

1 **Diastereomerically Pure Heterodi- and Heterotetrametallic (Pd and Pt) Compounds: A Study of**
2 **the Effect Induced by the Binding Mode of a Ferrocene-Containing Ligand on Their**
3 **Electrochemical Properties**
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43 compounds
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48 The reaction of (1*S*,2*R*)-[(η^5 -C₅H₅)Fe{(η^5 -C₅H₄)-CH=NCH(Me)-CH(OH)(C₆H₅)}] (1) with
49 Na₂[PdCl₄] in the presence of Na(OAc)·3H₂O produced three diastereomerically pure tetrametallic
50 cyclopalladated complexes (6*b*I–6*b*III). In two of them (6*b*I and 6*b*II), the imine 1 adopts the
51 [C(sp²,ferrocene), N]– mode of binding, but they differ in the planar chirality of the 1,2-ferrocenyl unit
52 (Sp in 6*b*I and Rp in 6*b*II), whereas ligand 1 in 6*b*III acts as a [C(sp²,phenyl),N]– group. Treatment of
53 6*b*I–6*b*III with PPh₃ gave [Pd{ κ^2 -C,N{(η^5 -C₅H₃)-CH=N-CH(Me)-CH(OH)(C₆H₅)}Fe(η^5 -
54 C₅H₅)}Cl(PPh₃)] (7*b*I, 7*b*II) and [Pd{ κ^2 -C,N{(C₆H₄)-CH(OH)-CH(Me)-N=CH-(η^5 -C₅H₄)}Fe(η^5 -
55 C₅H₅)}Cl(PPh₃)] (7*b*III). The PtII compounds [Pt{ κ^2 -C,N{(η^5 -C₅H₃)-
56 CH=NCH(Me)CH(OH)(C₆H₅)}Fe(η^5 -C₅H₅)}Cl(PPh₃)] [(Sp,1*S*,2*R*) and (Rp,1*S*,2*R*) diastereomers,
57 7*a*I and 7*a*II, respectively] have also been prepared. The results of electrochemical studies of 6*b*I–6*b*III,
58 7*b*I–7*b*III, 7*a*I, 7*a*II and related PtII complexes with 1 acting as an (N) or (N,O)– ligand are also
59 reported. Comparison of the results provides conclusive evidence for the relative influence of the mode
60 of binding of the ligand, the nature of the MII atom, the type of metallated atom C(sp²,phenyl or
61 ferrocenyl), the ancillary ligands and their relative disposition on the electrochemical properties of this
62 type of compound.

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68 INTRODUCTION

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70 One of the most exciting areas of modern organometallic chemistry is centred on the synthesis of novel
71 ferrocene derivatives, the study of their properties and their potential applications in a wide variety of
72 areas that include synthesis, catalysis, biology, advanced materials and biomedicine.[1–3] The existence
73 of a redox centre in these products makes them also especially useful for the design of electrochemical
74 devices such as molecular machines, switches and sensors..[4] In addition, the rich and versatile
75 chemistry of ferrocene permits the incorporation of substituents and functional groups into one or both
76 rings and at different sites.[1,2] The presence of heteroatoms (i.e., N, P, O or S) and/or unsaturated
77 groups with good donor abilities is particularly important due to their ability to act as ligands for other
78 metal ions to achieve heterodi-, heterotri- or, in general, heteropolymetallic complexes. In these systems,
79 the presence of proximal metals in different environments with different oxidation numbers and spin
80 states may influence their mutual cooperation in a variety of processes and, in particular, may allow not
81 only the modification of the electrochemical properties of the ferrocenyl unit, but also the introduction
82 or promotion of other properties or activities by external stimulus (e.g., light, pH) or vice versa.[1,5,6]

83 On the other hand, it is well known that 1) ferrocene derivatives with additional $-C(R)=N-$ or
84 heterocyclic rings are valuable ligands for PdII and PtII[5,6] and 2) ring–chain tautomeric equilibria
85 between imines and 1,3-(N,O) heterocycles (i.e., oxazolines or oxazines, Scheme 1) affect the reactivity
86 of the two species involved in this process.[7,8] This property is important not only because of their
87 utility in organic and organometallic synthesis, but also in physical and medicinal chemistry.[7,8]
88 Unfortunately, examples of ferrocenyl imines showing this type of behaviour are extremely scarce[9,10]
89 and studies on their reactivity with transition-metal salts are even less common. One of the latest
90 examples of ring–chain tautomerism of ferrocene derivatives is that of the imine (1S,2R)-[(η^5 -
91 C₅H₅)Fe{(η^5 -C₅H₄)-CH=NCH(Me)-CH(OH)C₆H₅}] (1)[10] and its closed form 2 (Scheme 2, step i).

92 Recent studies have shown that imine 1 can adopt a variety of binding modes, [(N),(N,O)]– or
93 [C(sp²,ferrocene), N]–,[11] and hapticities in PtII complexes. In fact, an accurate control of the
94 experimental conditions used in the reaction of 1 with cis-[PtCl₂(dms_o)₂][11] produced the preferential
95 formation of each of the six diastereomerically pure platinum(II) complexes 3aI, 3aII, 4aI, 4aII, 5aI and
96 5aII (Figure 1), some of them exhibiting greater anti-proliferative activity than cisplatin against lung
97 (A549), breast (MDA-MB-231) and colon (HCT-116) cancer cell lines.[11]

98 This outstanding versatility in the coordination of 1 with PtII, the relevance of enantio- and
99 diastereomerically pure PdII complexes in homogeneous catalysis and in asymmetric synthesis,[12] and
100 the increasing interest in the electrochemical properties of transition-metal complexes with ferrocenyl
101 ligands[1,2,6a,6e,13] prompted us to explore the reactivity of compound 1 with PdII salts or complexes
102 and to compare 1) the effects induced by the binding mode of 1 in the palladium(II) complexes on the
103 proclivity of the ferrocenyl ligand to oxidation and 2) their electrochemical behaviour with those of the
104 PtII derivatives depicted in Figure 1. Herein we present three types of diastereomerically pure
105 heterotetra- (Pd₂Fe₂) or heterodimetallic [(Pd,Fe) or (Pt,Fe)] complexes and a comparative study of
106 their electrochemical properties.

107

108 RESULTS AND DISCUSSION

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110 Heterotetrametallic Compounds

111 Treatment of (1*S*,2*R*)-[(η^5 -C₅H₅)Fe{(η^5 -C₅H₄)-CH=NCH(Me)-CH(OH)(C₆H₅)}] (1) with equimolar
112 amounts of Na₂[PdCl₄] and Na(OAc)·3H₂O in methanol at 298 K for 40 h followed by SiO₂ column
113 chromatography gave small amounts of ferrocenecarbaldehyde and three different di- μ -chlorido-bridged
114 cyclopalladated complexes 6bI, 6bII and 6bIII (Scheme 2, step ii) in a relative abundance 6bI/6bII/6bIII
115 of 1.0:0.9:0.4. The major components (6bI and 6bII) were isolated as garnet solids after elution with first
116 CHCl₃ (for 6bI) and then with a CHCl₃/MeOH (100:0.2) mixture (for 6bII). Note that the relative
117 abundance of the three isomers did not change substantially when the reaction period was increased
118 from 24 to 72 h.[14]

119 The characterization data for compounds 6bI–6bIII (see the Supporting Information) indicate that they
120 are formed by metallation of the (η^5 -C₅H₄) ring (for 6bI and 6bII) and the phenyl ring (6bIII). In these
121 isomers the two halves of the molecules could be in either a *cis* or *trans* disposition. Moreover, because
122 the formation of the σ [Pd–C(sp²,ferrocene)] bond induces planar chirality,[1–3,13a] for 6bI and 6bII the
123 two metallated units could have identical (Sp and Sp or Rp and Rp) or different (Sp and Rp) planar
124 chirality. The results obtained from the reactions of 6bI and 6bII with PPh₃ (see below) revealed that the
125 absolute configuration of the ferrocenyl unit was (Sp,Sp) in 6bI and (Rp,Rp) in 6bII,

126 The minor product, 6bIII [isolated after the elution with CHCl₃/MeOH (100:0.4) and concentration]
127 arose from the activation of the σ [C(sp²,phenyl)–H] bond. Its X-ray crystal structure[15] (Figure 2)
128 confirmed 1) the existence of a central and planar “Pd(μ -Cl)₂Pd” unit, 2) a *cis* disposition of the two
129 halves of the molecule, 3) the *syn* (*Z*) form adopted by the imine in the complex and 4) the
130 [C(sp²,phenyl),N]–mode of binding of the ligand.

131 In the crystal structure, the separation between the Cl1*S* (or Cl2*S*) atoms of the CH₂Cl₂ molecules and
132 the hydrogen atoms H9B (and H13B, respectively) is smaller than the van der Waals radii of these
133 atoms[16] and suggests C–H···Cl interactions that lead to supramolecular chains, as shown in Figure 3.

134 The results obtained in the reaction shown in Scheme 2 (step i) and, in particular, the formation of 6bIII,
135 are markedly different from those reported for [(η^5 -C₅H₅)Fe{(η^5 -C₅H₄)-CH=N-(CH₂)_n-(C₆H₅)}] (*n* =
136 0, 1 or 2), which, under identical experimental conditions, underwent cyclopalladation of the ferrocenyl
137 unit exclusively, even for *n* = 2.[17] These findings suggest that the presence of the –Me and –OH
138 substituents on the vicinal carbons of the –(CH₂)₂–chain is important for modifying the regioselectivity
139 of the cyclopalladation process.

140 Finally, note that despite the fact that 1) ligand 1 coexists with the closed form 2 in solution[10] and 2)
141 several examples of PdII complexes formed by the coordination of oxazines (involved in ring–chain
142 tautomeric processes) have been reported,[18] in our case no evidence of the presence of PdII complexes
143 containing any of the diastereomers of the closed form (2) as ligand has been provided by 1H NMR
144 studies of the crude of the reaction. This suggests that the open form 1 is more prone to bind to the PdII
145 centre than the heterocyclic form, in good agreement with the results obtained in the reaction of 1 with
146 *cis*-[PtCl₂(dmsO)₂].[11]

147

148 Heterodimetallic Compounds

149 The addition of PPh₃ to CH₂Cl₂ solutions of the corresponding di- μ -chlorido-bridged products 6bI, 6bII
150 or 6bIII in a molar ratio 2:1 produced the splitting of the central “Pd(μ -Cl)₂Pd” units and the formation
151 of the monomeric derivatives 7bI, 7bII and 7bIII, respectively (Scheme 2, step iii). The characterization

152 data (see the Supporting Information) agreed with the proposed formulae. Note that the signal observed
153 in the $^{31}\text{P}\{1\text{H}\}$ NMR spectrum of 7bIII ($\delta = 32.4$ ppm) appears at a higher field than in the spectra of
154 7bI and 7bII ($\delta = 37.4$ and 37.8 ppm, respectively). This may be due to the different influence of the
155 metallated carbon [C(sp²,phenyl) in 7bIII vs. C(sp²,ferrocene) in 7bI and 7bII). NMR studies of the
156 three products confirmed the cis arrangement of the phosphido ligand and the metallated carbon, in good
157 agreement with the transphobia effect.[19]

158 The X-ray crystal structure of 7bII [20] confirmed the formation of the heterodimetallic molecules
159 $[\text{Pd}\{\kappa^2\text{-C,N}\{(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-CH(Me)-CH(OH)(C}_6\text{H}_5)\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl-(PPh}_3)]$ (Figure 4).

160 In each molecule, the PdII is in a square-planar environment in which it is bound simultaneously to the
161 imine nitrogen {N(1)} and the ortho carbon {C(6)} of the substituted ring of the ferrocenyl unit. This
162 confirms the [C(sp²,ferrocene), N]- binding mode of ligand 1 in 7bII. A chlorido and the phosphorus of
163 the PPh₃ ligand complete the coordination sphere. The angle of C(6)-Pd(1)-P [$95.3(2)^\circ$] indicates a cis
164 arrangement to the metallated carbon, in good agreement with the results obtained from NMR studies
165 and the transphobia effect.[10]

166 To compare the effect induced by the PdII or PtII metals on the electrochemical behaviour of the
167 (Sp,1S,2R) and (Rp,1S,2R) diastereomers of $[\text{M}\{\kappa^2\text{-C,N}\{(\eta^5\text{-C}_5\text{H}_5)\text{-CH=NCH(Me)-CH(OH)}$
168 $(\text{C}_6\text{H}_5)\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl(PPh}_3)]$, we also prepared the PtII complexes. Treatment of the platinacycles
169 $[\text{Pt}\{\kappa^2\text{-C,N}\{(\eta^5\text{-C}_5\text{H}_5)\text{-CH=N-CH(Me)-CH(OH)(C}_6\text{H}_5)\}\text{-Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl(dmsO)}]$ (5aI or 5aII,
170 Scheme 3) with an equimolar amount of PPh₃ in CH₂Cl₂ at 298 K gave, after work-up, the desired
171 complexes 7aI and 7aII, respectively. The positions of the signals detected in the $^{31}\text{P}\{1\text{H}\}$ and
172 $^{195}\text{Pt}\{1\text{H}\}$ NMR spectra, as well the 1JPt,P coupling constant, are in good agreement with those
173 reported for related platinacycles such as the (Sp,SC) and (Rp,SC) diastereomers of $[\text{Pt}\{\kappa^2\text{-C,N}\{(\eta^5\text{-}$
174 $\text{C}_5\text{H}_5)\text{-CH=N-CH(R)-CH}_2(\text{OH})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl(PPh}_3)]$ (R = Me or iPr) in which the PPh₃ ligand
175 and the metallated carbon atom are in a cis disposition.[13a,13b]

176

177 Electrochemical Studies

178 In a first attempt to elucidate the effects produced by the mode of binding of the Schiff base to the MII
179 ions, the nature of the ancillary ligands bound to them and their relative arrangement in the electronic
180 environment of the iron(II), we decided to explore the electrochemical properties of the PtII and PdII
181 compounds 3aI, 3aII, 4aI, 4aII, 5aI, 5aII, 7aI, 7aII, 5bI-5bIII and 7bI-7bIII shown in Figure 1 and
182 Schemes 2 and 3. Note that the ^1H NMR spectra of all the products in CD₃CN revealed they are stable
183 in this solvent. The electrochemical studies were carried out by cyclic voltammetry of freshly prepared
184 solutions (10-3 m) in acetonitrile with (Bu₄N)[PF₆] as the supporting electrolyte. All these experiments
185 were carried out at different scan rates ν ($\nu = 0.05\text{-}1.0$ Vs⁻¹). The electrochemical data for all the
186 compounds under study are presented in Table 1 and the cyclic voltammograms (hereinafter referred to
187 as CVs) obtained at 298 K and a scan rate of $\nu = 0.1$ Vs⁻¹ for the PtII and PdII complexes are depicted
188 in Figures 5-7.

189 First, we will describe the results obtained for the monomeric PtII complexes. As shown in Figure 5 and
190 Figure 6, the CVs exhibit one anodic peak with a directly associated reduction in the reverse scan. The
191 $I_{\text{pa}}/I_{\text{pc}}$ ratios are close to 1 and the relationship between I_{pa} and $\nu^{1/2}$ is linear. According to the
192 literature, all these findings are consistent with those expected for a simple reversible one-electron
193 process.[21] The main differences between the CVs arise from the positions of the waves that shift
194 towards the anodic region as follows: 5aI 7aI 5aII 7aII 3aI 3aII 4aI 4aII (referred to hereafter
195 as sequence A).

196 It is well known that the proclivity of ferrocene derivatives to oxidation is strongly dependent on the
197 nature of the substituents.[1,10,13] In general, the presence of electronwithdrawing groups is reflected

198 by an increase in the Epa value, whereas donor groups produce the opposite effect. On this basis, several
199 conclusions can be reached from sequence A. First, the electrochemical properties of these PtII
200 complexes depend on several factors. One of them is the binding mode of the ligand. Compounds with 1
201 acting as a [C(sp²,ferrocene),N]- ligand (5aI, 5aII, 7aI and 7aII) are more prone to oxidation than 3aI
202 and 3aII in which the imine binds through the nitrogen atom exclusively, whereas complexes in which 1
203 acts as a (N,O)- ligand (4aI and 4aII) are less likely to undergo oxidation.

204 Secondly, the differences detected in the CVs of the pair of compounds 3aI and 3aII suggest that the
205 trans-“PdCl₂(dmsO)” moiety bound to the imine nitrogen has a greater electron-withdrawing effect than
206 if the two Cl- ligands are in a cis disposition. For the isomers 4aI and 4aII, the effect produced by the
207 relative arrangement of the dmsO and Cl- ligands (at a five-bond distance from the ferrocenyl unit) is
208 not as strong as in 3aI and 3aII, in which the monodentate groups are closer to the organometallic array.

209 For the cycloplatinated complexes 5aI, 5aII, 7aI and 7aII, replacement of the dmsO ligand of 5aI or 5aII
210 by PPh₃ to yield 7aI and 7aII, respectively, produced displacement of the wave to the anodic region.
211 The magnitude of this shift is greater than those observed for the other two pairs of isomeric PtII
212 complexes (i.e., 3aI and 3aII, 4aI and 4aII).

213 Furthermore, for compounds 7aI, 7aII, 7bI and 7bII, which differ in the planar chirality of the 1,2-
214 ferrocenyl unit, the differences are greater than those reported for related palladacycles, such as those
215 derived from (Sp,1SC)-and (Rp,1SC)-[Pt{κ²-C,N{(η⁵-C₅H₃)-CH=N-CH(R)-CH₂-(OH)}Fe(η⁵-
216 C₅H₅)}Cl(PPh₃)] (R = Me or iPr).[13b] In addition, comparison of the electrochemical properties of
217 compounds 7aI and 7bI indicate that the PdII complex is less prone to oxidation than its PtII analogue.
218 The same trend is found for the couple 7aII and 7bII.

219 The CVs of the dimeric and tetrametallic complexes 6bI– 6bIII (Figure 7) show one anodic peak with a
220 directly associated reduction peak in the reverse scan, which suggests that there is no electronic
221 communication between the two ferrocenyl units. Note that for 6bIII the wave is strongly shifted to the
222 anodic region when compared with those of 6bI and 6bII. Thus, on this basis, comparison of the
223 positions of the anodic peak for compounds 6bI, 6bII and 6bIII, or their partners 7bI, 7bII and 7bIII
224 (Figure 7), indicate that the metalation of the phenyl ring produces an electron-withdrawing effect on the
225 ferrocenyl unit.

226 For the couples 7aI, 7bI and 7aII, 7bII, which differ in the nature of the MII ion, the replacement of the
227 PtII in 7aI or 7aII by PdII (to yield 7bI or 7bII, respectively) produces a shift of the wave to the anodic
228 region. This means that the palladium(II) complexes are less prone to oxidation than their PtII
229 analogues.

230

231 **CONCLUSIONS**

232

233 The results presented herein have allowed us to prepare two series of three sets of diastereomerically
234 pure cyclopalladated complexes containing four (in 6bI–6bIII) or two (in 7bI–7bIII) metal centres. In
235 each series, the complexes differ in the nature of the metallated carbon [C(sp²),ferrocene in 6bI, 6bII,
236 7bI and 7bII, or C(sp²),phenyl in 6bIII and 7bIII] or in the planar chirality of the ferrocenyl unit (R_p in
237 6bI and 7bI, and S_p in 6bI and 7bI). Although the regio- and diastereoselectivity of the process is low, it
238 provides a simple method for achieving diastereomerically pure organometallic palladium(II) with two
239 stereogenic carbon centres with (in 6bI, 6bII, 7bI and 7bII) or without (in 6bIII and 7bIII) planar
240 chirality. The new PdII complexes presented herein appear to be excellent candidates for use not only as
241 precursors in asymmetric synthesis or catalysis, but also as electrochemical reagents.

242 Among the organic compounds that exhibit a similar rich and versatile chemistry in the presence of PdII
243 and PtII atoms, ligand 1 is, to the best of our knowledge, the first that can 1) generate a variety of
244 diastereomerically pure complexes with ferrocenyl units, 2) adopt up to four different binding modes
245 [(N),(N,O)]-, [C(sp²,ferrocene),N] or [C(sp²,phenyl),N]- and 3) produce different types of isomeric
246 forms of the PdII or PtII complexes.

247 In addition, a comparative study of the electrochemical behaviour of the new PdII and PtII complexes
248 prepared in this work (6bI–6bIII, 7bI–7bIII, 7aI and 7aII) and those closely related (3aI, 3aII, 4aI, 4aII,
249 5aI and 5aII) provide conclusive evidence of the relative important influence of 1) the binding mode of
250 the ligand to the metal centre {[C(sp²,ferrocene),N]- in 5aI, 5aII, 6bI, 6bII, 7aI, 7aII, 6bI and 6bII,
251 [C(sp²,phenyl),N]- in 6bIII and 7bIII, (N) in 3aI and 3aII or (N,O)- in 4aI and 4aII}, 2) the type of
252 metal ion (PdII or PtII), 3) the nature of the remaining ligands bound to the metal and 4) their relative
253 disposition on the electrochemical properties of the product. An accurate selection of the product allows
254 the fine-tuning of the anodic and cathodic potentials in a wide range (i.e., the maximum difference in the
255 E_{pa} values is ca. 0.45 V). Thus, these products are also attractive in view of their potential utility as
256 selective and specific electrochemical sensors or detectors.

257 Moreover, the presence of an –OH group in the pendant arm of most of these PdII and PtII complexes
258 (3aI, 3aII, 5aI, 5aII, 6bI, 6bII, 7aI, 7aII, 7bI and 7bII) opens up new possibilities and applications in
259 other interesting fields. These products are similar to the PtII complexes derived from [(η⁵-C₅H₅)Fe(η⁵-
260 C₅H₄)-CH=N-(C₆H₄-2-OH)], which exhibit behaviour typical of acid/base-dependent molecular
261 switches.[13b] The compounds presented herein are optically pure and consequently they appear to be
262 extremely useful for the development of pH-dependent chiral molecular switches. Further work in this
263 area is under way.

264

265 **Experimental Section**

266

267 **Preparation of the Compounds**

268 **Compounds 6bI and 6bII:** Na₂[PdCl₄] (237 mg, 8.06 × 10⁻⁴ mol) and NaOAc·3H₂O (110 mg,
269 8.06 × 10⁻⁴ mol) were added to a solution of ligand 1 (280 mg, 8.06 × 10⁻⁴ mol) in methanol (20 mL).
270 The reaction mixture was stirred at 298 K for 40 h. After this period, the solution was concentrated to
271 dryness on a rotary evaporator and the deep-red residue was dissolved in the minimum amount of
272 CHCl₃ and passed through a column of SiO₂ (25 × 50 mm). Elution with CHCl₃ produced two bands.
273 The first eluted was pale orange and gave, after concentration, small amounts of ferrocenecarbaldehyde.
274 The second was red-garnet and produced, after concentration, compound 6bI (122 mg). Further elution
275 with CHCl₃/MeOH (100:0.01) gave a mixture of the two diastereomers 6bI and 6bII (32 mg) in a 1:1
276 molar ratio. The subsequent use of CHCl₃/MeOH (100:0.02) as eluent produced compound 6bII (109
277 mg).

278 **Compound 6bIII:** This compound was isolated as a minor component during the preparation of the
279 palladacycles 6bI and 6bII. Once the band containing isomer 6bII had been collected, the eluent was
280 replaced by CHCl₃/MeOH (100:0.4). This produced an orange solution that gave, after evaporation of
281 the solvent, isomer 6bIII (54 mg).

282 **Compound 7bI:** PPh₃ (21 mg, 8.19 × 10⁻⁵ mol) was added to a solution of compound 6bI (40 mg,
283 4.10 × 10⁻⁵ mol) in CH₂Cl₂ and the mixture was stirred at 298 K for 30 min. After this period, the
284 mixture was concentrated to around 5 mL and passed through a short column of SiO₂ (15 × 20 mm)
285 using CH₂Cl₂ as eluent and the deeporange band produced was collected and concentrated to dryness
286 on a rotary evaporator to give complex 7bI, which was then dried in vacuo for 5 days (yield: 54 mg, 88
287 %).

288 **Compound 7bII:** This product was prepared by using the same procedure as described above for 7bI
289 but by using isomer 6bII (18 mg, 1.84 × 10⁻⁵ mol) and PPh₃ (10 mg, 3.69 × 10⁻⁵ mol) as the starting
290 materials (yield: 20 mg, 71%).

291 **Compound 7bIII: PPh₃** (8 mg, 3.07 × 10⁻⁵ mol) was added to a solution of 6bIII (20 mg, 1.54 × 10⁻⁵
292 mol) in CH₂Cl₂ (10 mL) and the mixture was stirred at 298 K for 30 min. After this period, the mixture
293 was filtered and the filtrate was concentrated to dryness on a rotary evaporator and the solid formed was
294 then collected and dried in vacuo for 5 days (yield: 19 mg, 83%).

295 **Compounds 7aI and 7aII:** The corresponding isomer, 5aI or 5aII (40 mg, 6.11 × 10⁻⁵ mol), was
296 dissolved in CH₂Cl₂ (10 mL) and then an equimolar amount of PPh₃ (18 mg) was added. The reaction
297 mixture was stirred at 298 K for 30 min, concentrated in vacuo to around 5 mL and then the solution
298 was passed through a short column of SiO₂ (20 × 30 mm). Elution with CH₂Cl₂ produced a red band
299 that gave, after concentration, a deep-red solid that was collected and dried in vacuo for 5 days (yields:
300 44 mg, 86% and 41 mg, 80% for 7bI and 7aII, respectively).

301 **CCDC-940607** (for 6bIII) and **-940608** (for 7bII) contain the supplementary crystallographic data for
302 this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre
303 via www.ccdc.cam.ac.uk/data_request/cif.

304 **Supporting Information** (see footnote on the first page of this article): Detailed characterization data
305 (elemental analyses, mass spectra, IR, UV/Vis, optical rotations, R_f values and NMR) for the PdII
306 compounds 6aI–6aIII and 7bI–7bIII, and the PtII complexes 7aI and 7aII.

307

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376 [15] Crystal data for 6bIII CH_2Cl_2 : $\text{C}_{40}\text{H}_{40}\text{Cl}_2\text{Fe}_2\text{N}_2\text{O}_2\text{Pd}_2 \cdot \text{CH}_2\text{Cl}_2$, $M = 1061.07$, $T = 100(2)$ K,
377 orthorhombic, space group = $P212121$, $a = 12.089(2)$, $b = 15.804(2)$, $c = 20.454(3)$ Å, $\alpha = \beta = \gamma$
378 $= 90^\circ$, $V = 3907.8(19)$ Å³, $D_{\text{calcd.}} = 1.80$ Mgm⁻³, $\mu = 2.441$ mm⁻¹, $F(000) = 2120$, no. of
379 reflections = 36791, no. of parameters = 480; final R indices [$\lceil 2\sigma(I) \rceil$]: $R1 = 0.0638$, $wR2 =$
380 0.1640 ; R indices (all data): $R1 = 0.0736$, $wR2 = 0.1692$.

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392 $P21$, $a = 7.668(7)$, $b = 10.523(6)$, $c = 20.377(13)$ Å, $\alpha = \beta = 90.0$, $\gamma = 94.48(4)^\circ$, $V = 1639(2)$ Å³,
393 $D_{\text{calcd.}} = 1.520$ Mgm⁻³, $\mu = 1.152$ mm⁻¹, $F(000) = 764$, number of reflections: 17447, number
394 of parameters: 399; final R indices [$\lceil 2\sigma(I) \rceil$]: $R1 = 0.0685$, $wR2 = 0.1644$; R indices (all data):
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400 **Legends to figures**

401

402 **Scheme 1.** Ring–chain tautomerism between imines and the 1,3-(N,O) heterocycles formed by a 5- or 6-
403 endo-trig process.

404

405 **Scheme 2.** Synthesis of tetra- and dimetallic cyclopalladated complexes 6bI–6bIII and 7bI–7bIII,
406 respectively. Reagents and conditions: i) tautomeric equilibrium between imine 1 and the closed forms
407 2; this process is solvent-dependent;[10] ii) Na₂[PdCl₄], Na(OAc)·3H₂O, MeOH, 298 K, 40 h; SiO₂
408 column chromatography; iii) PPh₃ {molar ratio PdII/PPh₃ = 0.5} in CH₂Cl₂ at 298 K.

409

410 **Figure 1** Diastereomerically pure platinum(II) complexes recently reported in which imine 1 adopts
411 different modes of binding (L represents dmsO).[11]

412

413 **Figure 2.** ORTEP plot of [Pd{κ²-C,N{(C₆H₄)-CH(OH)-CH(Me)-N=CH-(η⁵-C₅H₄)}Fe(η⁵-C₅H₄)}(μ-
414 Cl)]₂ (6bIII). Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]:
415 Pd1–C15 1.990(9), Pd1–N1 2.014(8), Pd1–Cl1 2.353(2), Pd1–Cl2 2.469(2), Pd2–Cl15B 2.020(7), Pd2–
416 N1B 2.020(7), Pd2–Cl1 2.355(2), Pd2–Cl2 2.469(2), N1–C11 1.264(12), N1–C12, 1.485(12), N1B–
417 C11B 1.270(12), N1B–C12B 1.478(12), O1–C13 1.444(11), O1B–C13B, 1.416(11).

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419 **Figure 3** Simplified view of the C–H···Cl contacts between molecules of [Pd{κ²-C,N{(C₆H₄)-
420 CH(OH)-CH(Me)-N=CH-(η⁵-C₅H₄)}Fe(η⁵-C₅H₄)}(μ-Cl)]₂ (6bIII) and CH₂Cl₂ in the crystals of 6bIII
421 CH₂Cl₂.

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423 **Fig. 4** ORTEP plot of compound (+)-(Rp,1S,2R)-[Pd{κ²-C,N{(η⁵-C₅H₃)-CH=N-CH(Me)-
424 CH(OH)(C₆H₅)}Fe(η⁵-C₅H₅)}Cl (PPh₃)] (7bII). Thermal ellipsoids are drawn at the 50% probability
425 level. Selected bond lengths [Å] and angles [°]: Pd(1)–C(6) 2.009(8), Pd(1)–N(1) 2.135(6), Pd(1)–P
426 2.259(2), Pd(1)–Cl(1) 2.369(3), N(1)–C(11) 1.323(10), N(1)–C(12) 1.486(10), C(6)–Pd(1)–N(1)
427 80.9(3), C(6)–Pd(1)–P 95.3(2), N(1)–Pd(1)–Cl(1) 92.32(19), P–Pd(1)–Cl(1) 92.90(8), C(10)–C(11)–
428 N(1) 114.2(7), C(11)–N(1)–C(12) 117.9(6).

429

430 **Scheme 3.** Synthesis of dimetallic complexes 7aI and 7aII. Reagents and conditions: i) Equimolar
431 amount of PPh₃, CH₂Cl₂, 298 K.

432

433 **Figure 5.** Cyclic voltammograms of the platinum(II) complexes with the Schiff base 1 acting as a
434 neutral N-donor ligand (3aI, 3aII) or as a monoanionic and bidentate (N,O)– ligand (4aI, 4aII).

435

436 **Figure 6.** Cyclic voltammograms of the (Sp,1S,2R) and (Rp,1S,2R) diastereomers of $[\text{Pt}\{\kappa^2\text{-C,N}\{(\eta^5\text{-C}_5\text{H}_3)\text{-CH=N-CH(Me)-CH(OH)(C}_6\text{H}_5)\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl(L)}]$ with L = dmsO (5aI, 5aII) or PPh₃ (7aI,
437 C₅H₃)-CH=N-CH(Me)-CH(OH)(C₆H₅)}Fe(η⁵-C₅H₅)}Cl(L)] with L = dmsO (5aI, 5aII) or PPh₃ (7aI,
438 7aII). Dotted vertical lines correspond to the E_{pa} value of 5aI and 5aII.

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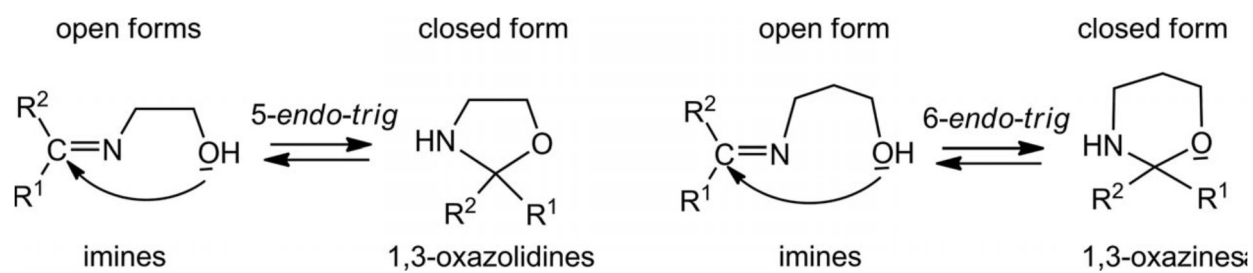
440 **Figure 7.** Cyclic voltammograms of the tetrametallic complexes 6bI–6bIII (top) and their corresponding
441 dimetallic derivatives 7bI–7bIII (bottom). The vertical lines correspond to the E_{pa} values of the parent
442 dimeric complexes (6bI–6bIII).

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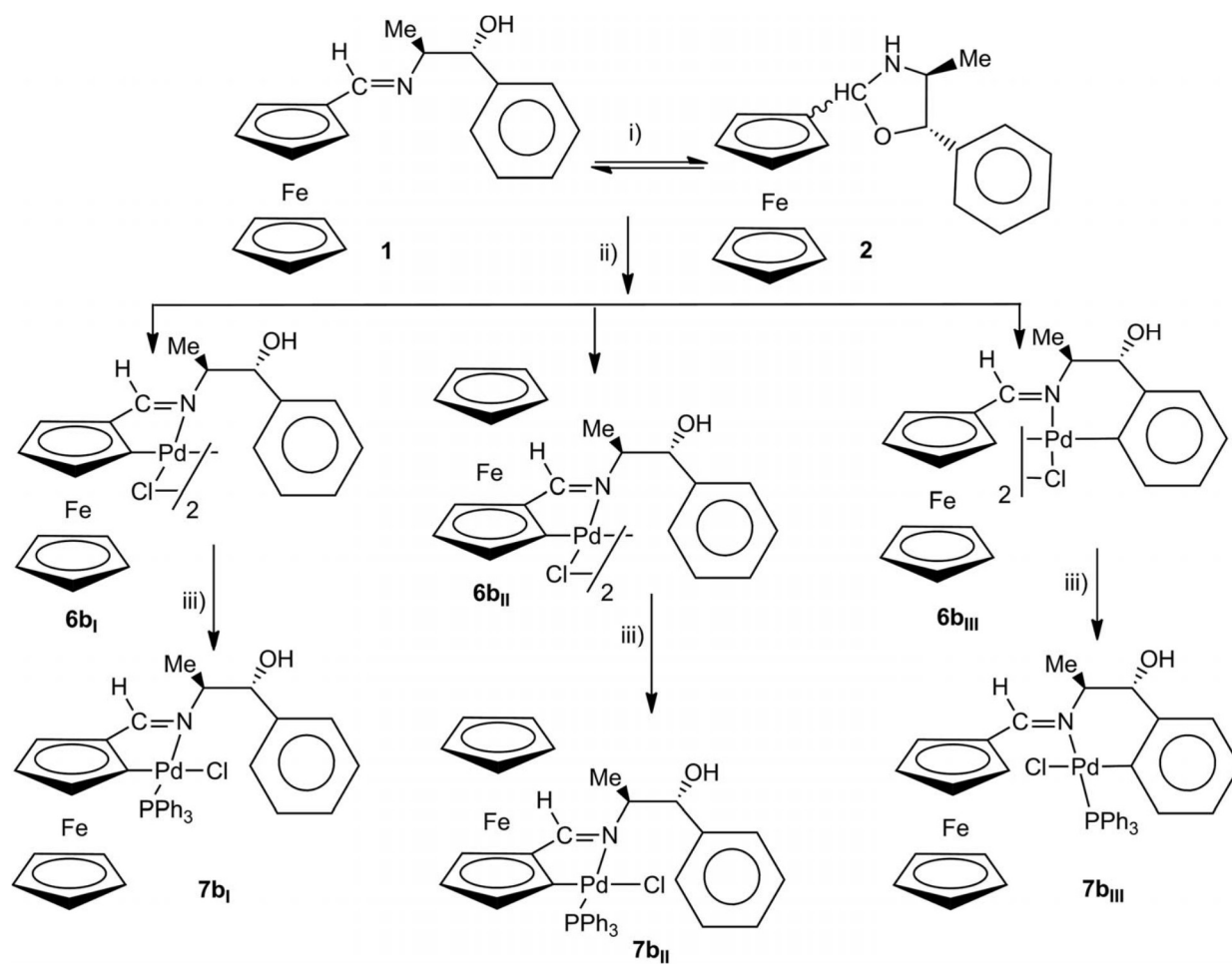
SCHEME 1



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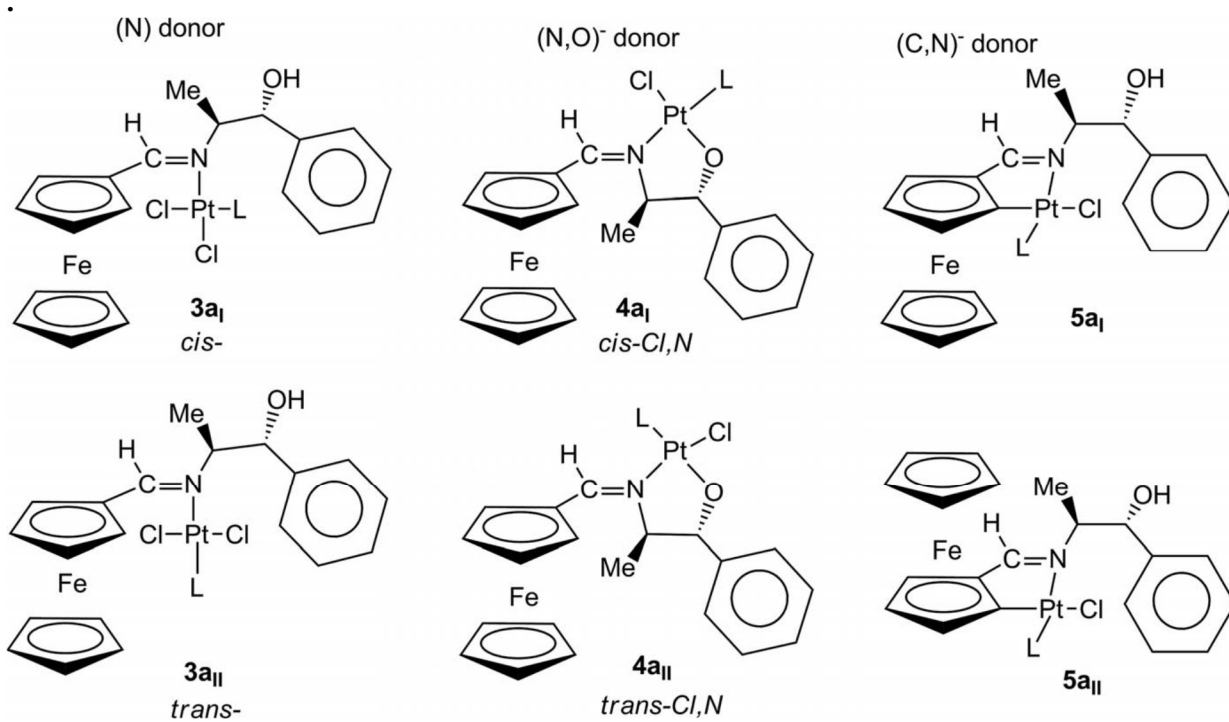
SCHEME 2



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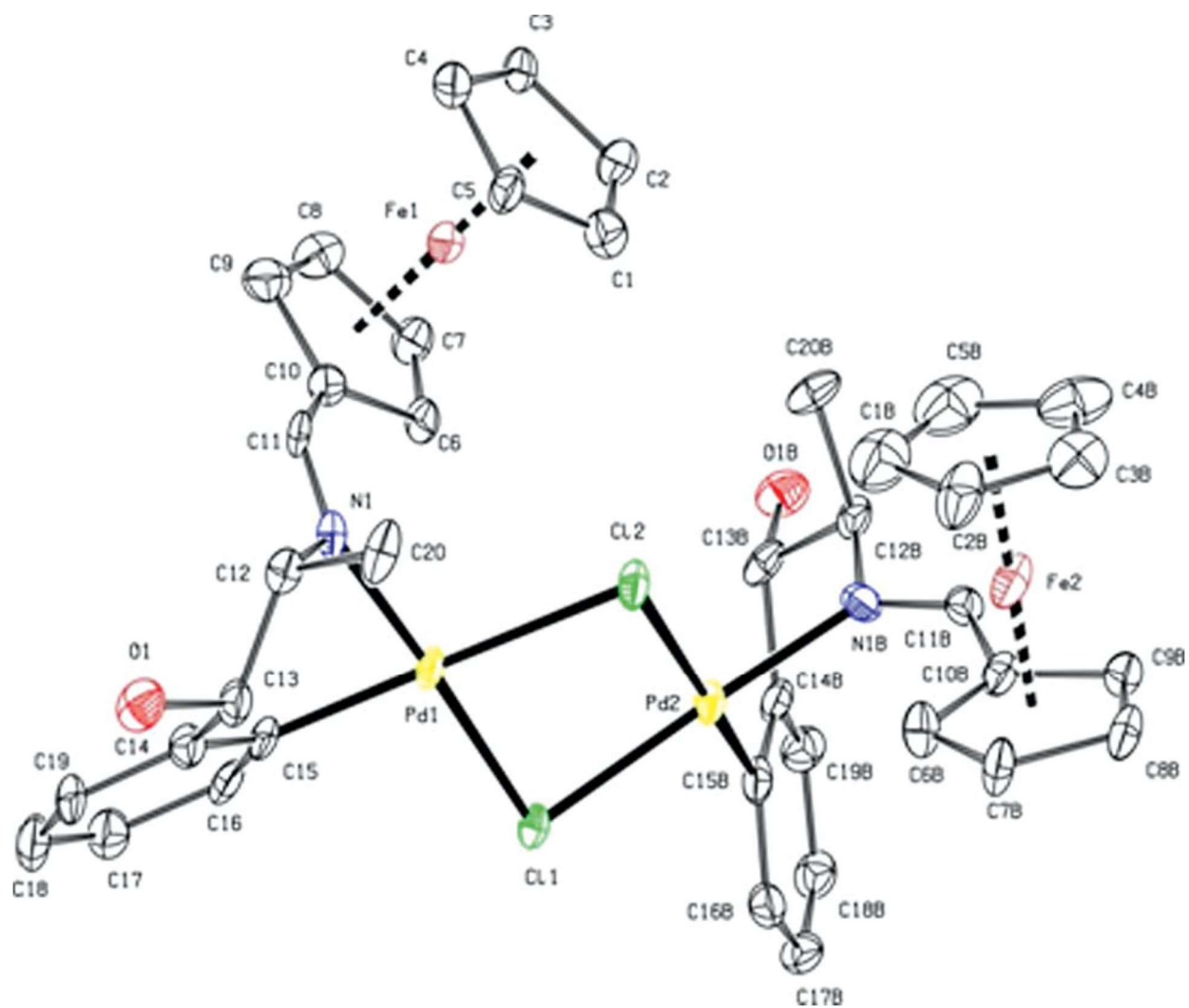
FIGURE 1



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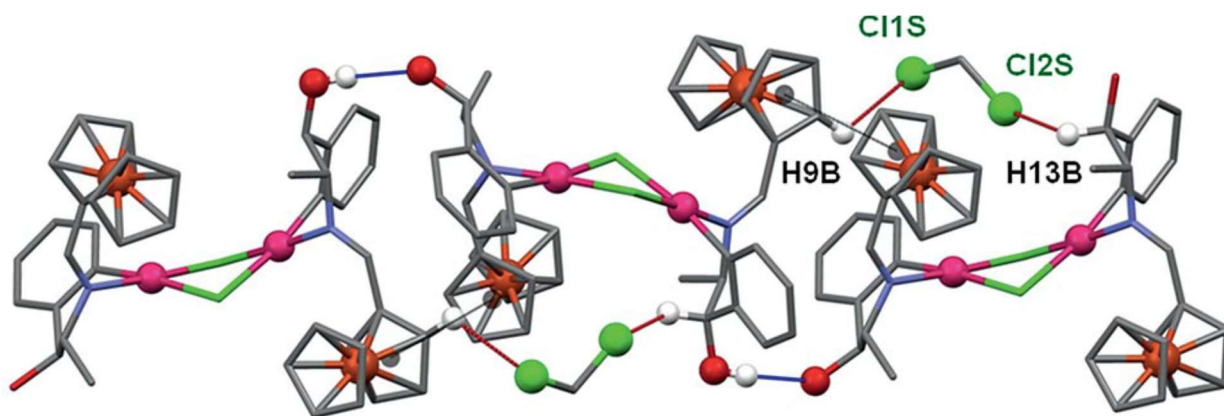
FIGURE 2



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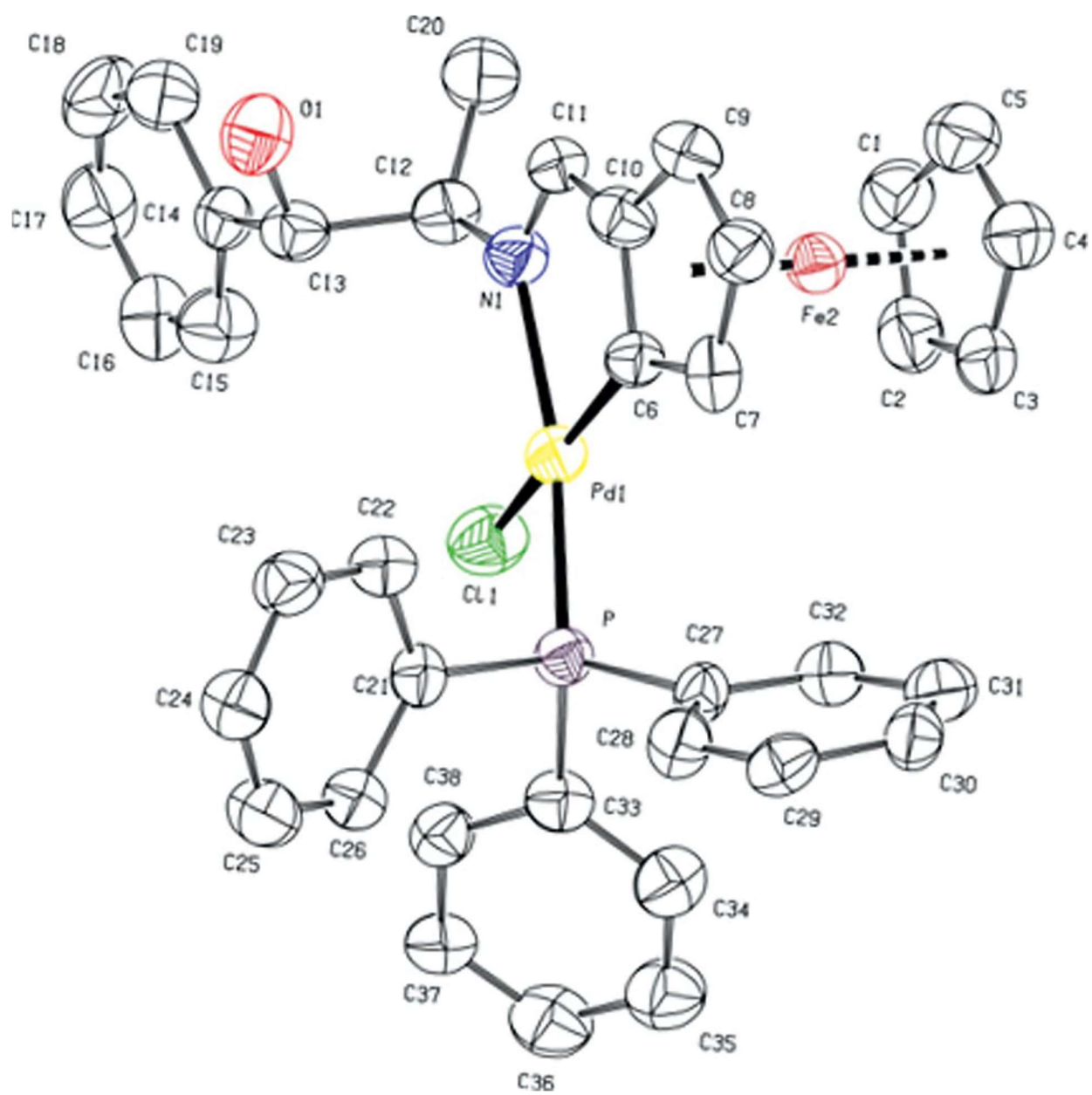
FIGURE 3



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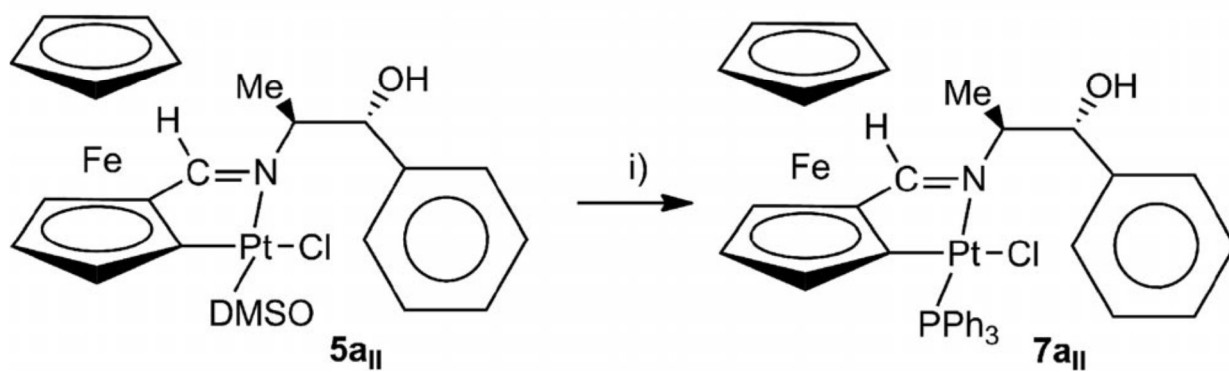
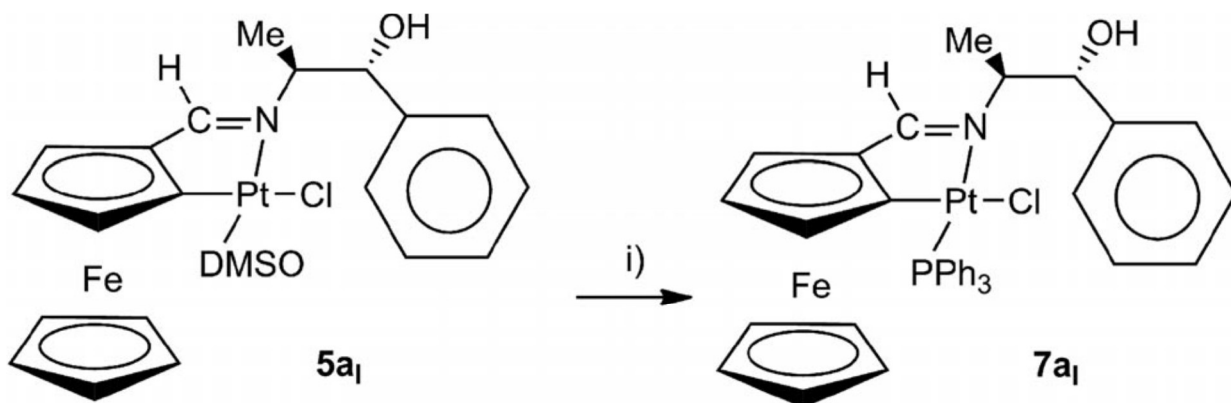
FIGURE 4



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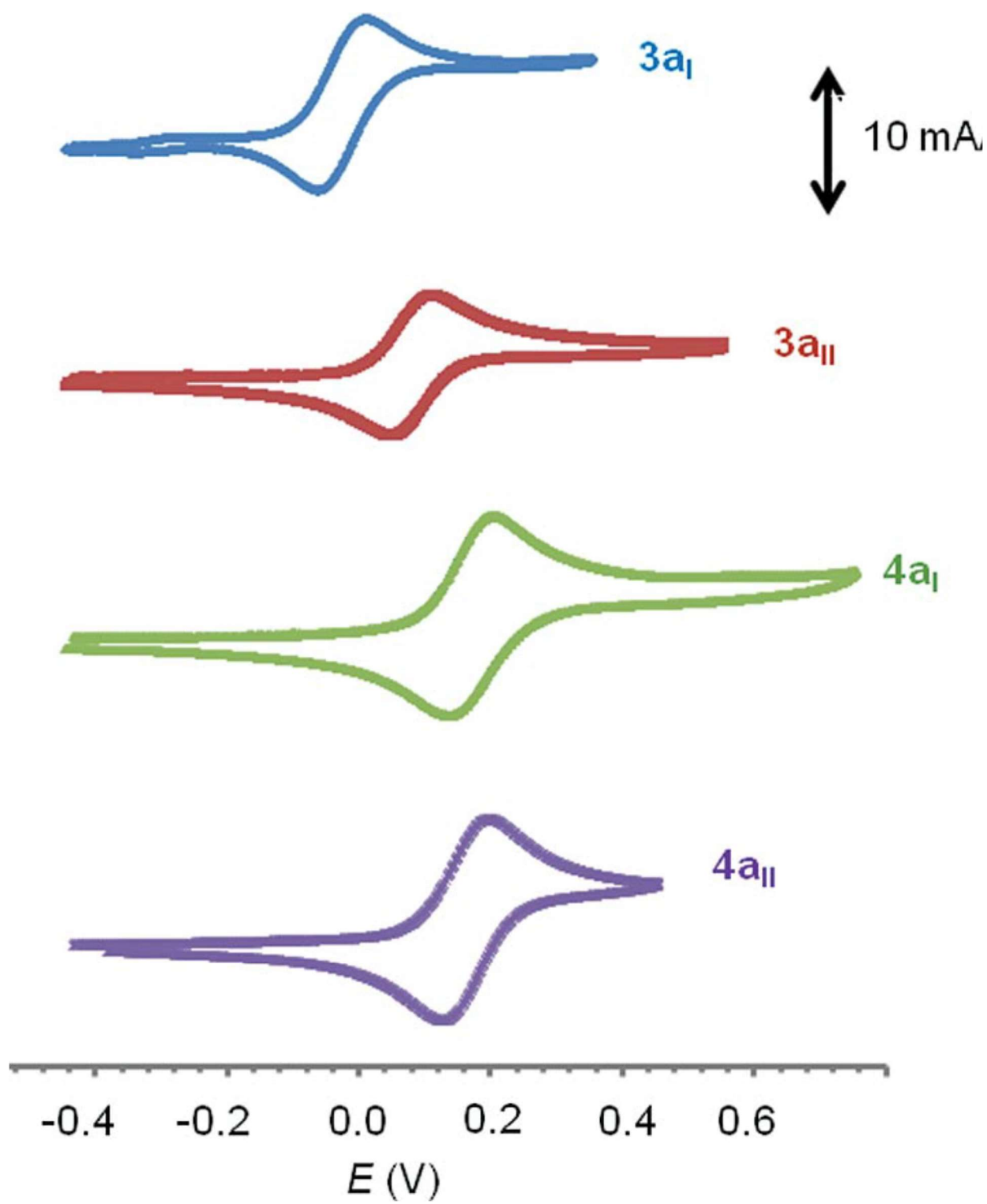
SCHEME 3



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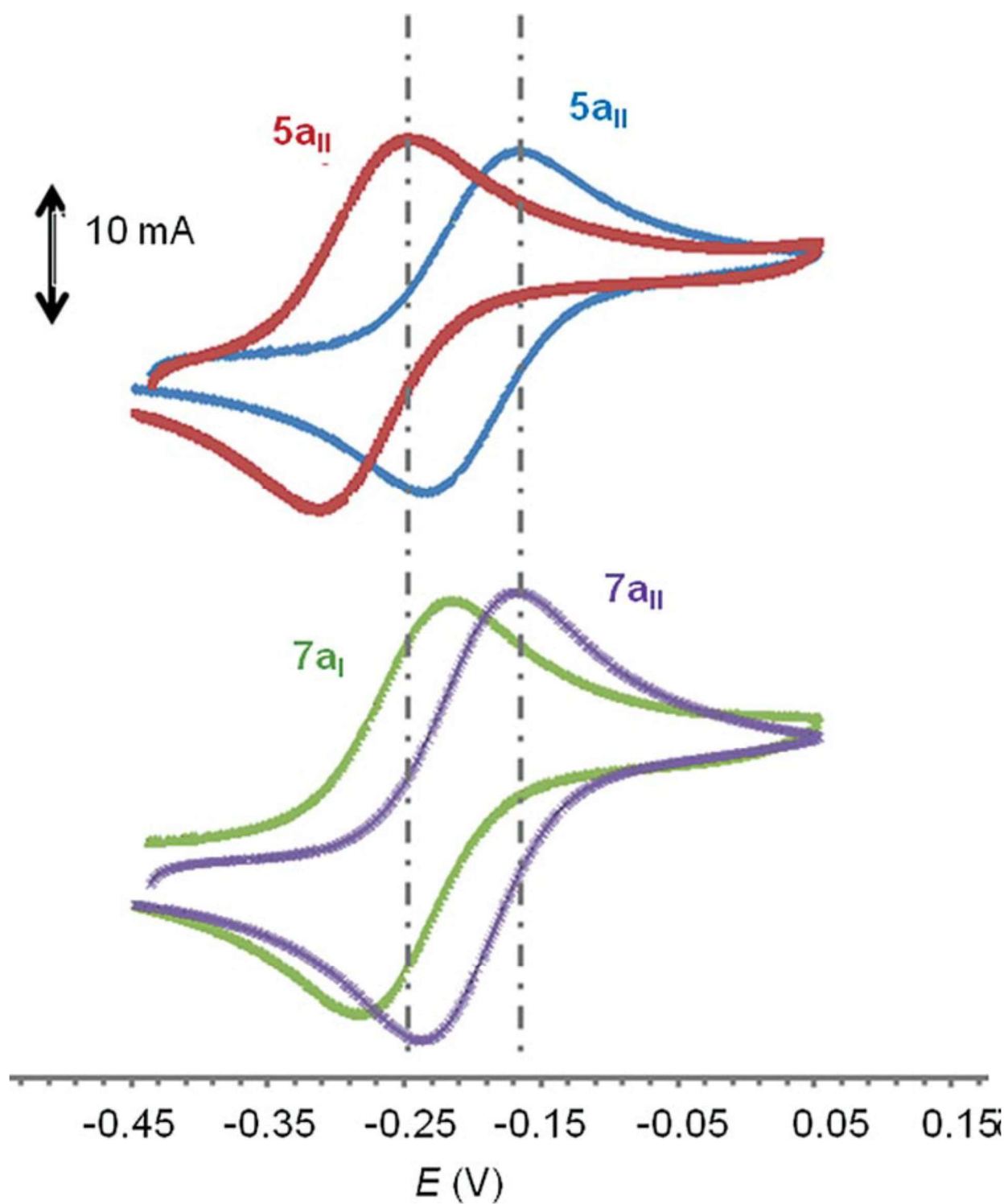
FIGURE 5



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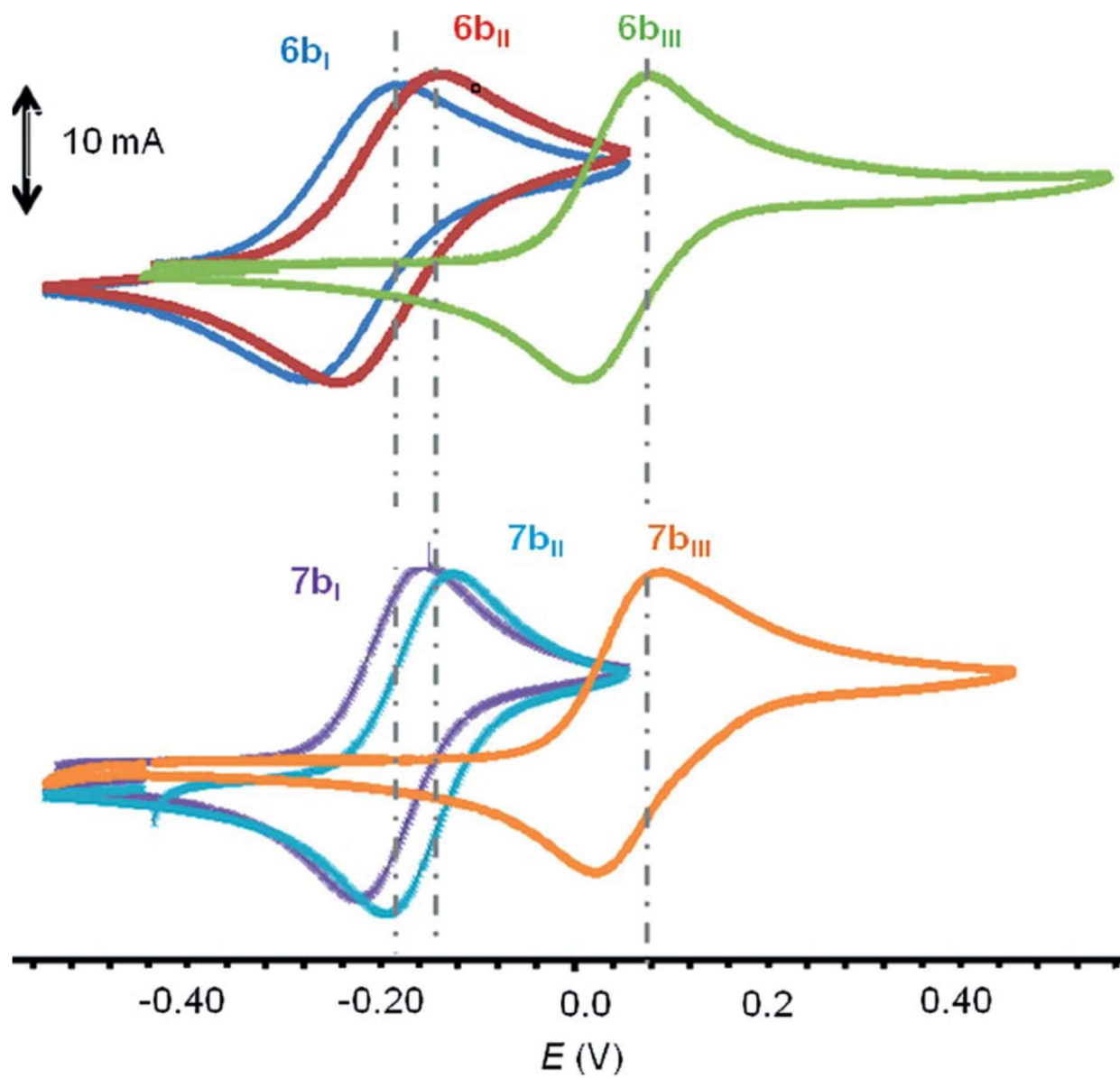
FIGURE 6



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FIGURE 7



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518 **Table 1.** Summary of the electrochemical data for the complexes studied.[a]

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Compound	Binding mode of ligand 1		Additional ligands	E_{pa} [V]	E_{pc} [V]	ΔE [V]	$E_{1/2}$ [V]	I_{pa}/I_{pc}
Platinum(II) complexes								
3a _I	(N)	<i>trans</i> -(Cl,Cl)	X = Cl, L = dmsO	0.108	0.042	0.066	0.075	1.012
3a _{II}	(N)	<i>cis</i> -(Cl,Cl)	X = Cl, L = dmsO	0.007	-0.084	0.091	-0.028	1.009
4a _I	(N,O) ⁻	<i>trans</i> -(Cl,N)	X = Cl, L = dmsO	0.197	0.125	0.072	0.160	0.958
4a _{II}	(N,O) ⁻	<i>cis</i> -(Cl,N)	X = Cl, L = dmsO	0.208	0.135	0.073	0.171	1.000
5a _I	[C(sp ² ,ferrocene),N] ⁻	(R _p)	X = Cl, L = dmsO	-0.250	-0.310	0.067	-0.249	0.900
5a _{II}	[C(sp ² ,ferrocene),N] ⁻	(S _p)	X = Cl, L = dmsO	-0.169	-0.237	0.070	-0.203	1.020
7a _I	[C(sp ² ,ferrocene),N] ⁻	(R _p)	X = Cl, L = PPh ₃	-0.224	-0.280	0.070	-0.201	0.941
7a _{II}	[C(sp ² ,ferrocene),N] ⁻	(S _p)	X = Cl, L = PPh ₃	-0.136	-0.180	0.063	-0.314	0.938
Palladium(II) complexes								
6b _I	[C(sp ² ,ferrocene),N] ⁻	(R _p)	(μ-Cl) ₂	-0.171	-0.263	0.097	-0.217	0.874
6b _{II}	[C(sp ² ,ferrocene),N] ⁻	(R _p)	(μ-Cl) ₂	-0.143	-0.242	0.099	-0.192	0.892
6b _{III}	[C(sp ² ,phenyl),N] ⁻	-	(μ-Cl) ₂	0.074	0.008	0.066	-0.049	1.000
7b _I	[C(sp ² ,ferrocene),N] ⁻	(R _p)	X = Cl, L = PPh ₃	-0.156	-0.222	0.056	-0.189	0.909
7b _{II}	[C(sp ² ,ferrocene),N] ⁻	(S _p)	X = Cl, L = PPh ₃	-0.128	-0.193	0.067	-0.283	0.909
7b _{III}	[C(sp ² ,phenyl),N] ⁻	-	X = Cl, L = PPh ₃	0.088	-0.021	0.066	0.055	1.056

[a] Anodic (E_{pa}) and cathodic (E_{pc}) potentials, the separation between peaks ($\Delta E = E_{pa} - E_{pc}$) and half-wave potentials ($E_{1/2}$) and the ratio between the intensities of the anodic and cathodic peaks (I_{pa}/I_{pc}) for the four pairs of Pt^{II} complexes (3a_I and 3a_{II}, 4a_I and 4a_{II}, 5a_I and 5a_{II}, 7a_I and 7a_{II}), in which ligand 1 exhibits different modes of binding [(N),(N,O)]⁻ or [C(sp²,ferrocene),N]⁻, and the tetra- (6b_I-6b_{III}) and dimetallic (7b_I-7b_{III}) palladium(II) compounds prepared in this work (Scheme 1). Data were obtained at a scan rate ν of 100 mV s⁻¹ and referenced to the ferrocene/ferricinium couple.

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