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

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The reactions of dinuclear [Pt2(4-RC6H4)4(μ-SEt2)2] (R = Me or F), or mononuclear [Pt(4-RC6H4)2(SMe2)2] (R = Me or H), platinum(II) compounds with imines of the general formula 2-X,6-YC6H3CHvNCH2Ph (X = Br, Y = F; X = Cl, Y = F; X = Br, Y = H) produced seven-membered [C,N]-platinacycles. The reaction consists of the initial formation of cyclometallated platinum(IV) compounds followed by a three step process: reductive elimination, isomerisation of the resulting non-cyclometallated intermediate and a final cycloplatination process. Combined 1H NMR and UV-Vis kinetico-mechanistic studies indicated that the rate determining step of the process depends on the nature of the aryl-Pt ligand (phenyl, p-tolyl or p-fluorophenyl).

INTRODUCTION

Cyclometallated platinum compounds containing N-donor ligands have attracted a great deal of interest due to their applications in several areas.1 In particular, cycloplatinated compounds with fluoro substituents are involved in fundamental processes of organometallic chemistry,2 in platinumcatalyzed cross coupling reaction of aryl fluorides3–6 and in the design of efficient light emitting devices.7,8 Moreover, the presence of fluoro substituents can be decisive in the regioselectivities and rates of metallacycle formation.9,10

In recent years, a novel class of seven-membered terdentate [C,Nimine,Namine] or bidentate [C,Nimine] platinacycles containing biaryl moieties has been reported.11–15 The mechanism of formation of this type of terdentate [C,Nimine,Namine] compounds has been carefully studied, including the isolation of several intermediates.16 As shown in Scheme 1, the initial step of the complete process corresponds to the formation of cyclometallated platinum(IV) compounds through intramolecular C–Br or C–Cl bond activation of the ligand at the platinum precursor. This step is followed by C–C bond formation via reductive elimination, involving one of the aryl ancillary ligands and the metallated aryl ring; isomerization of the resulting species and a final cyclometallation of the biaryl fragment result in the final cyclometallated complex. In the last step, the formation of seven-membered platinacycles is favoured over the formation of five-membered analogues for X = Cl. Moreover, the presence of a fluorine substituent (Y = F) at the ortho position, on the initially cyclometallated ligand, inhibits the formation of a five-membered platinacycle, thus favouring the seven-membered cycloplatination. Since the analogous bidentate [C,Nimine] seven-membered platinacycles have received less attention so far, we decided to undertake a study on the synthesis and mechanism for this class of compounds. With this aim the reactions of dinuclear [Pt2(4-RC6H4)4(μ-SEt2)2] (R = Me or F), or mononuclear [Pt(4-RC6H4)2(SMe2)2] (R = Me or H), organoplatinum(II) compounds with imines of the general formula 2-X,6-YC6H3CHvNCH2Ph (X = Br, Y = F; X = Cl, Y = F; X = Br, Y = H) were tested. In these systems, the role of the ancillary neutral (SEt2 or SMe2) ligands, as well as the substituents on the aryl (R = F, Me, H) ligands of the platinum precursor will be analysed both from a synthetic and a kinetico-mechanistic perspective.

RESULTS AND DISCUSSION

Preparation of seven-membered platinacycles

The general preparation procedure for the seven-membered cycloplatinated compounds studied is outlined in Scheme 2. Reactions of the corresponding platinum precursor and imine were carried out in refluxing toluene for six hours and produced the new seven-membered platinum(II) cyclometallated compounds 71-MeBrF, 71-MeClF, 71-FBrF, 71-FClF, 72-MeBrF, 72-MeBrH, and 72-HBrF as indicated. The uniform nature of the final products thus prepared, as well as the obtained yields (all within the 60–85% range), suggests that the reaction sequence is independent of the nature of the platinum compound and the imine ligand used. This result is in interesting contrast with the results obtained for the reaction of [Pt2(4-MeC6H4)4(μ-SEt2)2] with imines 2-XC6H4CHvNCH2CH2NMe2 where the formation of seven- and five-membered platinacycles is preferred for X = Cl and X = Br, respectively.16,17 NMR data obtained for these compounds are consistent with the proposed structures. Both the imine proton (JH–Pt in the 120–128 Hz range) and the Ha proton adjacent to the metalation site (JH–Pt in the 52–65 Hz range) are coupled with 195Pt. The latter signal appears as a singlet for 71-MeBrF, 71-MeClF, 72-MeBrF and 72-MeBrH, as a doublet (JH–F = 9.2) for 71-FBrF and 71-FClF, or as a doublet of doublets (JH–H = 7.6 and 1.2) for 72-HBrF, in agreement with the presence of a methyl, a fluoro or a hydrogen atom in ortho to Ha respectively.

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

Kinetico-mechanistic study

Given the fact that the general (5 → 7) sequence shown in Scheme 2 has been found to be very finely tuned by the presence of different substituents on the initial cyclometallating ligand, 3,16–18 a detailed mechanistic study has been conducted for the present system. The different steps involved in the full preparative process indicated have been often studied from a kinetico-mechanistic perspective.14,15,19 The behaviour is well-established for the initial oxidative addition reactions (4 → 5),10,20–24 as well as for the reductive elimination/oxidative addition follow up processes (5 → 7).16–18 From the data collected so far in the literature, it is clear that, despite the relative formal simplicity of the reactivity observed, the general mechanism is a compendium of multistep processes that include fast coordination/decoordination equilibria21,23,24 and isomerization reactions.16,17 Scheme 3 collects the kineticomechanistic sequential steps expected for the process.

For this purpose, complexes 5 were obtained from the reaction of 1 + 3 on a small scale; after workup the complexes were found to be of a high enough purity to study the 5 → 7 reaction without the presence of any remaining 1 or 3 species in solution. Nevertheless, in most of the cases some 1H NMR signals are also evident, which were assigned to some amounts of complex 6 as described in the Experimental part, their intensity increasing on workup as expected (see below). The detailed 1H NMR monitoring of the 5 → 7 reaction in CDCl3 solution was then conducted to ascertain the relative readiness of the 5 → 6 and 6 → 7 steps, as well as possible isomerisation processes of compounds 6, already observed for similar systems.16,17

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

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

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

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

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

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

For bidentate PtNimine/Namine systems some data are available,17 although comparison might be non-significant due to the different requirements of the ligands. In the present study the values of the activation enthalpies are much lower (within the 65–87 range versus 105–140 for the PtNimine/Namine systems) and the activation entropies are clearly negative (close to zero for the PtNimine/Namine systems) while keeping the value of $\Delta V^{\ddagger}$ at zero. Clearly the oxidative addition reaction leading from complex 6 (cis-Nimine/C) to 7, indicated in Scheme 3, proceeds via a better ordered transition state requiring less energy than that for the more encumbered bidentate PtNimine/Namine systems. The values are similar to those collected for the formation of complexes 5 from 1 + 3.21,24 The activation volumes should correspond to a compensation effect between a high degree of compression, due to the concerted nature of the oxidative addition, and an increase in bond distances, including the decoordination of the L ligand needed for the process.16,17,28–32

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

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

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

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

CONCLUSIONS

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

EXPERIMENTAL

General

Microanalyses were performed at the Centres Científics i Tecnològics (Universitat de Barcelona). NMR spectra were recorded at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using a Mercury-400 (1H, 400 MHz; 19F, 376.5 MHz) and referenced to SiMe4 (1H) or CFCl3 (19F). δ values are given in ppm and J values in Hz. Abbreviations used: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad.

Preparation of complexes

Platinum compounds [Pt2(4-RC6H4)4(μ-SEt2)2] (1-Me, R = Me35 or 1-F, R = F12), [Pt(4-RC6H4)2(SMe2)2] (2-Me, R = Me36 or 2-H, R = H37), ligands 2-X,6-FC6H3CHvNCH2P h (3-BrF, X = Br6 or 3-ClF, X = Cl38) and 2-BrC6H4CHvNCH2Ph (3-BrH)39 and the compound [PtBr{C6H4(C6H4)CHvNCH2Ph}SMe2] (72-HBrH)15 were prepared as reported elsewhere

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

[PtBr{(4-MeC6H3)(2-FC6H3)CHvNCH2Ph}SEt2] (71-MeBrF). 1H NMR (400 MHz, CDCl3), δ = 8.66 (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, 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, 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–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, 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 (ppm): −115.05 (ddd, 3JF–H = 9.0, 4JF–H = 5.6, 5JF–H = 2.0). EA (calc. for C25H27BrFNPtS): C: 45.21% (44.98%); H: 4.38% (4.08%); N: 2.32% (2.10%); S: 4.70% (4.80%).

[PtCl{(4-MeC6H3)(2-FC6H3)CHvNCH2Ph}SEt2] (71-MeClF). 1H NMR (400 MHz, CDCl3), δ = 8.67 (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, 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, 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–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), 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 NMR (376.5 MHz, CDCl3), δ (ppm): −115.07 (ddd, 3JF–H = 8.6, 4JF–H = 6.0, 5JF–H = 2.0). EA (calc. for C25H27ClFNPtS·0.5H2O): C: 47.50% (47.50%); H: 4.43% (4.46%); N: 2.46% (2.22%); S: 4.87% (5.07%).

[PtBr{(4-FC6H3)(2-FC6H3)CHvNCH2Ph}SEt2] (71-FBrF). 1H NMR (400 MHz, CDCl3), δ = 8.61 (s, 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,

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–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), 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), 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, CDCl3), δ (ppm): −114.73 (m), −116.94 (m). EA (calc. for C24H24BrF2NPtS): C: 42.92% (42.93%); H: 3.72% (3.60%); N: 2.20% (2.09%); S: 4.47% (4.77%).

[PtCl{(4-FC6H3)(2-FC6H3)CHvNCH2Ph}SEt2] (71-FClF). 1H NMR (400 MHz, CDCl3), δ = 8.64 (s, 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, 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–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), 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), 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, CDCl3), δ (ppm): −114.73 (m), −117.13 (m). EA (calc. for C24H24ClF2NPtS): C: 45.20% (45.97%); H: 3.84% (3.86%); N: 2.37% (2.23%); S: 4.63% (5.11%).

[PtBr{(4-MeC6H3)(2-FC6H3)CHvNCH2Ph}SMe2] (72-MeBrF). 1H NMR (400 MHz, CDCl3), δ = 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 (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, 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–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, CDCl3), δ (ppm): −114.81 (ddd, 3JF–H = 9.2, 4JF–H = 6.0, 5JF–H = 2.6). EA (calc. for C23H23BrFNPtS·1.5H2O): C: 41.30% (41.45%); H: 3.53% (3.93%); N: 2.26% (2.10%); S: 4.42% (4.81%).

[PtBr{(4-MeC6H3)(C6H4)CHvNCH2Ph}SMe2] (72-MeBrH). 1H NMR (400 MHz, CDCl3), δ = 8.44 (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 = 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, 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, 3H, Hi). EA (calc. for C23H24BrNPtS·H2O): C: 43.40% (43.20%); H: 3.87% (4.10%); N: 2.38% (2.19%); S: 4.72% (5.01%).

[PtBr{(C6H4)(2-FC6H3)CHvNCH2Ph}SMe2] (72-HBrF). 1H NMR (400 MHz, CDCl3), δ = 8.52 (s, 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 = 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, 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 (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, 3H, Hi), 2.00 (s, br, 3H, Hi). 19F NMR (376.5 MHz, CDCl3), δ (ppm): −114.84 (ddd, 3JF–H = 9.8, 4JF–H = 5.6, 5JF–H = 2.2). EA (calc. for C22H21BrFNPtS·H2O): C: 40.77% (41.06%); H: 3.35% (3.60%); N: 2.28% (2.18%); S: 4.72% (4.98%).

Compounds 5. Compounds [PtX(4-RC6H4)2(2-YC6H3CHv NCH2Ph)L] (51-MeBrF: R = Me, X = Br, Y = F, L = SEt2; 51-FBrF: R = F, X = Br, Y = F, L = SEt2; 52-MeBrF: R = Me, X = Br, Y = F, L = SMe2; 52-MeBrH: R = Me, X = Br, Y = H, L = SMe2; 52-HBrF: R = H, X = Br, Y = F, L = SMe2 and 52-HBrH: R = H, X = Br, Y = H, L = SMe2) were characterised by 1H NMR spectra. 10 mg of the corresponding platinum precursor 1-Me, 1-F, 2-Me or 2-H and the equivalent amount of the corresponding ligand 3-BrF or 3-BrH were mixed at 25 °C in a NMR tube and allowed to react for the reaction times stated below. 51-MeBrF: reaction time, 30 min; 1H NMR (400 MHz, CDCl3), δ = 8.26 (s, 3JH–Pt = 44, 1H, CHvN) (major isomer 2 : 1); 8.06 (s, 3JH–Pt = 44, 1H, CHvN) (minor isomer). 51-FBrF: reaction time, 30 min; 1H NMR (400 MHz, CDCl3), δ = 8.34 (s, 3JH–Pt = 44, 1H, CHvN), 5.47 (m, 2H, CH2Ph), 1.06 (t, 3JH–Pt = 16.0, 6H, SCH2CH3) (major isomer 1.6 : 1); 7.97 (s, 3JH–Pt = 44, 1H, CHvN), 5.05 (m, 2H, CH2Ph), 1.29 (t, 3JH–Pt = 16.0, 6H, SCH2CH3) (minor isomer). 52-MeBrF: reaction time, 180 min; 1H NMR (400 MHz, CDCl3), δ = 8.29 (s, 3JH–Pt = 44, 1H, CHvN), {5.65 (dd,

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 = 12.0, 6H, SMe2) (major isomer 2 : 1); δ = 8.05 (s, 3JH–Pt = 44, 1H, CHvN), {5.54 (dd, 2JH–H = 17.0, 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, SMe2) (minor isomer). 52-MeBrH: reaction time, 180 min; 1H NMR (400 MHz, CDCl3), δ = 7.92 (s, 3JH–Pt = 44, 1H, CHvN), {5.53 (dd, 2JH–H = 17.2, 4JH–H = 1.6, 1H), 5.42 (dd, 2JH–H = 17.2, 4JH–H = 1.6, 1H), CH2Ph}, 1.95 (s, 3JH–Pt = 12.0, 6H, SMe2) (major isomer 2 : 1); δ = 7.71 (s, 3JH–Pt = 48, 1H, CHvN); {5.45 (dd, 2JH–H = 17.0, 4JH–H = 1.6, 1H), 5.43 (dd, 2JH–H = 17.0, 4JH–H = 1.6, 1H), CH2Ph}, 2.07 (s, 3JH–Pt = 12.0, 6H, SMe2) (minor isomer). 52-HBrF: reaction time, 30 min; 1H NMR (400 MHz, CDCl3), δ = 8.29 (s, 3JH–Pt = 44, 1H, CHvN), {5.58 (dd, 2JH–H = 16.0, 4JH–H = 2.0, 1H), 5.44 (dd, 2JH–H = 16.0, 4JH–H = 2.0, 1H), CH2Ph}, 1.99 (s, 3JH–Pt = 12.0, 6H, SMe2) (major isomer 2 : 1); δ = 8.06 (s, 3JH–Pt = 48, 1H, CHvN); {5.48 (dd, 2JH–H = 16.0, 4JH–H = 2.0, 1H), 5.37 (dd, 2JH–H = 16.0, 4JH–H = 2.0, 1H), CH2Ph}, 2.07 (s, 3JH–Pt = 12.0, 6H, SMe2) (minor isomer). 52-HBrH: reaction time, 90 min; 1H NMR (400 MHz, CDCl3), δ = 7.95 (s, 3JH–Pt = 48, 1H, CHvN), {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 (s, 3JH–Pt = 12.0, 6H, SMe2) (major isomer 3.8 : 1); δ = 7.72 (s, 3JH–Pt = 44, 1H, CHvN), {5.47 (dd, 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 = 12.0, 6H, SMe2) (minor isomer).

Compounds 6. Compounds [PtX(4-RC6H4)(4-RC6H4–2- YC6H3CHvNCH2Ph)L] (61-MeBrF: R = Me, X = Br, Y = F, L = SEt2; 61-FBrF: R = F, X = Br, Y = F, L = SEt2; 62-MeBrF: R = Me, X = Br, Y = F, L = SMe2 and 62-MeBrH: R = Me, X = Br, Y = H, L = SMe2) were characterised by 1H NMR spectra. Solutions containing compounds 5 (see above) were concentrated to dryness, and the residues were washed with diethyl ether in order to remove excess of imine and dialkylsulfide ligands, and dried in vacuo. The obtained residues (crude compounds 5) were dissolved at 25 °C in a NMR tube and the reaction was monitored under the conditions stated below. 61-MeBrF: reaction time, 20–120 min, temperature 40 °C; 1H NMR (400 MHz, CDCl3), δ = 7.85 (s, 3JH–Pt = 44) (trans-Nimine/C); 8.56 (s, 3JH–Pt = 144) (cis-Nimine/C) (initial ratio ca. 1 : 1). 61-FBrF: reaction time, 40–80 min, temperature 25 °C; 1H NMR (400 MHz, CDCl3), δ = 8.10 (s, 3JH–Pt = 44) (trans-Nimine/C). 62-MeBrF: reaction time, 10–300 min, temperature 25 °C; 1H NMR (400 MHz, CDCl3), δ = 7.85 (s, 3JH–Pt = 44) (trans-Nimine/C); 8.48 (s, 3JH–Pt = 120) (cis-Nimine/C) (initial ratio ca. 1 : 1). 62-MeBrH: reaction time, 20–400 min, temperature 30 °C; 1H NMR (400 MHz, CDCl3), δ = 8.35 (s, 3JH–Pt = 124) (cis-Nimine/C).

X-ray structure analysis

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

Kinetics

The kinetic profiles for the reactions were followed by UV-Vis spectroscopy in the 700–300 nm range on HP8452A or Cary50 instruments equipped with thermostated multicell transports. The observed rate constants were derived from absorbance versus time traces at the wavelengths where a maximum increase and/or decrease of absorbance was observed. For the reactions carried out at varying pressure the previously described pillbox cell and pressurising system41–44 were used and final treatment of data was the same as described before. The calculation of the observed rate constants from the absorbance versus time monitoring of reactions was carried out using the SPECFIT or ReactLab softwares;45,46 typical errors of these values are within the 10–20% margin. The general kinetic technique is that previously described.15,20,47 Table S1† collects all the obtained kobs values for all the systems studied

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

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.

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.

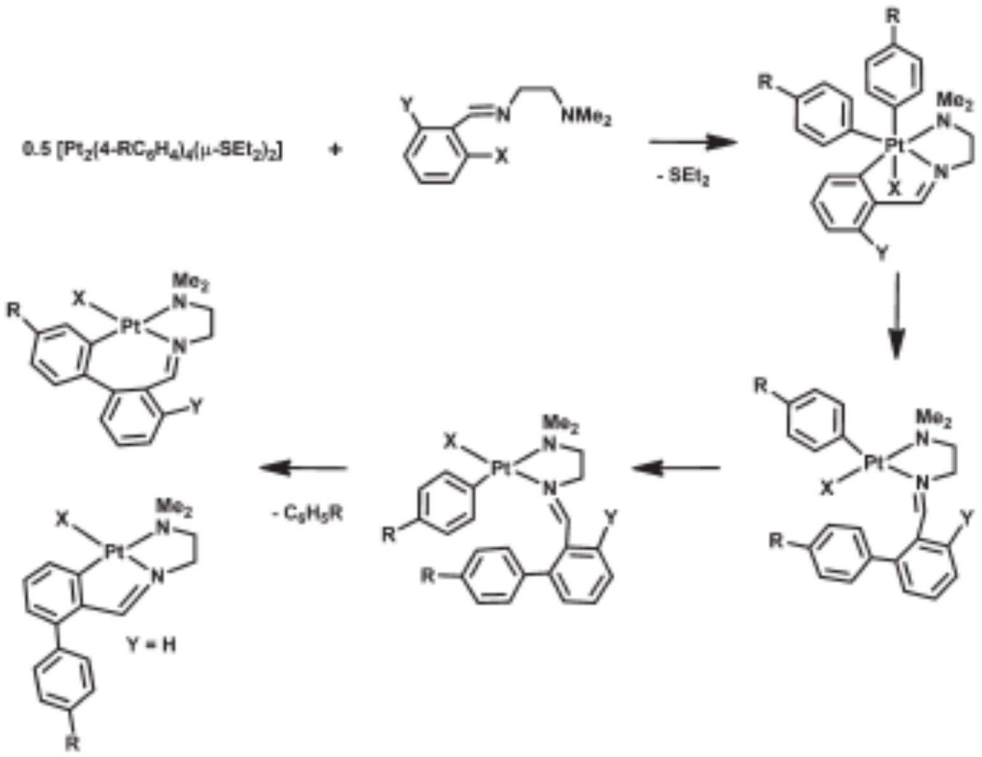
476

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.

480

481

SCHEME 1



SCHEME 2

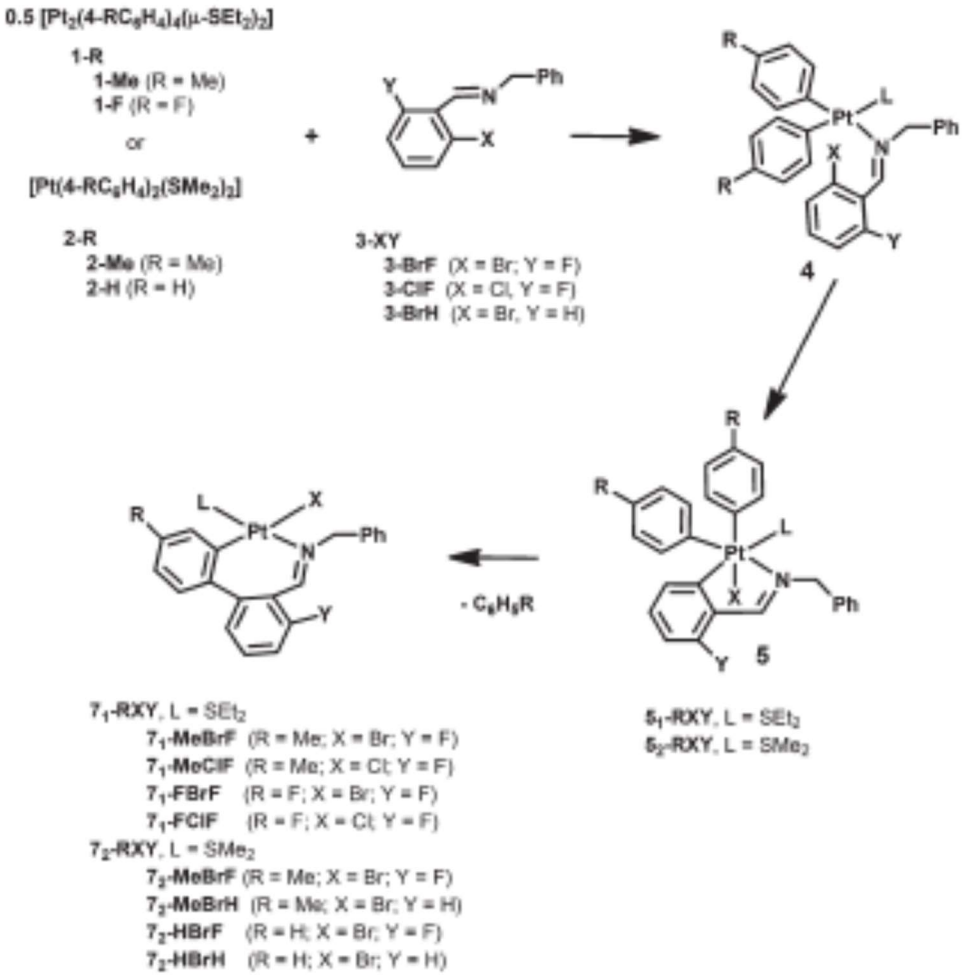
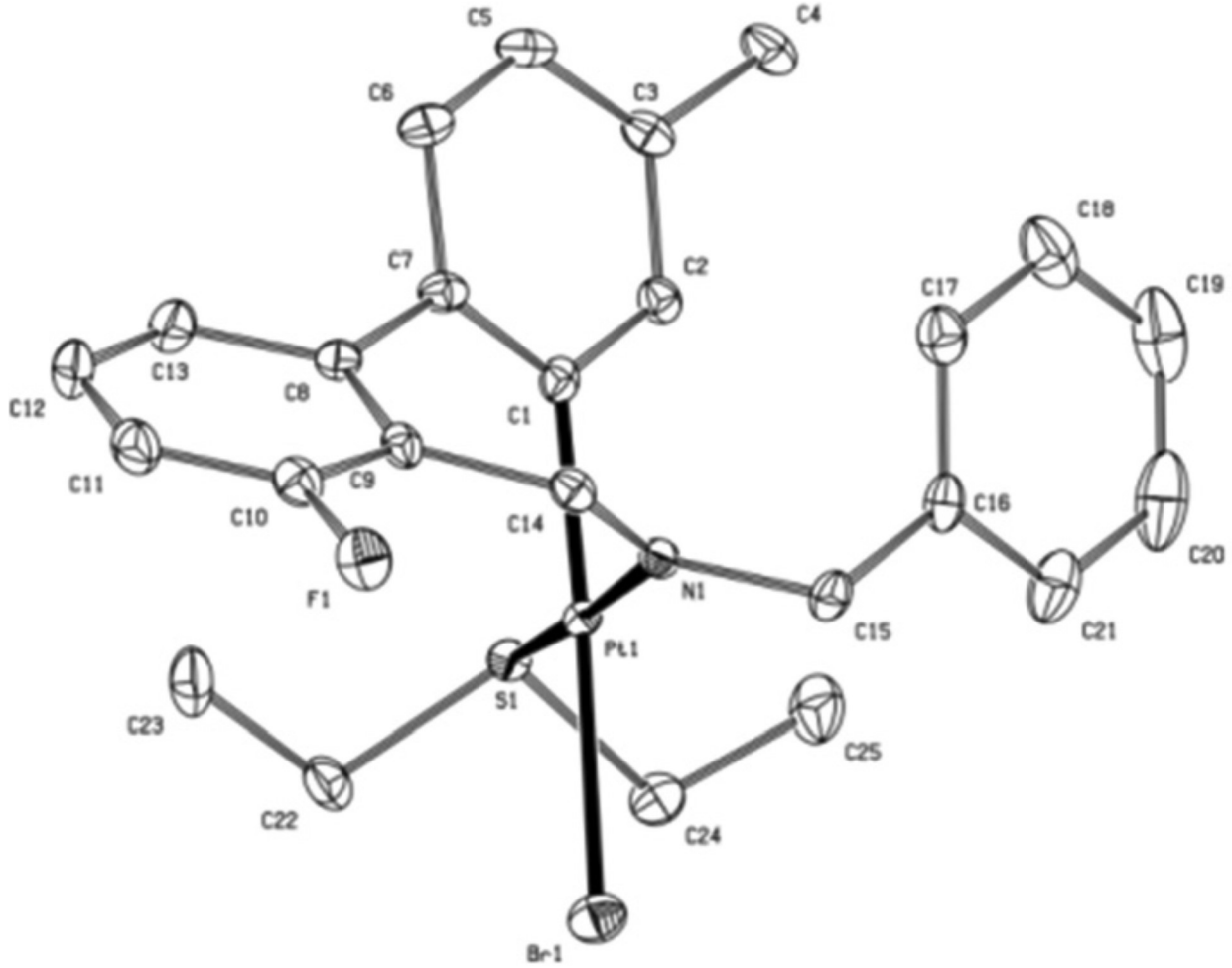

0.5 [Pt2(4-RC6H4)4(μ-SEt2)2]
1-R
1-Me (R = Me)
1-F (R = F)
or
[Pt(4-RC6H4)2(SMe2)2]
2-R
2-Me (R = Me)
2-H (R = H)
3-XY
3-BrF (X = Br; Y = F)
3-ClF (X = Cl, Y = F)
3-BrH (X = Br, Y = H)
4
5
- C6H5R
71-RXY, L = SEt2
71-MeBrF (R = Me; X = Br; Y = F)
71-MeClF (R = Me; X = Cl; Y = F)
71-FBrF (R = F; X = Br; Y = F)
71-FClF (R = F; X = Cl; Y = F)
72-RXY, L = SMe2
72-MeBrF (R = Me; X = Br; Y = F)
72-MeBrH (R = Me; X = Br; Y = H)
72-HBrF (R = H; X = Br; Y = F)
72-HBrH (R = H; X = Br; Y = H)
51-RXY, L = SEt2
52-RXY, L = SMe2

FIGURE 1.


C5
C4
C6
C3
C18
C7
C2
C17
C19
C13
C8
C1
C12
C11
C9
C16
C10
C14
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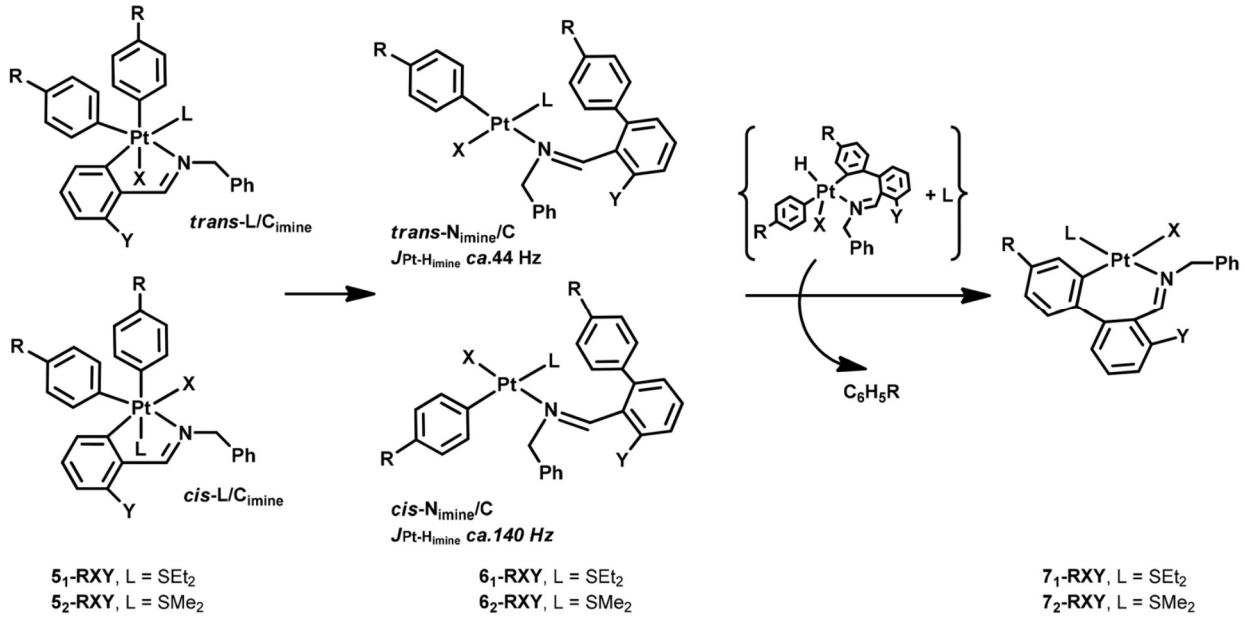
C15
C21
Pt1
S1
C23
C25
C22
C24
Br1

SCHEME 3



5_1-RXY, L = SEt_2
5_2-RXY, L = SMe_2

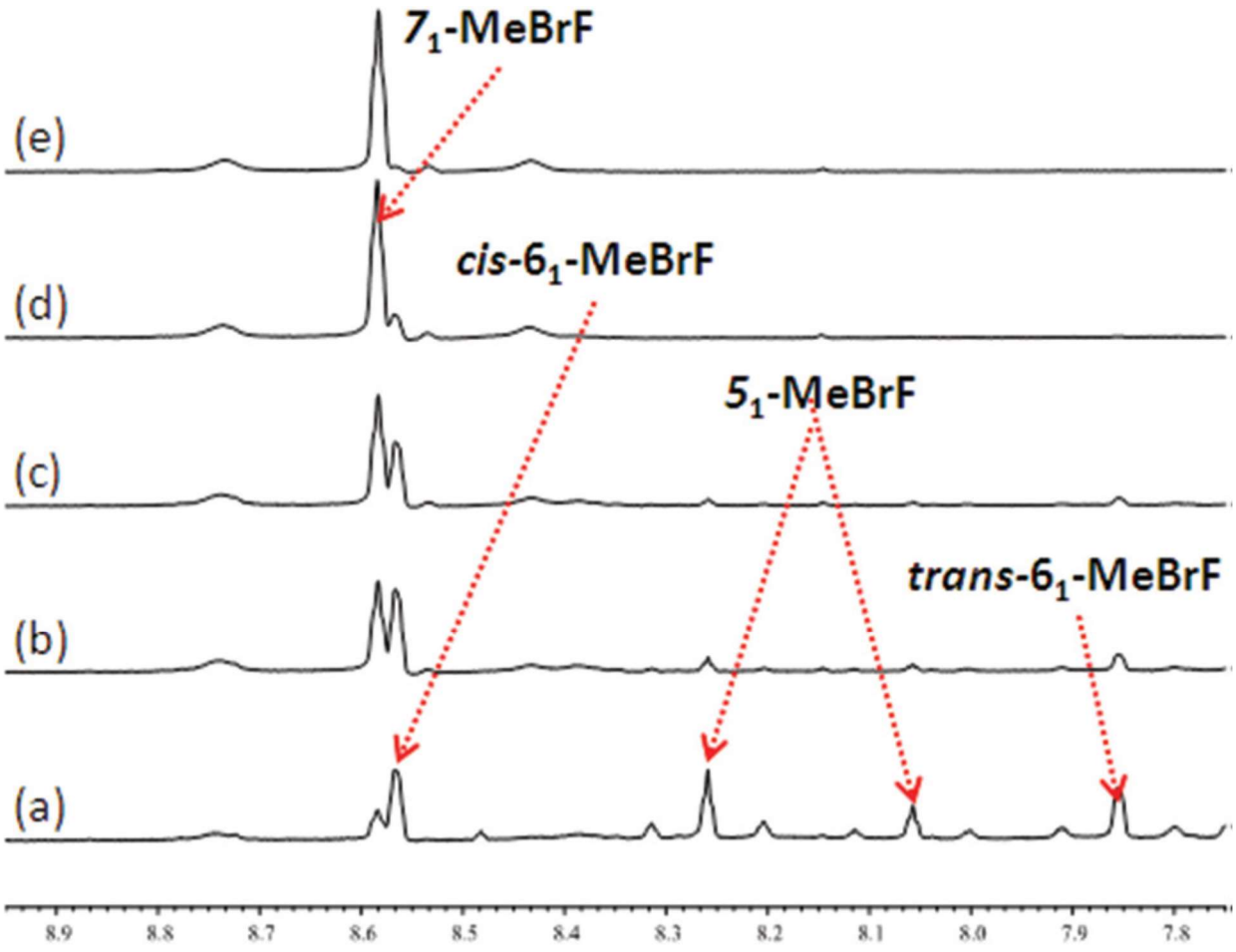
6_1-RXY, L = SEt_2
6_2-RXY, L = SMe_2

7_1-RXY, L = SEt_2
7_2-RXY, L = SMe_2

503 **FIGURE 2.**

504

505



506

507

FIGURE 3.

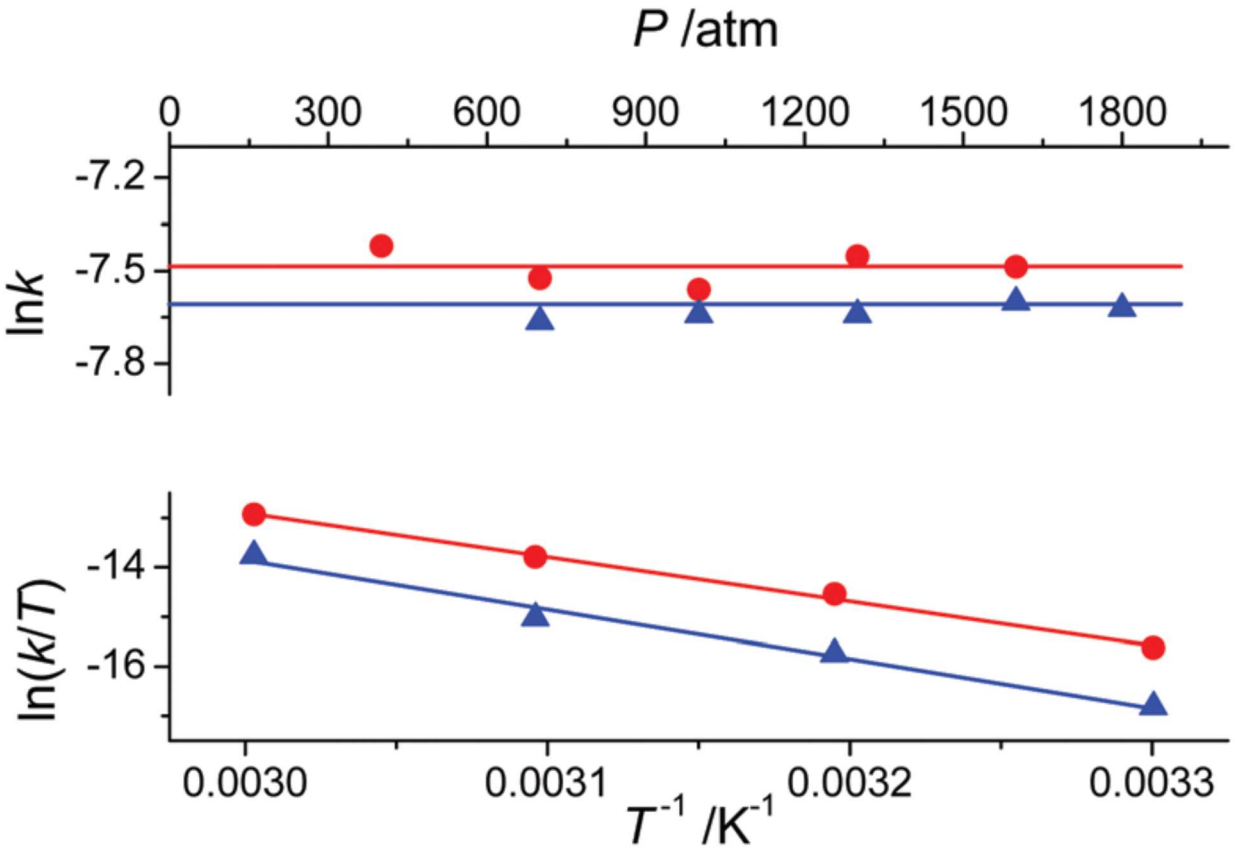
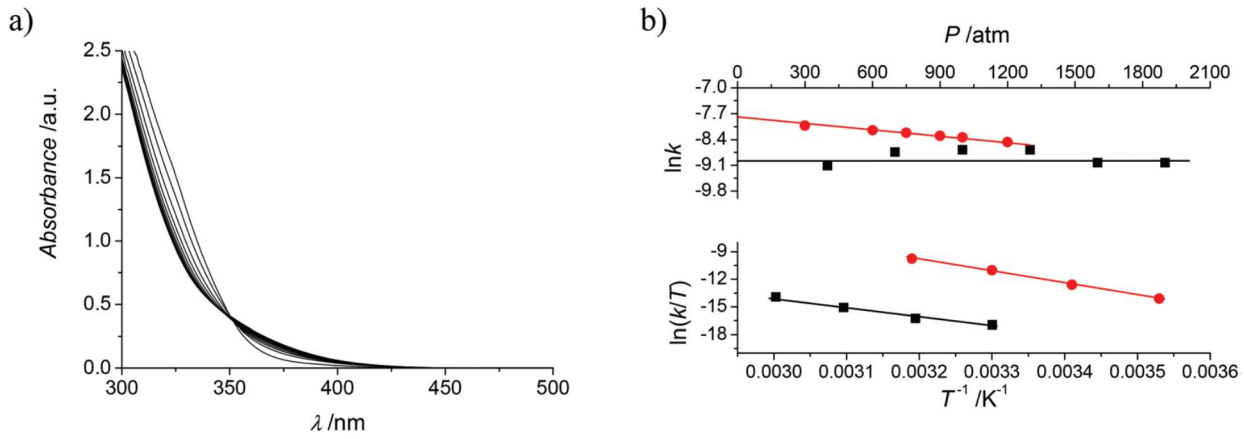

P /atm
0
300
600
900
1200
1500
1800
-7.2
-7.5
-7.8
lnk
-14
-16
ln(k/T)
0.0030
0.0031
0.0032
0.0033
T-1 /K-1

FIGURE 4.


a)
Absorbance /a.u.
2.5
2.0
1.5
1.0
0.5
0.0
300
350
400
450
500
λ /nm
b)
P /atm
0
300
600
900
1200
1500
1800
2100
-7.0
-7.7
-8.4
-9.1
-9.8
lnk
-9
-12
-15
-18
ln(k/T)
0.0030
0.0031
0.0032
0.0033
0.0034
0.0035
0.0036
T-1 /K-1

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	$10^4 \times {}^{340}k/s^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V^{\ddagger}_T$/cm^3 mol^{-1}$_K$
5_1-MeBrF	$6(cis\text{-}N_{imine}/C) \rightarrow 7$	9.5	65 ± 1	−115 ± 5	0_{313}
5_1-FBrF	$6(trans\text{-}N_{imine}/C) \rightarrow 6(cis\text{-}N_{imine}/C)$	2.3	84 ± 5	−71 ± 16	$-21 \pm 3_{323}$
5_2-HBrH	$5_2\text{-HBrH} \rightarrow 6(trans\text{-}N_{imine}/C)$	5200[a]	96 ± 3[a]	29 ± 10[a]	13 ± 1^a
5_2-HBrF	$5_2\text{-HBrF} \rightarrow 6(trans\text{-}N_{imine}/C)$	100	98 ± 4	2 ± 2	$27 \pm 2_{314}$
5_2-MeBrH	$6(cis\text{-}N_{imine}/C) \rightarrow 7$	13	75 ± 3	−83 ± 9	0_{335}
5_2-MeBrF	$6(cis\text{-}N_{imine}/C) \rightarrow 7$	6.7	83 ± 7	−65 ± 21	0_{335}

[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	$10^3 \times {}^{323}k$ (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta V^{\ddagger}_{T}$ (cm^3 mol^{-1} K)
5_1-MeBrF	2.1	72 ± 4	−76 ± 12	$4 \pm 2_{213}$
5_1-FBrF	0.34	88 ± 6	−42 ± 18	$5 \pm 2_{323}$
5_2-MeBrH	2.5	70 ± 3	−81 ± 10	$9 \pm 1_{303}$
5_2-MeBrF	1.7	50 ± 4	−146 ± 12	$16 \pm 1_{308}$

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Table 3 Crystallographic and refinement data for compound 71-MeBrF

Formula	$C_{22}H_{27}BrFNPtS$
Fw	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 [R_i(int) = 0.0318]
Data/restraint/parameter	7145/0/274
GOF on F^2	1.122
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0223$, w$R_2 = 0.0477$
R (all data)	$R_1 = 0.0268$, w$R_2 = 0.0490$
Peak and hole, e Å^{-3}	0.753 and −1.650