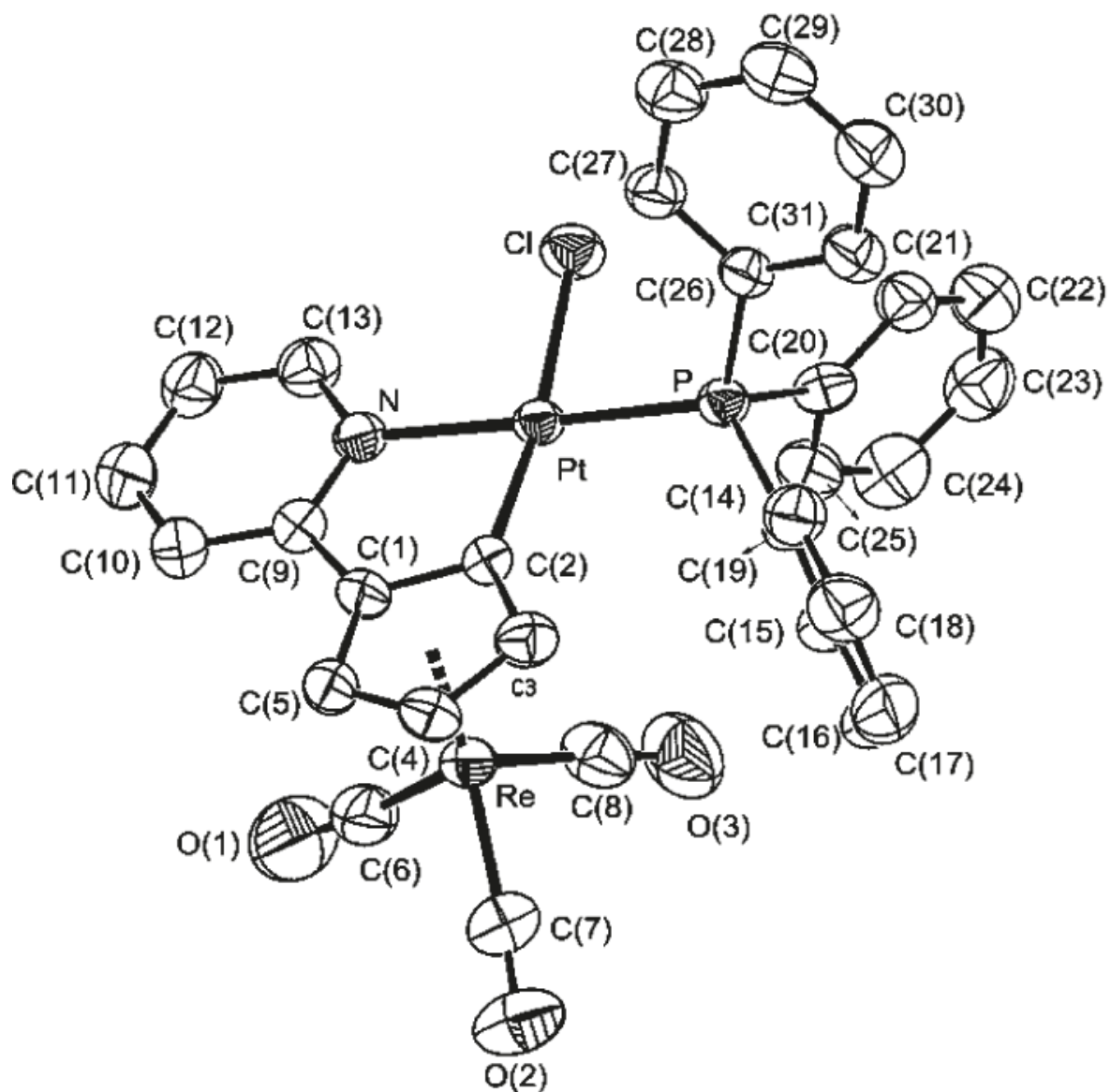877

Figure 7

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Figure 8

896   **Figure 9**

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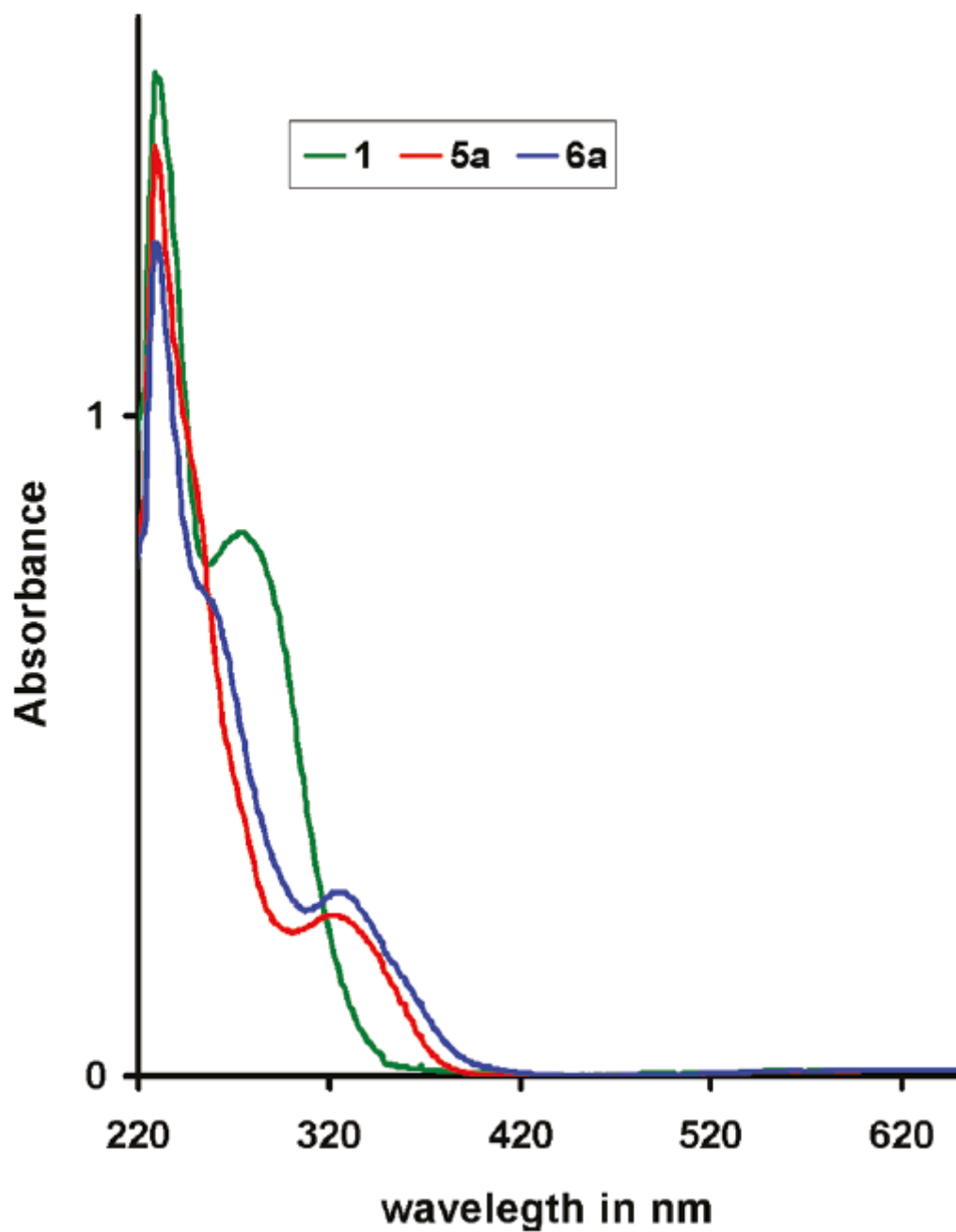
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905 **Figure 10**

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330   430   530

wavelength in nm

—5a —5b —6a —6b
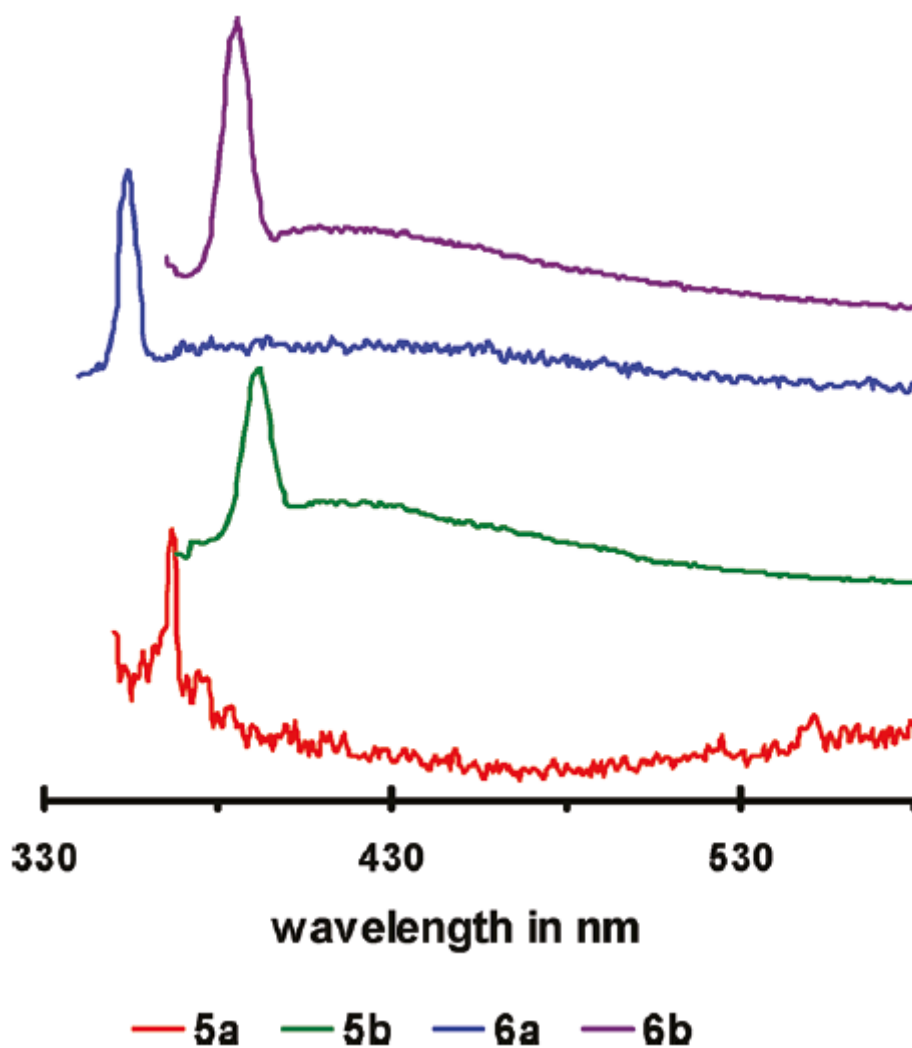
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