

1 **Kinetico-mechanistic studies on the formation of seven-membered [C,N]-platinacycles: the effect**
2 **of methyl or fluoro substituents on the aryl ancillary ligands†**

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35 The reactions of dinuclear $[\text{Pt}_2(4\text{-RC}_6\text{H}_4)_4(\mu\text{-SEt}_2)_2]$ (R = Me or F), or mononuclear $[\text{Pt}(4\text{-}$
36 $\text{RC}_6\text{H}_4)_2(\text{SMe}_2)_2]$ (R = Me or H), platinum(II) compounds with imines of the general formula 2-X,6-
37 $\text{YC}_6\text{H}_3\text{CH}=\text{NCH}_2\text{Ph}$ (X = Br, Y = F; X = Cl, Y = F; X = Br, Y = H) produced seven-membered [C,N]-
38 platinacycles. The reaction consists of the initial formation of cyclometallated platinum(IV) compounds
39 followed by a three step process: reductive elimination, isomerisation of the resulting non-
40 cyclometallated intermediate and a final cycloplatination process. Combined ^1H NMR and UV-Vis
41 kinetic-mechanistic studies indicated that the rate determining step of the process depends on the nature
42 of the aryl-Pt ligand (phenyl, p-tolyl or p-fluorophenyl).
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45 **INTRODUCTION**

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47 Cyclometallated platinum compounds containing N-donor ligands have attracted a great deal of interest
48 due to their applications in several areas.¹ In particular, cycloplatinated compounds with fluoro
49 substituents are involved in fundamental processes of organometallic chemistry,² in platinumcatalyzed
50 cross coupling reaction of aryl fluorides^{3–6} and in the design of efficient light emitting devices.^{7,8}
51 Moreover, the presence of fluoro substituents can be decisive in the regioselectivities and rates of
52 metallacycle formation.^{9,10}

53 In recent years, a novel class of seven-membered terdentate [C,Nimine,Namine] or bidentate [C,Nimine]
54 platinacycles containing biaryl moieties has been reported.^{11–15} The mechanism of formation of this
55 type of terdentate [C,Nimine,Namine] compounds has been carefully studied, including the isolation of
56 several intermediates.¹⁶ As shown in Scheme 1, the initial step of the complete process corresponds to
57 the formation of cyclometallated platinum(IV) compounds through intramolecular C–Br or C–Cl bond
58 activation of the ligand at the platinum precursor. This step is followed by C–C bond formation via
59 reductive elimination, involving one of the aryl ancillary ligands and the metallated aryl ring;
60 isomerization of the resulting species and a final cyclometallation of the biaryl fragment result in the
61 final cyclometallated complex. In the last step, the formation of seven-membered platinacycles is
62 favoured over the formation of five-membered analogues for X = Cl. Moreover, the presence of a
63 fluorine substituent (Y = F) at the ortho position, on the initially cyclometallated ligand, inhibits the
64 formation of a five-membered platinacycle, thus favouring the seven-membered cycloplatinated. Since
65 the analogous bidentate [C,Nimine] seven-membered platinacycles have received less attention so far,
66 we decided to undertake a study on the synthesis and mechanism for this class of compounds. With this
67 aim the reactions of dinuclear [Pt₂(4-RC₆H₄)₄(μ-SEt₂)₂] (R = Me or F), or mononuclear [Pt(4-
68 RC₆H₄)₂(SMe₂)₂] (R = Me or H), organoplatinum(II) compounds with imines of the general formula
69 2-X,6-YC₆H₃CH=NCH₂Ph (X = Br, Y = F; X = Cl, Y = F; X = Br, Y = H) were tested. In these
70 systems, the role of the ancillary neutral (SEt₂ or SMe₂) ligands, as well as the substituents on the aryl
71 (R = F, Me, H) ligands of the platinum precursor will be analysed both from a synthetic and a kinetic-
72 mechanistic perspective.

73

74 RESULTS AND DISCUSSION

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76 Preparation of seven-membered platinacycles

77 The general preparation procedure for the seven-membered cycloplatinated compounds studied is
78 outlined in Scheme 2. Reactions of the corresponding platinum precursor and imine were carried out in
79 refluxing toluene for six hours and produced the new seven-membered platinum(II) cyclometallated
80 compounds 71-MeBrF, 71-MeClF, 71-FBrF, 71-FClF, 72-MeBrF, 72-MeBrH, and 72-HBrF as
81 indicated. The uniform nature of the final products thus prepared, as well as the obtained yields (all
82 within the 60–85% range), suggests that the reaction sequence is independent of the nature of the
83 platinum compound and the imine ligand used. This result is in interesting contrast with the results
84 obtained for the reaction of $[\text{Pt}_2(4\text{-MeC}_6\text{H}_4)_4(\mu\text{-SEt}_2)_2]$ with imines $2\text{-XC}_6\text{H}_4\text{CH=NCH}_2\text{CH}_2\text{NMe}_2$
85 where the formation of seven- and five-membered platinacycles is preferred for $\text{X} = \text{Cl}$ and $\text{X} = \text{Br}$,
86 respectively.^{16,17} NMR data obtained for these compounds are consistent with the proposed structures.
87 Both the imine proton (JH-Pt in the 120–128 Hz range) and the Ha proton adjacent to the metalation
88 site (JH-Pt in the 52–65 Hz range) are coupled with ^{195}Pt . The latter signal appears as a singlet for 71-
89 MeBrF, 71-MeClF, 72-MeBrF and 72-MeBrH, as a doublet ($\text{JH-F} = 9.2$) for 71-FBrF and 71-FClF, or
90 as a doublet of doublets ($\text{JH-H} = 7.6$ and 1.2) for 72-HBrF, in agreement with the presence of a methyl,
91 a fluoro or a hydrogen atom in ortho to Ha respectively.

92 Compound 71-MeBrF was also characterised crystallographically (Fig. 1); the molecular structure
93 confirms the formation of a biaryl linkage producing a non-planar seven-membered platinacycle. As for
94 previously reported analogous structures,^{13,15} the metallated aryl ring is in a trans disposition to the
95 bromo ligand, while the nitrogen donor atom is situated trans to the SEt₂ ancillary ligand. Bond lengths
96 and angles are well within the range of values obtained for cyclometallated compounds, as indicated in
97 Fig. 1.

98

99 Kinetic-mechanistic study

100 Given the fact that the general ($5 \rightarrow 7$) sequence shown in Scheme 2 has been found to be very finely
101 tuned by the presence of different substituents on the initial cyclometallating ligand,^{3,16–18} a detailed
102 mechanistic study has been conducted for the present system. The different steps involved in the full
103 preparative process indicated have been often studied from a kinetic-mechanistic perspective.^{14,15,19}
104 The behaviour is well-established for the initial oxidative addition reactions ($4 \rightarrow 5$),^{10,20–24} as well as
105 for the reductive elimination/oxidative addition follow up processes ($5 \rightarrow 7$).^{16–18} From the data
106 collected so far in the literature, it is clear that, despite the relative formal simplicity of the reactivity
107 observed, the general mechanism is a compendium of multistep processes that include fast
108 coordination/decoordination equilibria^{21,23,24} and isomerization reactions.^{16,17} Scheme 3 collects the
109 kineticomechanistic sequential steps expected for the process.

110 For this purpose, complexes 5 were obtained from the reaction of 1 + 3 on a small scale; after workup
111 the complexes were found to be of a high enough purity to study the $5 \rightarrow 7$ reaction without the
112 presence of any remaining 1 or 3 species in solution. Nevertheless, in most of the cases some ^1H NMR
113 signals are also evident, which were assigned to some amounts of complex 6 as described in the
114 Experimental part, their intensity increasing on workup as expected (see below). The detailed ^1H NMR
115 monitoring of the $5 \rightarrow 7$ reaction in CDCl_3 solution was then conducted to ascertain the relative
116 readiness of the $5 \rightarrow 6$ and $6 \rightarrow 7$ steps, as well as possible isomerisation processes of compounds 6,
117 already observed for similar systems.^{16,17}

118 In all cases the initial ^1H NMR spectra indicate the presence of two isomeric forms of compounds 5 in a
119 2 : 1 ratio, characterised by a JH-Pt value for the imine proton within the 44–48 Hz range. These forms

120 can be associated with the relative positions of the L and X ligands in the structure (Scheme 3). This
121 isomeric distribution has already been observed for complexes of the same family,^{25,26} even the
122 isomerization on substitution of the dialkylsulfide by phosphine has been quantified, as well as the
123 formation of dimeric species.^{25,27} Scrambling between these two isomeric forms is known to be fast on
124 the NMR time-scale for the bis-methyl analogue of 52-HBrH and, consequently, should not be relevant
125 to the follow up 5 → 6 reductive elimination.²⁶ Effectively the disappearance of the two isomers of
126 species 5 occurs simultaneously, indicating its rapid scrambling. From this point the appearance of two
127 reductive eliminated forms of complex 6 at rather different chemical shifts is evident in the ¹H NMR
128 spectra for compounds 51-MeBrF and 52-MeBrF. The initial spectra show a signal at a higher field that
129 evolves into another one at a lower field as indicated below and in the Experimental part. For the 52-
130 MeBrH complex only the evolved signal at a lower field is observed; the absence of a fluoro substituent
131 in the cyclometallated ligand, 3, produces a general high field shift in the imine resonances (as observed
132 for both isomers of 52-MeBrH, which display signals at 7.92 and 7.71 ppm), and the high field imine
133 signal is expected to overlap under the aromatic signals. Interestingly, for complex 51-FBrF a single
134 reductively eliminated complex 6 is observed, showing the iminic proton signal at a higher field that is
135 not seen to evolve in the lower field signal. For complexes 52-HBrH and 52-HBrF no reductively
136 eliminated species 6 are observed in the ¹H NMR spectra.

137 The disappearance of the signals of compounds 6 (as a mixture or as a single species) is accompanied by
138 the expected increase of a new signal due to seven-membered metallacycle compounds 7, characterised
139 by a J_{H-Pt} in the 120–130 Hz range. Evidently for complexes 52-HBrH and 52-HBrF a simple
140 appearance of compounds 7 is observed, as stated above. As indicated in the previous paragraph, the two
141 sets of signals of compounds 6 (Scheme 3) show a definite trend in their relative intensity; after the
142 initial formation of the trans-Nimine/C isomer increasing quantities of the cis-Nimine/C form are
143 observed (Fig. 2). The relatively fast evolution of these forms prevents isolation of these intermediates;
144 nevertheless, the distinct J_{Pt-H} values observed for the imine proton, 44 Hz and 120–144 Hz for the
145 trans- and cis-Nimine/C isomers allows unequivocal identification (Scheme 3). No other intermediates
146 were observed, not even those corresponding to E–Z isomerisation of the imine group. After build up,
147 complexes 6 in the cis-Nimine/C isomeric form disappear in favour of the final compound 7.

148 As a comparison, it is interesting to indicate that for compounds of the same family where the
149 dialkylsulfide ligands (L) have been replaced with a –CH₂–CH₂–NMe₂ group attached to the imine
150 nitrogen (thus forming a PtNimine/Namine chelate), the final oxidative addition on compounds of type 6
151 has also been proved to take place through the cis-Nimine/C form after isomerisation of the kinetically
152 preferred trans-Nimine/C isomer formed from the corresponding platinum(IV) compound and both
153 isomers have been structurally characterised.¹⁷

154 One should note that, given the fact that for 52-HBrH and 52-HBrF no accumulation of complexes of
155 type 6 occurs, the reactions taking place after the rate limiting initial reductive elimination have to be
156 relatively fast in this case. In the same respect, for complex 51-FBrF the build-up of species 6 in a
157 cisNimine/C form does not occur (see Fig. 2 for the expected trend), indicating that the cis-61-FBrF →
158 71-FBrF is faster than the trans-61-FBrF → cis-61-FBrF isomerisation reaction, which should be rate
159 limiting in this case. Table 1 collects the nature of the rate limiting reactions observed according to ¹H
160 NMR spectroscopy.

161 In view of these results, time-resolved monitoring of the UV-Vis spectral changes occurring in toluene
162 solutions of compounds 5 was conducted at different temperatures to fully quantify the time-dependence
163 observed. For compounds 51-MeBrF, 52-MeBrH and 52-MeBrF, a two-step sequence (Fig. S1, ESI[†])
164 was observed for the time span used, as expected from the above NMR data.^{14,15} The data collected in
165 Table 1 correspond to the rate constants of the rate limiting process of formation of compound 7 from
166 complex 6 in a cis-Nimine/C form, as measured by ¹H NMR spectroscopy. The values determined for
167 ΔH^\ddagger , ΔS^\ddagger and ΔV^\ddagger are the first ones determined for the oxidative addition reaction leading to the
168 formation of seven-membered metallacycles with monodentate ligands indicated in Scheme 3 (Fig. 3).

169 For bidentate PtNimine/Namine systems some data are available,¹⁷ although comparison might be non-
170 significant due to the different requirements of the ligands. In the present study the values of the
171 activation enthalpies are much lower (within the 65–87 range versus 105–140 for the PtNimine/Namine
172 systems) and the activation entropies are clearly negative (close to zero for the PtNimine/Namine
173 systems) while keeping the value of ΔV^\ddagger at zero. Clearly the oxidative addition reaction leading from
174 complex 6 (cis-Nimine/C) to 7, indicated in Scheme 3, proceeds via a better ordered transition state
175 requiring less energy than that for the more encumbered bidentate PtNimine/Namine systems. The
176 values are similar to those collected for the formation of complexes 5 from 1 + 3.^{21,24} The activation
177 volumes should correspond to a compensation effect between a high degree of compression, due to the
178 concerted nature of the oxidative addition, and an increase in bond distances, including the
179 decoordination of the L ligand needed for the process.^{16,17,28–32}

180 For complexes 52-HBrF and 52-HBrH the data collected for the rate determining single step in Table 1
181 (Fig. 4a) are very different, which is not surprising in view of the results indicated in the previous
182 paragraphs and in the second column of the table.^{14,15} In this case it is the reductive elimination
183 reaction step that has been quantified, showing rather high values of ΔH^\ddagger , practically zero values of ΔS^\ddagger
184 and positive volumes of activation (Fig. 4b). The latter is clearly due to the lengthening of the Pt–C
185 distances due to reductive elimination, despite an increased ordering. The data are definitively in line
186 with those observed for the reductive elimination occurring on the analogous PtNimine/Namine
187 systems.¹⁷ It is clear that the presence of a chelate does not seem to affect the process in an important
188 way; dissociation of the L or Namine ancillary ligands is not required according to the microreversibility
189 principle.^{28–34}

190 Finally the data collected in Table 1 for compound 51-FBrF, where only species trans-61-FBrF has been
191 detected by ¹H NMR, show that the dominant rate determining step corresponds to the isomerisation
192 reaction from trans-61-FBrF to cis-61-FBrF, as indicated above. The values collected for the activation
193 parameters can thus be compared with the equivalent isomerisation occurring on the PtNimine/Namine
194 analogous systems.¹⁷ In the present case the value of ΔH^\ddagger is larger, while that of ΔS^\ddagger is less negative;
195 the value of ΔV^\ddagger parallels that of the activation entropy. Clearly, in the present system decoordination of
196 the dialkylsulfide ligand seems to be playing a more important role in the reaction than its back
197 coordination, as was found for the amine back coordination on the PtNimine/Namine mentioned
198 systems. Interestingly, by UV-Vis (a much more concentration-sensitive technique) a faster step is also
199 detected, which is not observed by ¹H NMR spectroscopy, that probably corresponds to the 5 → 6
200 process, although its nature cannot be guaranteed.

201 In this respect, the faster steps detected during the monitoring of the UV-Vis spectral changes of the
202 toluene solution of compounds 51-MeBrF, 52-MeBrH and 52-MeBrF should correspond to the
203 respective 6(trans-Nimine/C) → 6(cis-Nimine/C) isomerisation reactions, to the 5 → 6 reductive
204 elimination reaction, or to a composite of both steps (see Fig. S1†). Table 2 collects the relevant data
205 obtained as indicated in the Experimental section. For complex 51-FBrF, the measured step should
206 correspond either to the reductive elimination to produce trans-61-FBrF or to the final oxidative addition
207 reaction to produce compound 71-FBrF; data are also collected in Table 2.

208 From the data collected in Table 1 it seems rather obvious that none of the processes involved in the
209 values determined corresponds to the 6(trans-Nimine/C) → 6(cis-Nimine/C) isomerisation reactions,
210 characterised by a negative value of ΔV^\ddagger . The reductive 5 → 6(trans-Nimine/C) step does not either
211 seem to be the effective process measured, by comparison of the relevant data also collected in Table 1.
212 Probably the measured values correspond to a mixture of both steps occurring at rather similar rates.
213 This sort of unresolved behaviour has already been observed in some other related systems, although in
214 some cases the choice of different temperature ranges has allowed for a comprehensive study.^{16,17} In
215 the present case the existence of a follow up reaction (Table 1) has not allowed for such techniques and
216 any further discussion on these non-rate determining values would be meaningless.

217

218 **CONCLUSIONS**

219

220 In summary, the comprehensive ¹H NMR spectroscopy study of the 5 → 7 process, indicated in Scheme
221 2, shows that this is a three step process involving an initial 5 → 6(trans-Nimine/C) reductive
222 elimination step, followed by a 6(trans-Nimine/C) → 6(cis-Nimine/C) isomerisation reaction, to finish
223 up with a 6(cis-Nimine/C) → 7 cycloplatination process via an oxidative addition/reductive elimination
224 sequence (Scheme 3). Interestingly, while for the phenyl 52-HBrH and 52-HBrF derivatives the rate
225 determining step corresponds to the reductive elimination 5 → 6(trans-Nimine/C) reaction, for the p-
226 tolyl 51-MeBrF, 52-MeBrH and 52-MeBrF the reactions are limited by the final 6(cis-Nimine/C) → 7
227 oxidative addition step. For the p-fluoro 51- FBrF complex the trans-61-MeBrF → cis-61-MeBrF
228 isomerisation, prior to the final oxidative addition, is the process limiting the reactivity of the system.
229 The kinetic and thermal and pressure activation parameters measured for these limiting processes agree
230 with the expected, as does the isomerisation sequence already established for similar PtNimine/Namine
231 systems. Clearly the nature of the substituent at the para position of the ancillary aryl ligand (R) plays a
232 decisive role during the process, as the X substituent has been proved to have in the five- versus seven-
233 membered cycloplatination reactions.^{16,17} Electron donating Me should slow-down any reductive
234 elimination process, either that leading to the 6(cis-Nimine/C) complex, or that producing the final
235 compound 7 by elimination of C₆H₅R (see Scheme 3); clearly the latter is the one more affected in this
236 case. The electron withdrawing F hampers the dissociation of the ancillary L ligand in Pt(II) compound
237 6 to undergo the 6(trans-Nimine/C) → 6(cis-Nimine/C) reaction. In the same respect, the differences
238 between the SMe₂ and SEt₂ derivatives do not seem to be relevant for the rate-determining step, as seen
239 for 51-MeBrF and 52-MeBrF in Table 1. The differences, if existing, should be appearing in the faster
240 non-rate determining steps observed.

241

242 EXPERIMENTAL

243

244 General

245 Microanalyses were performed at the Centres Científics i Tecnològics (Universitat de Barcelona). NMR
246 spectra were recorded at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using a
247 Mercury-400 (1H, 400 MHz; 19F, 376.5 MHz) and referenced to SiMe₄ (1H) or CFC1₃ (19F). δ values
248 are given in ppm and J values in Hz. Abbreviations used: s = singlet; d = doublet; t = triplet; m =
249 multiplet; br = broad.

250

251 Preparation of complexes

252 Platinum compounds [Pt₂(4-RC₆H₄)₄(μ -SEt₂)₂] (1-Me, R = Me³⁵ or 1-F, R = F¹²), [Pt(4-
253 RC₆H₄)₂(SMe₂)₂] (2-Me, R = Me³⁶ or 2-H, R = H³⁷), ligands 2-X,6-FC₆H₃CHvNCH₂Ph (3-BrF, X
254 = Br⁶ or 3-ClF, X = Cl³⁸) and 2-BrC₆H₄CHvNCH₂Ph (3-BrH)³⁹ and the compound
255 [PtBr{C₆H₄(C₆H₄)CHvNCH₂Ph}SMe₂] (72-HBrH)¹⁵ were prepared as reported elsewhere

256 **Compounds 7.** Compounds [PtX{(4-RC₆H₃)(2-YC₆H₃)CHvNCH₂Ph}L] (71-MeBrF: R = Me, X =
257 Br, Y = F, L = SEt₂; 71-MeClF: R = Me, X = Cl, Y = F, L = SEt₂; 71-FBrF: R = F, X = Br, Y = F, L =
258 SEt₂; 71-FCIF: R = F, X = Cl, Y = F, L = SEt₂; 72-MeBrF: R = Me, X = Br, Y = F, L = SMe₂; 72-
259 MeBrH: R = Me, X = Br, Y = H, L = SMe₂; 72-HBrF: R = H, X = Br, Y = F, L = SMe₂) were obtained
260 after stirring under reflux for 6 hours a solution containing 0.090 g of compounds 1-Me (0.096 mmol) or
261 1-F (0.095 mmol), or 50 mg of compounds 2-Me (0.100 mmol) or 2-H (0.105 mmol) and the equivalent
262 amount of the corresponding ligand 3-BrF (56 mg for 71-MeBrF, 55 mg for 71-FBrF, 29 mg for 72-
263 MeBrF and 31 mg for 72-HBrF), 3-ClF (48 mg for 71-MeClF and 47 mg for 71-FCIF) or 3-BrH (31 mg
264 for 72-HBrF) in toluene. The solvent was evaporated and the residue was treated with diethyl ether. The
265 white or light yellow solids were filtered and dried in a vacuum. Yield: 77 mg (60%) for 71-MeBrF; 72
266 mg (61%) for 71-MeClF; 77 mg (61%) for 71-FBrF; 86 mg (72%) for 71-FCIF; 54 mg (85%) for 72-
267 MeBrF; 43 mg (69%) for 72-MeBrH and 50 mg (76%) for 72-HBrF (Chart 1).

268 [PtBr{(4-MeC₆H₃)(2-FC₆H₃)CHvNCH₂Ph}SEt₂] (71-MeBrF). 1H NMR (400 MHz, CDCl₃), δ = 8.66
269 (s, 3JH-Pt = 128.0, 1H, Hg), 7.45 (td, 3JH-H = 8.0, 4JH-F = 6.0, 1H, He), 7.30 (m, 1H), 7.22–7.21 (m,
270 4H), 7.14 (d, 3JH-H = 7.6 Hz, 1H, Hd), 7.05 (t, 3JH-H = 3JH-F = 8.8, 1H, Hf), 6.83 (d, 3JH-H = 7.6,
271 1H, Hc), 6.70 (d, 3JH-H = 7.6, 1H, Hb), 6.24 (s, 3JH-Pt = 64.8, 1H, Ha), 5.69 (dd, 2JH-H = 12.8, 4JH-
272 H = 1.6, 1H, Hh), 5.03 (d, 2JH-H = 13.2, 1H, Hh), 3.08 (s, br, 1H, Hi), 2.67 (s, br, 2H, Hi), 2.38 (s, br,
273 1H, Hi), 2.11 (s, 3H, Me), 1.28 (s, br, 3H, Hj), 0.98 (s, br, 3H, Hj). 19F NMR (376.5 MHz, CDCl₃), δ
274 (ppm): -115.05 (ddd, 3JF-H = 9.0, 4JF-H = 5.6, 5JF-H = 2.0). EA (calc. for C₂₅H₂₇BrFNpS): C:
275 45.21% (44.98%); H: 4.38% (4.08%); N: 2.32% (2.10%); S: 4.70% (4.80%).

276 [PtCl{(4-MeC₆H₃)(2-FC₆H₃)CHvNCH₂Ph}SEt₂] (71-MeClF). 1H NMR (400 MHz, CDCl₃), δ = 8.67
277 (s, 3JH-Pt = 120.4, 1H, Hg), 7.45 (td, 3JH-H = 8.0, 4JH-F = 6.0, 1H, He), 7.29 (m, 1H), 7.24–7.18 (m,
278 4H), 7.14 (d, 3JH-H = 7.6 Hz, 1H, Hd), 7.04 (t, 3JH-H = 3JH-F = 8.8, 1H, Hf), 6.82 (d, 3JH-H = 7.6,
279 1H, Hc), 6.69 (dd, 3JH-H = 7.6, 4JH-H = 1.2, 1H, Hb), 6.31 (s, 3JH-Pt = 54.8, 1H, Ha), 5.63 (dd, 2JH-
280 H = 13.2, 4JH-H = 2.0, 1H, Hh), 5.01 (d, 2JH-H = 13.2, 3JH-Pt = 43.2, 1H, Hh), 3.08 (s, br, 1H, Hi),
281 2.62 (s, br, 2H, Hi), 2.35 (s, br, 1H, Hi), 2.11 (s, 3H, Me), 1.25 (s, br, 3H, Hj), 0.97 (s, br, 3H, Hj). 19F
282 NMR (376.5 MHz, CDCl₃), δ (ppm): -115.07 (ddd, 3JF-H = 8.6, 4JF-H = 6.0, 5JF-H = 2.0). EA (calc.
283 for C₂₅H₂₇ClFNpS·0.5H₂O): C: 47.50% (47.50%); H: 4.43% (4.46%); N: 2.46% (2.22%); S: 4.87%
284 (5.07%).

285 [PtBr{(4-FC₆H₃)(2-FC₆H₃)CHvNCH₂Ph}SEt₂] (71-FBrF). 1H NMR (400 MHz, CDCl₃), δ = 8.61 (s,
286 3JH-Pt = 120.0, 1H, Hg), 7.39 (td, 3JH-H = 8.0, 4JH-F = 6.0, 1H, He), 7.25 (m, 1H), 7.17–7.13 (m,

287 4H), 7.05 (d, 3JH-H = 8.0 Hz, 1H, Hd), 7.04 (t, 3JH-H = 3JH-F = 8.8, 1H, Hf), 6.83 (t, 3JH-H = 4JH-
288 F = 6.4, 1H, Hc), 6.52 (t, 3JH-H = 3JH-F = 8.4, 1H, Hb), 6.01 (d, 3JH-F = 9.2, 3JH-Pt = 59.2, 1H, Ha),
289 5.62 (d, 2JH-H = 12.8, 1H, Hh), 4.94 (d, 2JH-H = 12.8, 3JH-Pt = 58.4, 1H, Hh), 3.00 (s, br, 1H, Hi),
290 2.62 (s, br, 2H, Hi), 2.38 (s, br, 1H, Hi), 1.13 (s, br, 3H, Hj), 0.88 (s, br, 3H, Hj). 19F NMR (376.5 MHz,
291 CDCl₃), δ (ppm): -114.73 (m), -116.94 (m). EA (calc. for C₂₄H₂₄BrF₂NPtS): C: 42.92% (42.93%);
292 H: 3.72% (3.60%); N: 2.20% (2.09%); S: 4.47% (4.77%).

293 [PtCl{(4-FC₆H₃)(2-FC₆H₃)CHvNCH₂Ph}SEt₂] (71-FCIF). 1H NMR (400 MHz, CDCl₃), δ = 8.64 (s,
294 3JH-Pt = 120.0, 1H, Hg), 7.40 (td, 3JH-H = 8.0, 4JH-F = 5.4, 1H, He), 7.25 (m, 1H), 7.24-7.12 (m,
295 4H), 7.05 (d, 3JH-H = 7.6 Hz, 1H, Hd), 7.01 (t, 3JH-H = 3JH-F = 8.8, 1H, Hf), 6.83 (t, 3JH-H = 4JH-
296 F = 6.4, 1H, Hc), 6.52 (t, 3JH-H = 3JH-F = 8.4, 1H, Hb), 6.09 (d, 3JH-F = 9.6, 3JH-Pt = 54.8, 1H, Ha),
297 5.55 (d, 2JH-H = 12.8, 1H, Hh), 4.92 (d, 2JH-H = 12.0, 3JH-Pt = 50.4, 1H, Hh), 3.01 (s, br, 1H, Hi),
298 2.55 (s, br, 2H, Hi), 2.32 (s, br, 1H, Hi), 1.19 (s, br, 3H, Hj), 0.90 (s, br, 3H, Hj). 19F NMR (376.5 MHz,
299 CDCl₃), δ (ppm): -114.73 (m), -117.13 (m). EA (calc. for C₂₄H₂₄ClF₂NPtS): C: 45.20% (45.97%); H:
300 3.84% (3.86%); N: 2.37% (2.23%); S: 4.63% (5.11%).

301 [PtBr{(4-MeC₆H₃)(2-FC₆H₃)CHvNCH₂Ph}SMe₂] (72-MeBrF). 1H NMR (400 MHz, CDCl₃), δ =
302 8.53 (s, 3JH-Pt = 120.0, 1H, Hg), 7.40 (td, 3JH-H = 8.0, 4JH-F = 6.0, 1H, He), 7.22 (m, 1H), 7.18-7.09
303 (m, 5H), 6.99 (t, 3JH-H = 3JH-F = 8.0, 1H, Hf), 6.78 (d, 3JH-H = 8.0, 1H, Hc), 6.65 (d, 3JH-H = 8.0,
304 1H, Hb), 6.29 (s, 3JH-Pt = 56.0, 1H, Ha), 5.60 (dd, 2JH-H = 12.0, 4JH-H = 2.0, 1H, Hh), 5.01 (d, 2JH-
305 H = 12.0, 3JH-Pt = 56.0, 1H, Hh), 2.33 (s, br, 3H, Hi), 1.97 (s, br, 3H, Hi). 19F NMR (376.5 MHz,
306 CDCl₃), δ (ppm): -114.81 (ddd, 3JF-H = 9.2, 4JF-H = 6.0, 5JF-H = 2.6). EA (calc. for
307 C₂₃H₂₃BrFNPtS·1.5H₂O): C: 41.30% (41.45%); H: 3.53% (3.93%); N: 2.26% (2.10%); S: 4.42%
308 (4.81%).

309 [PtBr{(4-MeC₆H₃)(C₆H₄)CHvNCH₂Ph}SMe₂] (72-MeBrH). 1H NMR (400 MHz, CDCl₃), δ = 8.44
310 (s, 3JH-Pt = 124.0, 1H, Hg), 7.44-7.40 (m, 1H), 7.33-7.21 (m, 4H), 7.18-7.12 (m, 4H), 6.78 (d, 3JH-H
311 = 8.0, 1H, Hc), 6.66 (d, 3JH-H = 8.0, 1H, Hb), 6.32 (s, 3JH-Pt = 56.0, 1H, Ha), 5.58 (dd, 2JH-H = 12.0,
312 4JH-H = 2.0, 1H, Hh), 4.98 (d, 2JH-H = 12.0, 3JH-Pt = 52.0, 1H, Hh), 2.28 (s, br, 3H, Hi), 1.97 (s, br,
313 3H, Hi). EA (calc. for C₂₃H₂₄BrNPtS·H₂O): C: 43.40% (43.20%); H: 3.87% (4.10%); N: 2.38%
314 (2.19%); S: 4.72% (5.01%).

315 [PtBr{(C₆H₄)(2-FC₆H₃)CHvNCH₂Ph}SMe₂] (72-HBrF). 1H NMR (400 MHz, CDCl₃), δ = 8.52 (s,
316 3JH-Pt = 120.0, 1H, Hg), 7.45-7.39 (m, 1H), 7.21-7.20 (m, 2H), 7.17-7.11 (m, 4H), 7.02 (t, 3JH-H =
317 8.0, 1H), 6.90 (td, 3JH-H = 8.0; 4JH-H = 1.6, 1H), 6.86 (td, 3JH-H = 7.2; 4JH-H = 1.2, 1H), 6.73 (td,
318 3JH-H = 7.2; 4JH-H = 1.6, 1H), 6.60 (dd, 3JH-H = 7.6; 4JH-H = 1.2, 3JH-Pt = 52.0, 1H, Ha), 5.57
319 (dd, 2JH-H = 13.6, 4JH-H = 2.0, 1H, Hh), 5.06 (d, 2JH-H = 13.6, 3JH-Pt = 49.2, 1H, Hh), 2.31 (s, br,
320 3H, Hi), 2.00 (s, br, 3H, Hi). 19F NMR (376.5 MHz, CDCl₃), δ (ppm): -114.84 (ddd, 3JF-H = 9.8,
321 4JF-H = 5.6, 5JF-H = 2.2). EA (calc. for C₂₂H₂₁BrFNPtS·H₂O): C: 40.77% (41.06%); H: 3.35%
322 (3.60%); N: 2.28% (2.18%); S: 4.72% (4.98%).

323 **Compounds 5.** Compounds [PtX(4-RC₆H₄)₂(2-YC₆H₃CHvNCH₂Ph)L] (51-MeBrF: R = Me, X = Br,
324 Y = F, L = SEt₂; 51-FBrF: R = F, X = Br, Y = F, L = SEt₂; 52-MeBrF: R = Me, X = Br, Y = F, L =
325 SMe₂; 52-MeBrH: R = Me, X = Br, Y = H, L = SMe₂; 52-HBrF: R = H, X = Br, Y = F, L = SMe₂ and
326 52-HBrH: R = H, X = Br, Y = H, L = SMe₂) were characterised by 1H NMR spectra. 10 mg of the
327 corresponding platinum precursor 1-Me, 1-F, 2-Me or 2-H and the equivalent amount of the
328 corresponding ligand 3-BrF or 3-BrH were mixed at 25 °C in a NMR tube and allowed to react for the
329 reaction times stated below. 51-MeBrF: reaction time, 30 min; 1H NMR (400 MHz, CDCl₃), δ = 8.26
330 (s, 3JH-Pt = 44, 1H, CHvN) (major isomer 2 : 1); 8.06 (s, 3JH-Pt = 44, 1H, CHvN) (minor isomer). 51-
331 FBrF: reaction time, 30 min; 1H NMR (400 MHz, CDCl₃), δ = 8.34 (s, 3JH-Pt = 44, 1H, CHvN), 5.47
332 (m, 2H, CH₂Ph), 1.06 (t, 3JH-Pt = 16.0, 6H, SCH₂CH₃) (major isomer 1.6 : 1); 7.97 (s, 3JH-Pt = 44,
333 1H, CHvN), 5.05 (m, 2H, CH₂Ph), 1.29 (t, 3JH-Pt = 16.0, 6H, SCH₂CH₃) (minor isomer). 52-MeBrF:
334 reaction time, 180 min; 1H NMR (400 MHz, CDCl₃), δ = 8.29 (s, 3JH-Pt = 44, 1H, CHvN), {5.65 (dd,

335 2JH–H = 17.2, 4JH–H = 1.6, 1H), 5.52 (dd, 2JH–H = 17.2, 4JH–H = 1.6, 1H), CH₂Ph}, 2.14 (s, 3JH–Pt
336 = 12.0, 6H, SMe₂) (major isomer 2 : 1); δ = 8.05 (s, 3JH–Pt = 44, 1H, CH_vN), {5.54 (dd, 2JH–H = 17.0,
337 4JH–H = 1.6, 1H), 5.43 (dd, 2JH–H = 17.0, 4JH–H = 1.6, 1H), CH₂Ph}, 2.06 (s, 3JH–Pt = 12.0, 6H,
338 SMe₂) (minor isomer). 52–MeBrH: reaction time, 180 min; 1H NMR (400 MHz, CDCl₃), δ = 7.92 (s,
339 3JH–Pt = 44, 1H, CH_vN), {5.53 (dd, 2JH–H = 17.2, 4JH–H = 1.6, 1H), 5.42 (dd, 2JH–H = 17.2, 4JH–H
340 = 1.6, 1H), CH₂Ph}, 1.95 (s, 3JH–Pt = 12.0, 6H, SMe₂) (major isomer 2 : 1); δ = 7.71 (s, 3JH–Pt = 48,
341 1H, CH_vN); {5.45 (dd, 2JH–H = 17.0, 4JH–H = 1.6, 1H), 5.43 (dd, 2JH–H = 17.0, 4JH–H = 1.6, 1H),
342 CH₂Ph}, 2.07 (s, 3JH–Pt = 12.0, 6H, SMe₂) (minor isomer). 52–HBrF: reaction time, 30 min; 1H NMR
343 (400 MHz, CDCl₃), δ = 8.29 (s, 3JH–Pt = 44, 1H, CH_vN), {5.58 (dd, 2JH–H = 16.0, 4JH–H = 2.0, 1H),
344 5.44 (dd, 2JH–H = 16.0, 4JH–H = 2.0, 1H), CH₂Ph}, 1.99 (s, 3JH–Pt = 12.0, 6H, SMe₂) (major isomer
345 2 : 1); δ = 8.06 (s, 3JH–Pt = 48, 1H, CH_vN); {5.48 (dd, 2JH–H = 16.0, 4JH–H = 2.0, 1H), 5.37 (dd,
346 2JH–H = 16.0, 4JH–H = 2.0, 1H), CH₂Ph}, 2.07 (s, 3JH–Pt = 12.0, 6H, SMe₂) (minor isomer). 52–
347 HBrH: reaction time, 90 min; 1H NMR (400 MHz, CDCl₃), δ = 7.95 (s, 3JH–Pt = 48, 1H, CH_vN),
348 {5.44 (dd, 2JH–H = 17.0, 4JH–H = 2.0, 1H), 5.42 (dd, 2JH–H = 17.0, 4JH–H = 2.0, 1H), CH₂Ph}, 1.95
349 (s, 3JH–Pt = 12.0, 6H, SMe₂) (major isomer 3.8 : 1); δ = 7.72 (s, 3JH–Pt = 44, 1H, CH_vN), {5.47 (dd,
350 2JH–H = 17.0, 4JH–H = 2.0, 1H), 5.36 (dd, 2JH–H = 17.0, 4JH–H = 2.0, 1H), CH₂Ph}, 2.07 (s, 3JH–Pt
351 = 12.0, 6H, SMe₂) (minor isomer).

352 **Compounds 6.** Compounds [PtX(4-RC₆H₄)(4-RC₆H₄-2-YC₆H₃CH_vNCH₂Ph)L] (61–MeBrF: R =
353 Me, X = Br, Y = F, L = SEt₂; 61–FBrF: R = F, X = Br, Y = F, L = SEt₂; 62–MeBrF: R = Me, X = Br, Y
354 = F, L = SMe₂ and 62–MeBrH: R = Me, X = Br, Y = H, L = SMe₂) were characterised by 1H NMR
355 spectra. Solutions containing compounds 5 (see above) were concentrated to dryness, and the residues
356 were washed with diethyl ether in order to remove excess of imine and dialkylsulfide ligands, and dried
357 in vacuo. The obtained residues (crude compounds 5) were dissolved at 25 °C in a NMR tube and the
358 reaction was monitored under the conditions stated below. 61–MeBrF: reaction time, 20–120 min,
359 temperature 40 °C; 1H NMR (400 MHz, CDCl₃), δ = 7.85 (s, 3JH–Pt = 44) (trans-Nimine/C); 8.56 (s,
360 3JH–Pt = 144) (cis-Nimine/C) (initial ratio ca. 1 : 1). 61–FBrF: reaction time, 40–80 min, temperature 25
361 °C; 1H NMR (400 MHz, CDCl₃), δ = 8.10 (s, 3JH–Pt = 44) (trans-Nimine/C). 62–MeBrF: reaction time,
362 10–300 min, temperature 25 °C; 1H NMR (400 MHz, CDCl₃), δ = 7.85 (s, 3JH–Pt = 44) (trans-
363 Nimine/C); 8.48 (s, 3JH–Pt = 120) (cis-Nimine/C) (initial ratio ca. 1 : 1). 62–MeBrH: reaction time, 20–
364 400 min, temperature 30 °C; 1H NMR (400 MHz, CDCl₃), δ = 8.35 (s, 3JH–Pt = 124) (cis-Nimine/C).

365

366 X-ray structure analysis

367 A crystal of approximate dimensions 0.074 mm × 0.105 mm × 0.254 mm was selected and intensity data
368 were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo
369 microfocus. The structure was solved using the Bruker SHELXTL Software Package, and refined using
370 SHELXL.40 Further details are given in Table 3 and Fig. 1.

371

372 Kinetics

373 The kinetic profiles for the reactions were followed by UV-Vis spectroscopy in the 700–300 nm range
374 on HP8452A or Cary50 instruments equipped with thermostated multicell transports. The observed rate
375 constants were derived from absorbance versus time traces at the wavelengths where a maximum
376 increase and/or decrease of absorbance was observed. For the reactions carried out at varying pressure
377 the previously described pillbox cell and pressurising system^{41–44} were used and final treatment of data
378 was the same as described before. The calculation of the observed rate constants from the absorbance
379 versus time monitoring of reactions was carried out using the SPECFIT or ReactLab softwares;^{45,46}
380 typical errors of these values are within the 10–20% margin. The general kinetic technique is that
381 previously described.^{15,20,47} Table S1† collects all the obtained k_{obs} values for all the systems studied

382 as a function of the starting complex, process studied, pressure and temperature. All post-run fittings
383 were carried out using the standard available commercial programs.

384

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386

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463 .

464 **Legends to figures**

465

466 **Figure 1** Molecular structure of compound 71-MeBrF. Selected bond lengths (Å) and angles (°) with
467 estimated standard deviations are: Pt(1)–C (1): 2.001(3); Pt(1)–N(1): 2.028(2); Pt(1)–S(1): 2.2701(6);
468 Pt(1)–N(1): 2.028 (2); Pt(1)–Br(1): 2.5456(3); C(1)–Pt(1)–N(1): 86.01(9); C(1)–Pt(1)–S(1): 88.90(7);
469 N(1)–Pt(1)–Br(1): 91.04(6); S(1)–Pt(1)–Br(1): 94.268(18).

470

471 **Figure 2.** Evolution of the ¹H NMR spectra (imine region) of a CDCl₃ solution of compound 51MeBrF
472 at 40 °C. (a) 20 minutes; (b) 40 minutes; (c) 60 minutes; (d) 80 minutes; (e) 120 minutes.

473

474 **Figure 3** Eyring and ln k versus P plots of the rate determining step observed in the 5 → 7 reaction in
475 the 52-MeBrH (●, 54 °C) and 52-MeBrF (▲, 62 °C) systems.

476

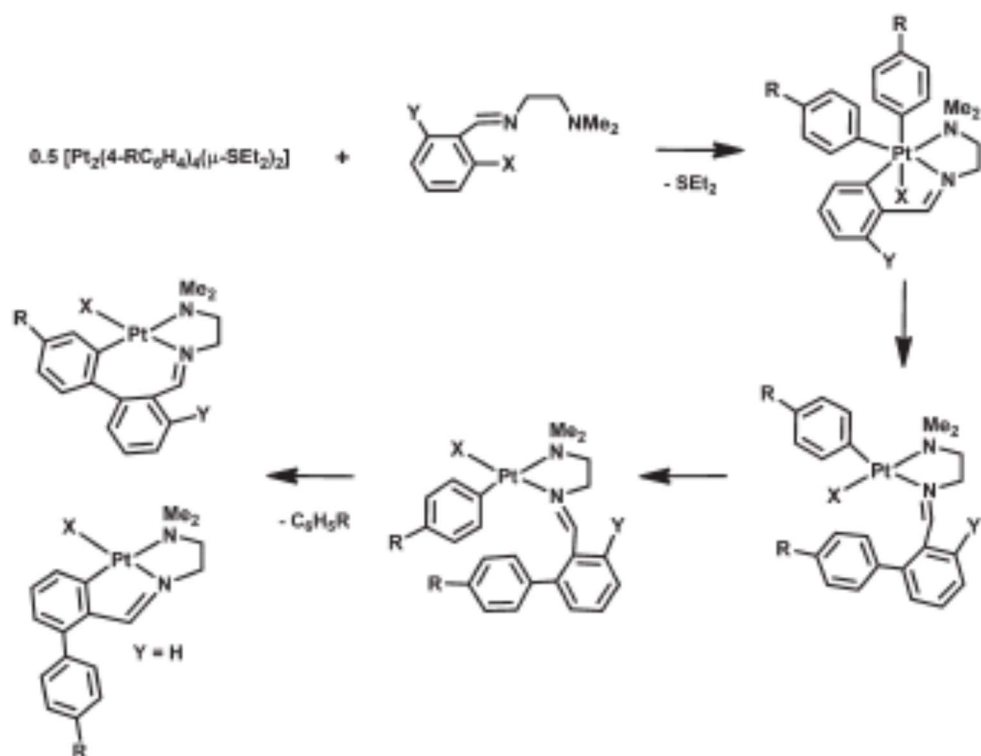
477 **Fig. 4** (a) Single step UV-Vis spectral changes observed in a 5 × 10⁻⁴ M toluene solution of 52-HBrF
478 (40 °C 4.5 hours). (b) Eyring and ln k versus P plots of the rate determining step observed in the 5 → 7
479 reaction in the 52-HBrF (□, 45 °C) and 52-HBrH (○, data from ref. 14) systems.

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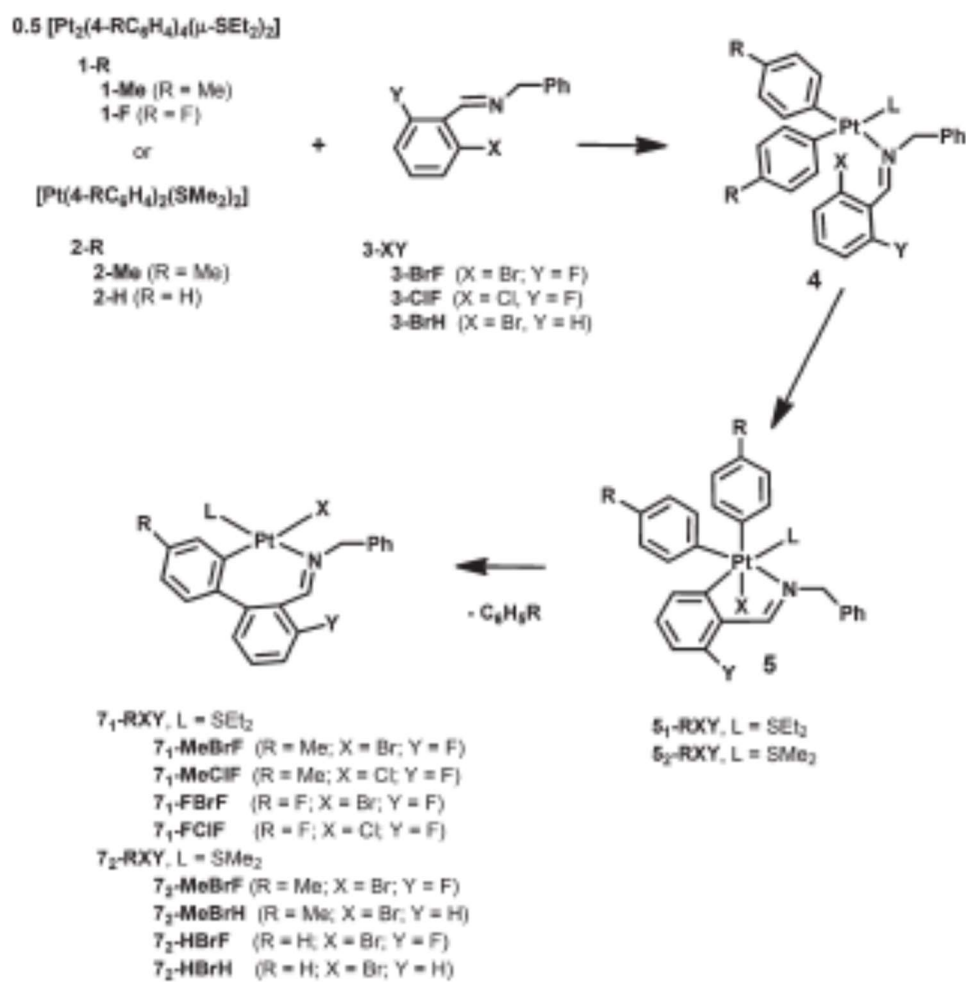
SCHEME 1



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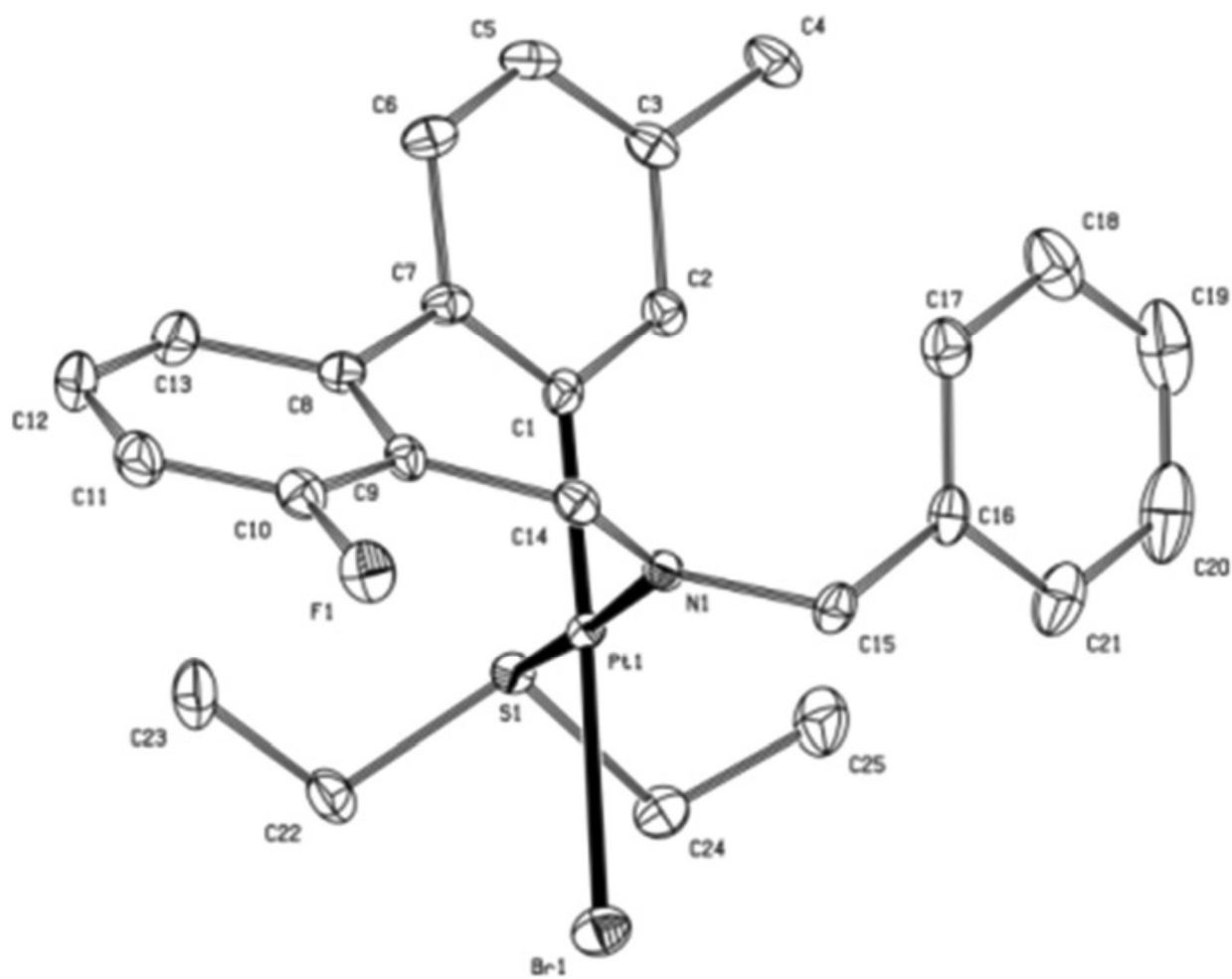
SCHEME 2



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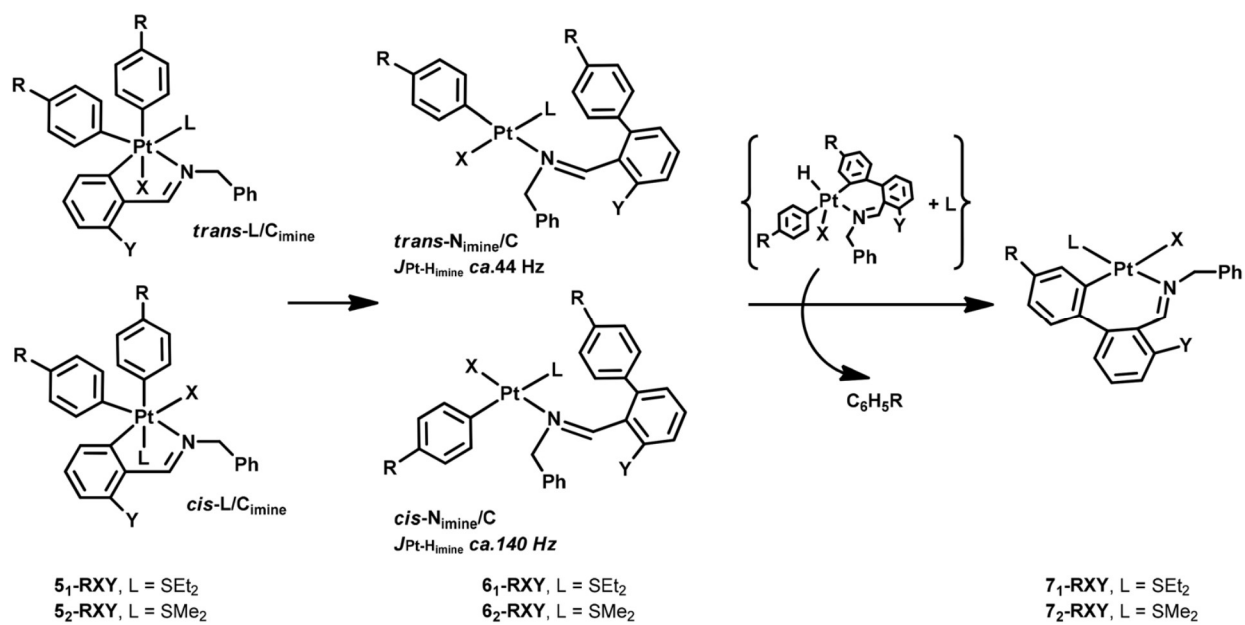
FIGURE 1.



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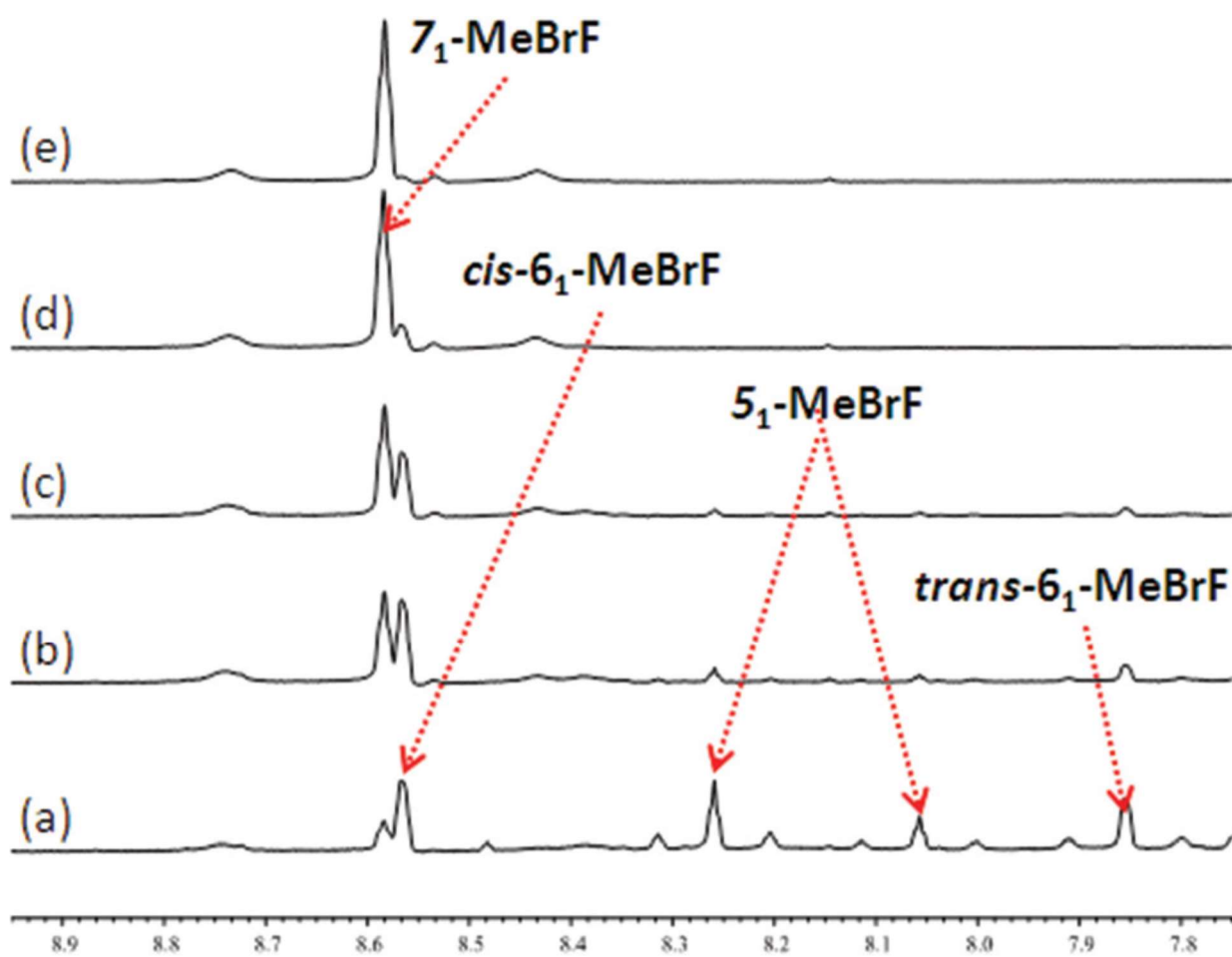
SCHEME 3



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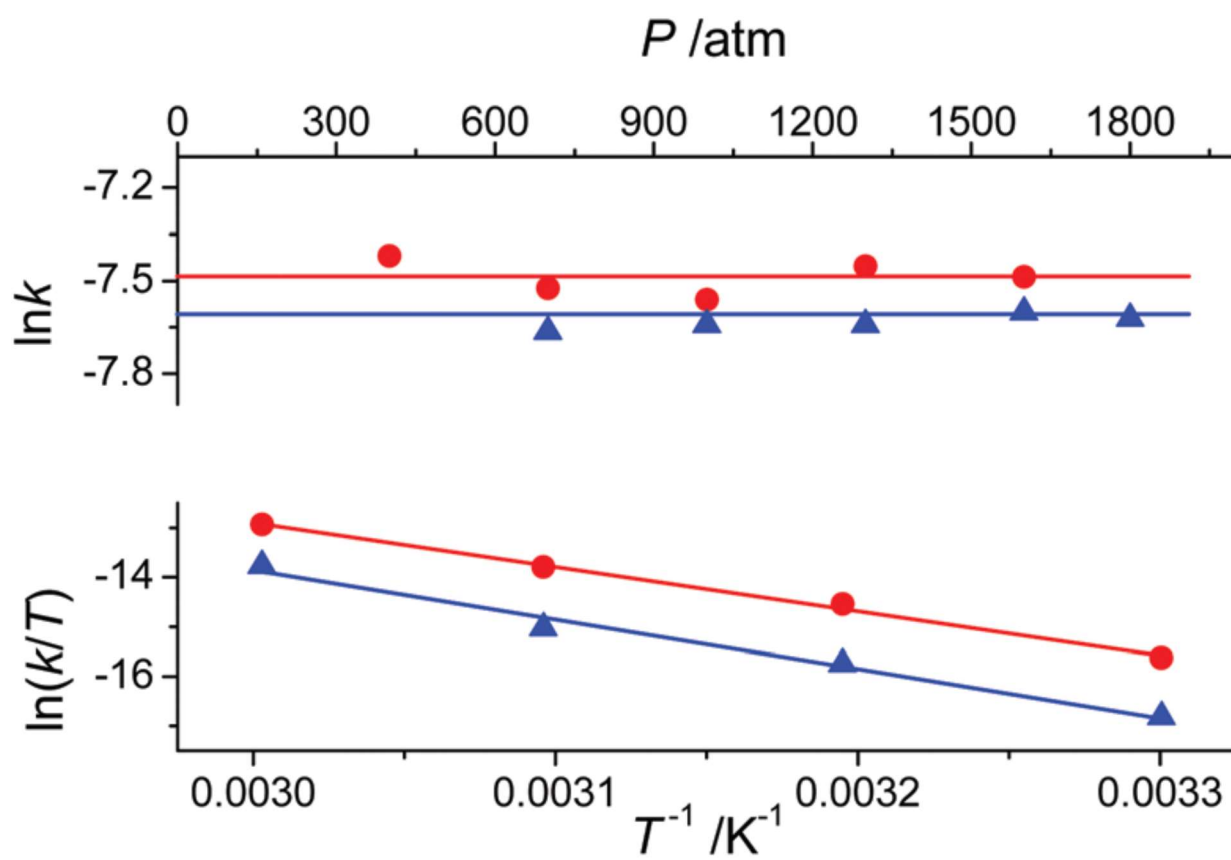
FIGURE 2.



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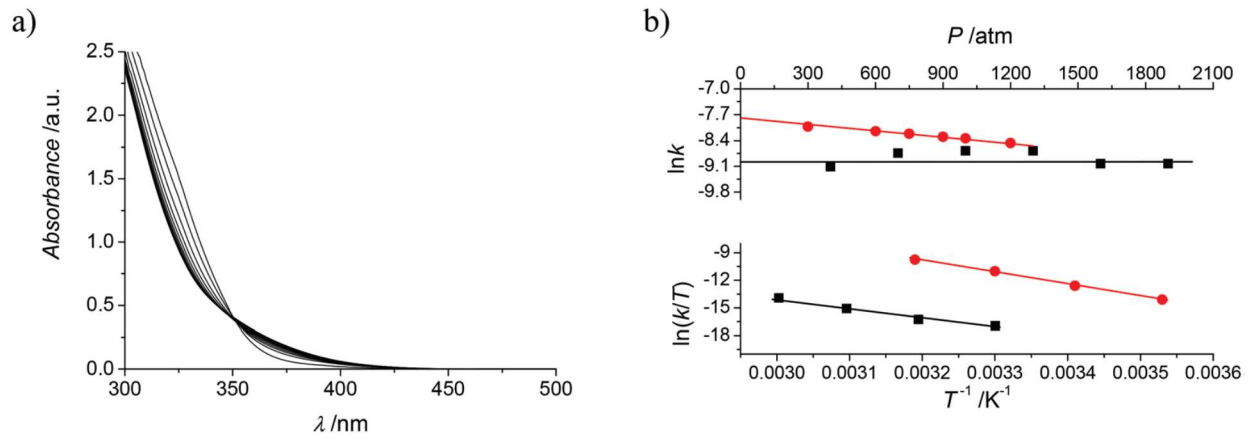
FIGURE 3.



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FIGURE 4.



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519 **Table 1.** Summary of the kinetic and activation parameters determined for the rate determining step
 520 measured during the UV-Vis monitoring of toluene solution of compounds 5 leading to complexes 7.
 521

Starting complex	Rate limiting reaction, as observed by ¹ H NMR	10 ⁴ × ²⁹⁰ k/s ⁻¹	ΔH [‡] /kJ mol ⁻¹	ΔS [‡] /J K ⁻¹ mol ⁻¹	ΔV [‡] /cm ³ mol ⁻¹ K
5 ₁ -MeBrF	6(<i>cis</i> -N _{imine} /C) → 7	9.5	65 ± 1	-115 ± 5	0 ₃₁₂
5 ₁ -FBrF	6(<i>trans</i> -N _{imine} /C) → 6(<i>cis</i> -N _{imine} /C)	2.3	84 ± 5	-71 ± 16	-21 ± 3 ₂₂₂
5 ₂ -HBrH	5 ₂ -HBrH → 6(<i>trans</i> -N _{imine} /C)	5200 ^a	96 ± 3 ^a	29 ± 10 ^a	13 ± 1 ^a
5 ₂ -HBrF	5 ₂ -HBrF → 6(<i>trans</i> -N _{imine} /C)	100	98 ± 4	2 ± 2	27 ± 2 ₃₁₈
5 ₂ -MeBrH	6(<i>cis</i> -N _{imine} /C) → 7	13	75 ± 3	-83 ± 9	0 ₂₂₅
5 ₂ -MeBrF	6(<i>cis</i> -N _{imine} /C) → 7	6.7	83 ± 7	-65 ± 21	0 ₂₂₅

^a Kinetic data estimated from ref. 14 and 15 in chloroform solution.

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527 **Table 2** Summary of the kinetic and activation parameters determined for the faster step measured
528 during the UV-Vis monitoring of toluene solution of compounds 5 leading to complexes 7
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Starting complex	$10^3 \times k$ (s ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J K ⁻¹ mol ⁻¹)	$\Delta V^\ddagger_{\ddagger}$ (cm ³ mol ⁻¹)
5 _{1'} -MeBrF	2.1	72 ± 4	-76 ± 12	4 ± 2 _{21.2}
5 _{1'} -FBrF	0.34	88 ± 6	-42 ± 18	5 ± 2 _{22.2}
5 _{2'} -MeBrH	2.5	70 ± 3	-81 ± 10	9 ± 1 _{20.2}
5 _{2'} -MeBrF	1.7	50 ± 4	-146 ± 12	16 ± 1 _{20.8}

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535 **Table 3** Crystallographic and refinement data for compound 71-MeBrF

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Formula	C ₂₅ H ₂₇ BrFNpS
Pw	667.53
Temp, K	100(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /c
a, Å	7.5163(3)
b, Å	29.5093(14)
c, Å	10.5848(5)
β , °	96.773(2)
V, Å ³ ; Z	2331.33(18); 4
d (calcd), Mg m ⁻³	1.902
Abs coeff, mm	7.842
F(000)	1288
Rflns coll./independent	69 060/7145 [<i>R</i> (int) = 0.0318]
Data/restraint/parameter	7145/0/274
GOF on F^2	1.122
Final <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0223, w <i>R</i> ₂ = 0.0477
<i>R</i> (all data)	<i>R</i> ₁ = 0.0268, w <i>R</i> ₂ = 0.0490
Peak and hole, e Å ⁻³	0.753 and -1.650

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