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Isomerization in substitution processes of cyclometallated dimethylhaloplatinum(IV) complexes †

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Cyclometallated imine platinum(IV) derivatives of general formula $[PtX(Me)_2(\boldsymbol{C}–\boldsymbol{N})(SMe_2)]$, being X = Br and Cl with $\boldsymbol{C}–\boldsymbol{N} = \boldsymbol{C}C_5H_4CH_2\boldsymbol{N}CH(2,4,6\text{-}Me_3C_6H_2)$ (**1** and **2**); X = I with $\boldsymbol{C}–\boldsymbol{N} = \boldsymbol{C}C_5H_4CH\boldsymbol{N}Bzl$ (**3**); X = Br with $\boldsymbol{C}–\boldsymbol{N} = \boldsymbol{C}C_5H_4CH\boldsymbol{N}Ph$ and $\boldsymbol{C}C_5H_4CH_2\boldsymbol{N}(2,4,6\text{-}Me_3C_6H_2)$ (**4** and **5**), and X = I with $\boldsymbol{C}–\boldsymbol{N} = \boldsymbol{C}C_5H_4CH_2\boldsymbol{N}(2,4,6\text{-}Me_3C_6H_2)$ (**6**) have been characterised as having different *fac*(Me/Me/SMe_2) to *mer*(Me/Me/SMe_2) geometrical disposition ratios. The isomeric *fac*(Me/Me/SMe_2) form is present at various percentages depending on the rigidity of the system, from a maximum of 100% for complexes **1** and **2** as proved from the X-ray crystal structure determination of both complexes and selective NOE experiments, to a minimum of 30% in the case of **3**. SMe_2 by PPh_3 substitution has been studied for these *fac* complexes where, in comparison to similar compounds with a *mer*(Me/Me/SMe_2) disposition, the strong *trans*-influence of the methyl group is avoided. The results indicate that there are more important effects than the simple *trans*-influence of the methyl ligand, the reactions are found to be much faster than their equivalent with complexes with *mer* geometries. In some of the cases, the final phosphine substituted products show the full isomerization to expected less hindered *mer*(Me/Me/PPh_3) geometry, while in others, a mixture of the *fac* and *mer* arrangements is found in the final reaction products. For the $2,4,6Me_3C_6H_2$-containing imines the isomerization takes place during substitution from a postulated pentacoordinated intermediate, for the remaining complexes the final reaction mixture is obtained in a process that takes place after substitution. For these two cases (products **3** and **4**), the presence of an intermediate with a *fac*(Me/Me/PPh_3) geometry, that further evolves to the final *mer* complex, has been characterised by low temperature NMR, and the isomerization reactions have been studied as a function of temperature and pressure. The results agree with a process involving a very energetically demanding turnstile twist type reorganization of the molecule, after a significant degree of dissociation of the ligands ($\Delta H^{\ddagger}$ = 109 and 100 kJ mol^{-1}; $\Delta S^{\ddagger}$ = 88 and 49 J K^{-1} mol^{-1}; $\Delta V^{\ddagger}$ = 14.9 and 20.0 cm^3 mol^{-1} for compounds **3** and **4** respectively).

Introduction

Substitution reactions on potentially inert Pt(IV) t_{2g}^6 octahedral complexes have always been a controversial subject.[1,2] The extreme inertness of some of these processes has been a difficult task to deal with, specially due to the easy availability of the Pt(II) catalysis that enhances the reaction rate and masks the proper reaction mechanism.[3–6] For organometallic Pt(IV), the early studies of substitution reactions on these type of complexes indicated an important dissociative lability that could be related to a dramatic *trans*-influence of the good σ-donor methyl group on the Pt(IV) centre.[7,8] Consequently, the substitution process seems to be directed by a dissociative activation process; even some pentacoordinated species have been detected and characterised.[9–11] The importance of this lability in reductive elimination and carbon–carbon bond formation reactions cannot be overstressed.[12]

We have been lately involved in the study of the substitution processes of cyclometallated dimethylhaloplatinum(IV) octahedral complexes.[13–15] In most cases a limiting dissociative activation process has been found to operate, with the existence of a pentacoordinated intermediate that is not too discriminating with respect to the entering ligand. Surprisingly, in one case, an associatively activated substitution path has been found, and has been related to an increased acidic character of the Pt(IV) centre.[14] Given the fact that all the previously studied $[Pt(Me)_2X(\boldsymbol{C}C_5H_5CH\boldsymbol{N}Bzl)(SMe_2)]$ complexes have a *trans*-methyl/leaving ligand geometrical arrangement (Scheme 1), which seems the responsible of the labilisation of the complex, we intended to study the same substitution reactions on complexes with an equivalent *cis*-arrangement.

We report in this paper the study of the SMe_2 by PPh_3 substitution reaction on six *cis*(Me/SMe_2) arranged cyclometallated dimethylhaloplatinum(IV) complexes (**1**, **2**, *fac*-**3**, *fac*-**4**, *fac*-**5**, and *fac*-**6**, Scheme 1). Lability and geometrical distribution of the ligands are dependent not only on the *trans*-influence of the methyl ligands, we have found that the overall steric and electronic characteristics to be crucial. The transient formation of not thermodynamically stable isomers of the phosphine substituted compounds[16] has also been established by low temperature proton and phosphorus NMR.

Results and discussion

Dimethylsulfide compounds

Complexes **1** and **2** were prepared by the method described in the literature for these type of compounds,[17,18] their ^{1}H NMR spectra (**1** and **2**) and elemental analysis (**1**) were used as a proof for their characterisation. On standing, their solutions produced crystals that were of good X-ray quality, and their

† Electronic supplementary information (ESI) available: k_{obs}, the ^{ax}Me signal intensity of **1**, the ^{1}H NMR spectrum of **3**, and the temperature evolution of ^{1}H NMR signals of SMe_2 in isomers of **5**. See http://www.rsc.org/suppdata/dt/b2/b209844j/

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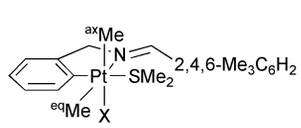
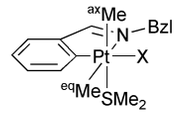
fac(Me/Me/SMe_2) *mer*(Me/Me/SMe_2)

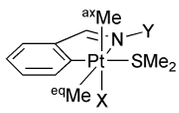


100% **1: X = Br**

100% **2, X = Cl**



100% [Pt(Me)$_2$X(***C***C_5H_5CH***N***Bzl)(SMe_2)]

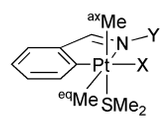


30% *fac***3: X = I, Y = Bzl**

34% *fac***4: X = Br, Y = Ph**

50% *fac***5: X = Br, Y = 2,4,6-$Me_3C_6H_2$**

75% *fac***6: X = I, Y = 2,4,6-$Me_3C_6H_2$**



70% *mer***3: X = I, Y = Bzl**

66% *mer***4: X = Br, Y = Ph**

50% *mer***5: X = Br, Y = 2,4,6-$Me_3C_6H_2$**

25% *mer***6: X = I, Y = 2,4,6-$Me_3C_6H_2$**

Scheme 1 Scheme of the complexes involved in this study. The different stereochemistries involved are indicated for the complexes where two isomers are present in the reaction medium.

structures were determined; Fig. 1 and Table 1 collect the relevant data for the structures. In both cases only a *fac*(Me/Me/SMe_2) geometrical arrangement is observed, as would be expected for the simple concerted oxidative ^{arm}C–X addition mechanism operating for the preparation of these complexes.[17,19] For the chloro derivative **2**, both optical isomers (derived from the concerted addition of the ^{arm}C–Cl bond onto the top or the bottom of the Pt(II) square-planar precursor centre) are crystallized. The *exo* nature of the cycle, or the presence of three methyl substituents on the non-metallated moiety of the molecule, cannot be the sole reason for the *fac*(Me/Me/SMe_2) geometrical arrangement found. For other *exo* or mesityl-containing complexes a *mer*(Me/Me/SMe_2) arrangement has been established by its structure determination, both *via* X-ray and selective NOE experiments.[13,14] Only the combination of both steric hindrance on the ligand, and the *exo* nature of the metallacycle seem to play the trick for the complete maintenance of the expected *fac*(Me/Me/SMe_2) arrangement. Probably the existence of the double bond in the non-metallated moiety of the imine ligand in the *Z* form adds up enough steric rigidity[20,21] to the system for the geometrical distribution found. The structures show a novel arrangement for these type of cyclometallated complexes, characterised by a general shortening of both Pt–^{ax}Me and Pt–^{eq}Me bonds (see Scheme 1) when compared with the values found for similar *mer*(Me/Me/SMe_2) complexes.[13] Surprisingly, despite the increase in the length of the Pt–halogen bond, as expected from the important *trans*-influence of the methyl ligand, the Pt–S bond distance does not suffer important variations, when compared with the known similar structures. As for the octahedral angles, the X–Pt–S decreases with respect to the *mer*(Me/Me/SMe_2) complexes, while the N–Pt–S increases, as expected from the hindrance of the molecule.

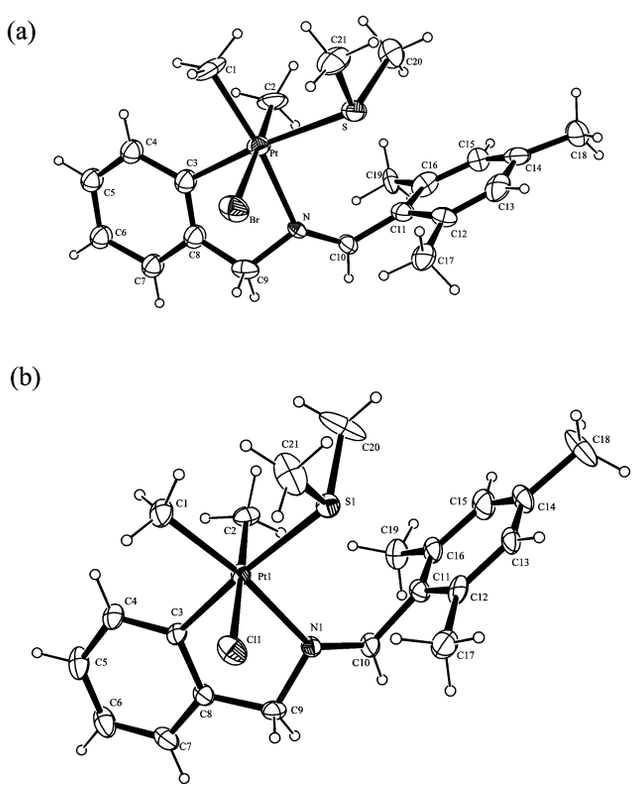


Fig. 1 View of the structures of complexes **1** (a) and **2** (b). Ellipsoids indicate 20% probability.

Selective 1D NOE experiments were carried out on the complexes in solution in order to establish the nature of the isomeric (*fac*/*mer*) form in solution.[14] Selective irradiation of anyone of the two platinum bound methyl group signals at 210 K (at which the inversion/rotation of the sulfide ligand is slow enough to resolve the two sulfur bound methyl signals), resulted in a NOE effect on the two SMe_2 signals for both complexes (**1** and **2**), confirming so that solely a *fac*(Me/Me/SMe_2) arrangement occurs in solution (see Scheme 1). In fact, the ^{ax}Me signal appears in the proton NMR spectra at a rather higher field than that found for the complexes in which a *mer*(Me/Me/SMe_2) structure has been established (see experimental part);[13,14] the change from X to SMe_2 as *trans* ligand to this methyl group seems to be the reason for this shift.[16] Some interaction must exist in the complex that produces such an important increase in the stability of this encumbered geometrical distribution. In this respect, the two SMe_2 proton NMR signals at low temperature for compound **1** (see above) appear at very different fields (1.12, 2.30 ppm in acetone at 210 K) when compared with the same signals for the *mer*(Me/Me/SMe_2) structures (1.94, 2.02 ppm and 1.89, 2.08 ppm for the

Table 1 Crystal data, and relevant bond angles (deg) and distances (Å) for the crystal structure of compounds **1** and **2**

Compound	**1**	**2**
Space group	$P2_1/n$	$P2_1/a$
Formula	$(C_{21}H_{30}BrNPtS)1/2(C_3H_6O)$	$C_{21}H_{30}ClNPtS$
a/Å	12.014(10)	16.15(2)
b/Å	10.321(10)	11.726(6)
c/Å	21.277(10)	23.075(18)
β/deg	92.256(1)	94.16(8)
V/Å^3	2636.23	4359
Fw	632.56	559.06
Z	4	8
μ/cm^{-1}	6.926	6.660
N	4664	8307
N_o (F_o>2σ)	2527	6406
$R(F_o)$, $wR_2(F_o^2)$ ($I > 2\sigma(I)$)	0.0676, 0.1865	0.0442, 0.0940
Goodness of fit	1.033	0.942
Pt(1)–C(1)	2.044(11)	1.992(8)
Pt(1)–C(2)	1.939(15)	2.005(8)
Pt(1)–C(3)	2.131(13)	2.009(8)
Pt(1)–N(1)	2.206(9)	2.150(6)
Pt(1)–S(1)	2.482(3)	2.453(3)
Pt(1)–X(1)	2.5915(13)	2.425(3)
C(2)–Pt(1)–C(1)	84.6(7)	87.4(4)
C(2)–Pt(1)–C(3)	83.3(6)	88.1(3)
C(1)–Pt(1)–C(3)	93.8(6)	91.6(3)
C(2)–Pt(1)–N(1)	94.6(6)	92.8(3)
C(1)–Pt(1)–N(1)	171.8(5)	171.3(3)
C(3)–Pt(1)–N(1)	78.0(4)	79.7(3)
C(2)–Pt(1)–S(1)	97.5(5)	95.5(3)
C(1)–Pt(1)–S(1)	91.3(4)	91.3(3)
C(3)–Pt(1)–S(1)	174.9(3)	175.4(2)
N(1)–Pt(1)–S(1)	96.9(2)	97.28(18)
C(2)–Pt(1)–X(1)	177.7(5)	179.2(2)
C(1)–Pt(1)–X(1)	93.4(5)	91.8(3)
C(3)–Pt(1)–X(1)	95.9(3)	92.0(2)
N(1)–Pt(1)–X(1)	87.3(2)	88.02(18)
S(1)–Pt(1)–X(1)	83.48(8)	84.36(10)

analogous *mer*(Me/Me/SMe_2) complexes [$PtBr(Me)_2$(***C***C_5H_4–CH_2–***N***=CH–Ph)(SMe_2)] and [$PtBr(Me)_2$(***C***C_5H_4–CH=*N*–CH_2-(2,4,6-$Me_3C_6H_2$)(SMe_2)], respectively, at 210 K),[13] indicating somehow the rigidity of the system even in solution.

Further information about the rigidity of the molecule can be extracted from the rate of the inversion/exchange process of the methyl groups at the sulfide ligand, as seen in Fig. 2.

The coalescence of the two sulfur-bound methyl group signals at *ca.* 250 K, is indicative of one of the slowest processes of this type found in the literature, ^{298}k = 34000 s^{-1}.[22] Thermal activation enthalpies and entropies are not available for many of such reactions,[23] but in our case the determined value of the activation enthalpy, 56 ± 2 kJ mol^{-1}, is relatively large and the entropy of activation, 27 ± 7 J K^{-1} mol^{-1}, is definitively positive indicating a certain degree of dissociativeness in the process. This is in line with the expected, according to the transition state suggested in the literature,[24] where the SMe_2 inverts without having to go to a planar geometry, a further rotation produces the final exchange of the two methyl groups.[25] In our case, the activation parameters indicate a certain extend of dissociation of the sulfide ligand, as proved necessary for similar systems[26] (or even for isomerization reactions of nitrito to

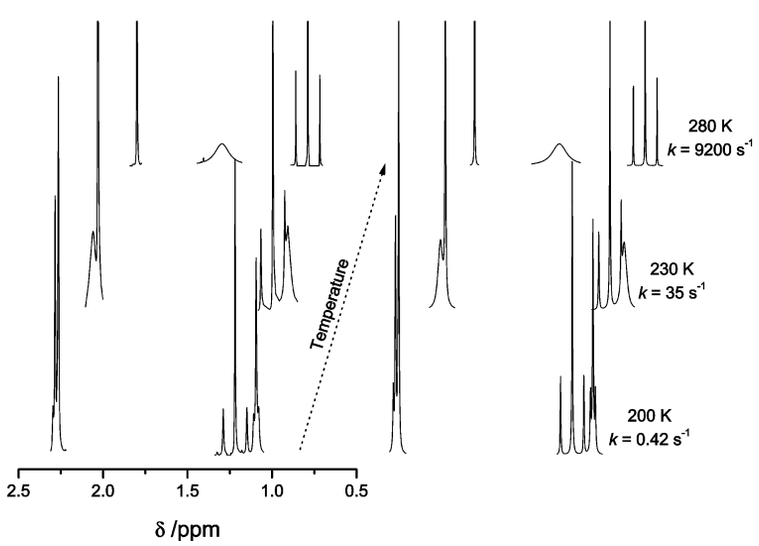


Fig. 2 Changes of the proton NMR spectra of the two temperature resolved sulfide methyl signals of compound **1** with temperature (left), and their gNMR fitted exchange spectrum (right). [**1**] = 2 × 10^{-3} M; 500 MHz; acetone-d_6.

nitro complexes where a parallelism exist between dissociative activated substitutions and isomerization processes),[27] given the fact that no available empty coordination positions exist.

Being steric rigidity parallel to the preference of the extremely encumbered arrangement observed for complexes **1** and **2**, oxidative addition of MeI to the Pt(II) complex [Pt(Me)(***C***C_5H_4–CH=***N***–CH_2–Ph)(SMe_2)],[28] was carried out in order to obtain product **3**. The new complex prepared, **3** (Scheme 1), although with a high tendency to form halogen bridged dimeric forms,[13,29] can be easily kept in solutions containing free SMe_2 as a 1 : 2.5 mixture of isomers. The two pairs of methyl signals of equal intensity (0.61 and 1.29 ppm and 1.15 and 1.45 ppm, respectively) and the relative high field of the signal at 0.61 ppm, are a clear indicative of the presence of a *fac*(Me/Me/SMe_2) isomer as the minor compound in the mixture. Low temperature 1D NOE experiments, as those mentioned above,[14] effectively indicated that the two isomers exist in solution. In the same line, preparation of compounds **4**, **5** and **6** (Scheme 1) has also been achieved. While bromo and iodo complexes, **5** and **6**, have been prepared *via* oxidative addition of MeBr or MeI to the corresponding Pt(II) derivative, [Pt(Me)(***C***C_5H_4–CH=***N***-(2,4,6-$Me_3C_6H_2$)(SMe_2)], complex **4** has been prepared *via* oxidative addition of the corresponding imine, (2-BrC_6H_4)–CH=N–Ph, to the [{Pt(Me)$_2$(μ-SMe_2)}$_2$] dimer. For all these complexes a mixture of *fac*(Me/Me/SMe_2) and *mer*(Me/Me/SMe_2) geometrical arrangements is found in the final reaction mixture, the assignment of the definite geometries has been done by using the ^{1}H NMR signal appearing at higher field as a spectroscopic handle (see above and experimental part). The varying proportions of the two isomers in the equilibrated reaction medium can be easily related both with the hindrance of the imine substituent and with the nature of the halo ligand. That is, while for compound **3** the *fac*/*mer* ratio is 0.3, the value is 0.4, 1.0 and 1.3 for compounds **4**, **5** and **6**, respectively, at room temperature. It is important to note that for all these complexes the dimeric (μ-X)$_2$ forms, with no SMe_2 ligands, are formed on intensive workup, and that solution of these insoluble forms in acetone, containing dimethylsulfide, produced in all cases the same initial thermodynamically equilibrated isomeric ratios.

The hindrance introduced for the bromo derivatives on going from the previously described Bzl compound,[30] to the one having a Ph substituent (**4**) on the cyclometallated imine ligand, produces the disappearance of a 34% of the *mer* isomer. Moving to an even more hindered 2,4,6-$Me_3C_6H_2$ substituent (**5**) has the effect of a 50% disappearance. For the studied iodo complexes the effect introduced by the iminic substituent is the same, from a 70% of *mer* isomer for compound **3**, to a 25% in the case of the 2,4,6-$Me_3C_6H_2$ substituent (compound **6**). It is very clear that extremely fine steric and electronic tuning characteristics have to be present in these systems. In this respect, the position of the SMe_2 signal in the proton NMR spectrum for the *fac* isomers appears at lower fields (2.21 and 2.14 ppm *versus* 2.03 and 2.03 ppm for the *fac*(Me/Me/SMe_2) and *mer*(Me/Me/SMe_2) isomers of **3** and **4**, respectively), which seems to indicate a certain degree of interaction with the dangling phenyl ring of the imine ligand. This effect has not been observed for the systems for which the X ligand changes from Br to F,[13,14] indicating that the effect is not related with the electronegativity of the halogen ligand. This type of non-bonding interactions between the sulfide ligand and the rest of the cyclometallated molecule, have already been kinetically established on similar complexes.[14]

Dimethylsulfide lability

Previous studies of SMe_2 substitution by different phosphines on this type of complexes have indicated a high lability of the ligand.[13–15] Given the fact that the appearance of an empty coordination position in the octahedral complex has been found the key step for reductive elimination of these complexes, producing new carbon–carbon bonds, the relative lability of the SMe_2 ligand on the *fac* and *mer* geometries has been tried. For the isomerically pure complex **1**, the substitution reaction has been found too fast and with too little changes in the electronic spectrum to be followed by UV-Vis spectroscopy. Consequently, the approximate rate of exchange of SMe_2 was measured instead by full line-shape analysis of the ^{1}H NMR spectra at different temperatures. Fig. 3 shows the analysis carried out with the gNMR software[31] for the methyl signals of free and coordinated dimethylsulfide. No activation parameters could be derived from the exchange with free SMe_2, given the very narrow range of temperatures (less than 10 °C) where neither the exchange of the two coordinated methyl groups interfere with the process, nor the concentration of free SMe_2 are reliable (due to solvent and/or ligand evaporation). The approximate value found for the $^{298}k_{ex}$ rate constant, 29, is of *ca.* 2–3 orders of magnitude larger than that found for complexes having a *mer*(Me/Me/SMe_2) geometry. This fact does not agree with a larger *trans*-influence of the methyl ligand, when compared with the cyclometallated[1,2,14] or non-cyclometallated[15] phenyl ligand. The SMe_2 ligand can be found in the *fac*(Me/Me/SMe_2) form as the most stable position in complexes **1** and **2**, but the rate at which it leaves the Pt(IV) is by far the largest.

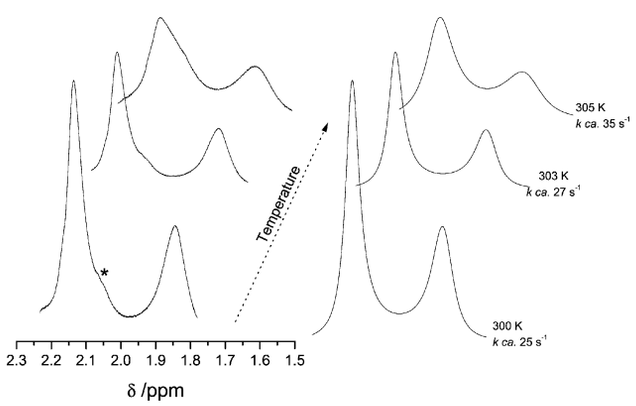
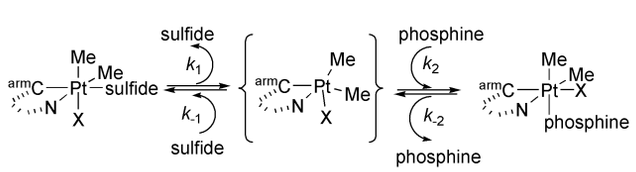


Fig. 3 Changes of the proton NMR spectra of the free (2.14 ppm) and coordinated (1.84 ppm) unresolved SMe_2 methyl signals with temperature for compound **1** (left), and their gNMR fitted exchange spectrum (right). [**1**] = 2 × 10^{-3} M; [SMe_2] = 3 × 10^{-3} M; 250 MHz; chloroform-d_1; * indicates solvent impurities.

Low temperature (250–270 K) recording of the time evolution of spectra at different [PPh_3]/[SMe_2] ratios indicated that the substitution reaction rate, effectively, depends on this concentration ratio (Fig. S1 †), and that no intermediate species are formed during the process. The results agree perfectly with the already established reaction mechanism and rate law[32,33] found for these complexes [eqn. (1)] where the limiting rate constant, k_1, corresponds to the rate of exchange of the SMe_2 ligand.



$$k_{obs} = \frac{k_{-1}k_{-2}[\text{sulfide}] + k_1k_2[\text{phosphine}]}{k_{-1}[\text{sulfide}] + k_2[\text{phosphine}]} \quad (1)$$

In the same way, the two proton SMe_2 signals of the mixtures of isomers for compounds **3** and **5** were studied with respect to their dynamic behaviour. These signals show interesting differences depending on the isomer to which they are associated.

Although at room temperature for compound **3** the signal at 2.03 ppm, associated to the *mer* isomer, appears narrow and clearly coupled with ^{195}Pt, the corresponding *fac* signal, at 2.21 ppm, is much wider (Fig. S2 †) indicating a relatively (to the *mer* isomer) fast SMe_2 exchange. The same applies to the mixture of isomers of **5**, although in this case the spectrum is further complicated by the presence of the methyl signals of the 2,4,6-$Me_3C_6H_2$ group. For both systems the two signals are too close, and the spectra are too complex, for a correct estimation of the value of k_{ex} using the above mentioned full line-shape spectrum analysis. Nevertheless, Fig. S3 † shows the temperature evolution of the signals associated to the two SMe_2 groups present in solution for compound **5**; it is clear that the SMe_2 group corresponding to the *fac* isomer is much more labile, and that, at room temperature, its exchange with free SMe_2 is fast relative to that of the *mer* isomer; at only 50 °C a relative widening of the signal associated to the *mer* isomer is observed. This is again surprising, as for compound **1**, given the lack of the strong *trans*-influence of the methyl group on the SMe_2 ligand in a dissociative substitution mechanism.

Taking these facts into account, the substitution processes of complexes **3**, **4**, **5** and **6** are much more complex than expected, given the above mentioned important differences in lability of the dimethylsulfide ligand of the two isomers present in solution. While for complexes **3** and **4** the final reaction mixture is isomerically pure, for compounds **5** and **6** the final reaction products correspond to a mixture of two isomers that do not held the same isomeric ratio that the unsubstituted complexes. For all the systems it seems clear, from the NMR data that the only measurable substitution process corresponds to that occurring on the *mer*(Me/Me/SMe_2) isomer. The general substitution process was found, again, to follow the reaction rate law indicated by eqn. (1), as expected. Consequently the value of the SMe_2 dissociation can be calculated from the data; Table 2 collects the relevant kinetic and thermal activation parameters derived for the substitution processes of complexes *mer*-**3**, *mer*-**4** and *mer*-**5**.

The kinetic parameters for *mer*-**3** are larger than those known for the same compounds with fluoro, chloro or bromo ligands, while the derived thermal activation parameters produce enthalpies and entropies of activation that are in the same margin. The trend observed for the series ligands is maintained;[13,14] the process is accelerated on the increase of the size and the decrease of electronegativity of the halogen ligand. Comparison of the kinetic parameters for the *mer*-**4** and *mer*-**5** substitution processes, shows the expected trend derived from the increased encumbrance on the *mer*-**5** complex, which produces a much easier dissociation of the leaving SMe_2 ligand. The values of the thermal activation parameters for these substitution processes indicate that they must have a less dissociative character as derived from the value of $\Delta S^{\ddagger}$. This can be related both to a certain degree of interaction of the leaving dimethylsulfide with the rest of the molecule, as already been found in other systems with high electronegativity,[14] or to an ordering of the pentacoordinated intermediate, induced by the steric relief produced on dissociation of the sulfide ligand in such hindered systems.

Table 2 Kinetic (extrapolated at 298 K) and thermal activation parameters in acetone solution for the dissociation reaction of SMe_2 on complexes **1**, **3**, **4** and **5**

Compound	^{298}k/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1	29[a]	not determined	not determined
mer-**3**	0.66	90 ± 3	71 ± 10
mer-**4**	0.084	76 ± 6	−2 ± 19
mer-**5**	1.6	80 ± 2	26 ± 7

[a] Corresponds to the value of k_{ex} measured by NMR experiments.

Triphenylphosphine compounds

Given the complicated isomeric mixture of the starting material and substituted products, further investigation of the substitution reaction mixtures was carried out. Preparative procedures of the PPh_3 derivatives for the set of these four compounds produced important differences; while for complexes **1**, **3** and **4**, the only isolated compound is the *mer*(Me/Me/PPh_3) isomer (determined by the important decrease of the ^{ax}Me–Pt coupling constant),[18] in the case of complexes **5** and **6**, although with a larger relative amount of the *mer*(Me/Me/PPh_3) arranged isomer, both isomers of the phosphine derivative are present in the final reaction mixture. No further conversion to the major *mer*(Me/Me/PPh_3) compound is observed during days, as detected in other complexes.[16] In consequence ^{1}H and ^{31}P NMR experiments were carried out on reaction mixtures just after addition of the PPh_3 ligand. While for complexes **1**, **5** and **6** the phosphine derivative immediately produced already has the final isomeric composition (100% of *mer*(Me/Me/PPh_3) for **1**, 88% for **5**, and 66% for **6**), for compounds **3** and **4** the initial substitution products have the same isomeric composition as the starting material (75% of *mer*(Me/Me/PPh_3) for **3**, 71% for **4**), on standing these isomeric mixtures slowly evolve to the final 100% of *mer*(Me/Me/PPh_3) for both complexes.

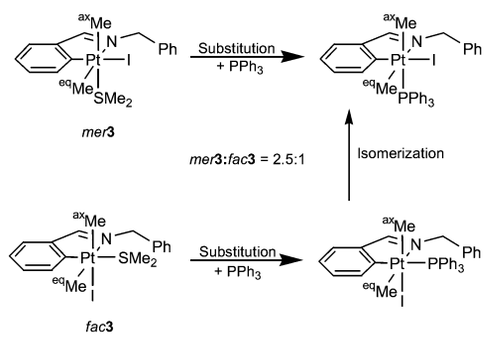
The results agree very well with the 2D NOESY experiments carried on the complexes **1**, **3** and **5**. These experiments indicated that, while for compounds **1**, *mer*-**3**, and the *fac*-**5**/*mer*-**5** mixture there is an exchange process of the two platinum-bound methyl groups during the experiment mixing time, for the *fac*-**3** complex this exchange is much slower, and no cross-peaks are found under the same conditions. That is, while the *fac*-**3** complex maintains its structure on dissociation of the SMe_2 ligand, allowing the coordination of the phosphine ligand in the same facial position, for compounds **1**, *mer*-**3**, and the *fac*-**5**/*mer*-**5** mixture dissociation of the dimethylsulfide ligand produces a turnstile twist of the Me/Me/X ligands in the pentacoordinated intermediate and the phosphine ligand coordinates only in the thermodynamically most stable position, which implies isomerization for compounds **1**, the *fac*-**5**/*mer*-**5** mixture, while retention for compound *mer*-**3**. At 270 K and in chloroform solution, the phosphorus spectra recorded for **3** and **4** just after mixing indicated the presence of two types of platinum-bound phosphines [−7.70 ppm (J_{PPt} = 1026 Hz) and −3.87 ppm (J_{PPt} = 1221 Hz) for **3**; 0.47 ppm (J_{PPt} = 1245 Hz) and 1.09 ppm (J_{PPt} = 1035 Hz) for **4**]. The maintenance of the same isomeric composition than the starting material (see above), indicated that the substitution on the two isomers takes place separately, and that are followed by a slow isomerization process, as indicated in Scheme 2 in the case of compound **3**.

These processes for complexes **3** and **4** were so related with further small and slow electronic spectral changes occurring after the substitution reactions indicated above. The reactions rates were found independent on the concentrations of entering (SMe_2) and leaving ligand (PPh_3) and the dependence of these on the temperature and pressure were studied. Table 3 collects the kinetic and activation parameters determined for this intramolecular isomerization process.

These parameters are the first ones measured for this type of reaction on these complexes. The data collected in Table 3 indicates that the process is highly enthalpic and has an extremely significant degree of dissociativeness, as found from the very positive values of the activation volumes and entropies. Taking into account the definitive intramolecular character of this isomerization process (as proved by the independence of the rate constants on the concentrations of the entering and leaving ligands), it might imply a turnstile twist type reorganization of the molecule, after a significant degree of dissociation

Table 3 Kinetic (extrapolated at 298 K) and thermal activation parameters in acetone solution for the intramolecular isomerization processes involved in the substitution reaction of SMe_2 by PPh_3 on complexes **3** and **4**

Compound	$^{298}k/s^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}
3	0.024	109 ± 3	88 ± 10	14.9 ± 0.3 (303 K)
4	0.0081	100 ± 2	49 ± 8	20.0 ± 0.4 (293 K)



*mer***3**; ^{ax}Me, 1.49 ppm (J_{PtH}= 70.3 Hz);
^{eq}Me, 1.28 ppm (J_{PtH}= 69.2 Hz)

Substituted *mer***3**; ^{ax}Me, 1.21 ppm (J_{PtH}= 59.6 Hz, J_{PH}= 7.5 Hz);
^{eq}Me, 1.58 ppm (J_{PtH}= 69.6 Hz, J_{PH}= 7.6 Hz);
P, -7.70 ppm (J_{PtP}= 1026 Hz)

*fac***3**; ^{ax}Me, 0.65 ppm (J_{PtH}= 70.2 Hz);
^{eq}Me, 1.32 ppm (J_{PtH}= 70.3 Hz)

Substituted *fac***3**; ^{ax}Me, 0.28 ppm (J_{PtH}= 68.8 Hz, J_{PH}= 7.1 Hz);
^{eq}Me, 1.38 ppm (J_{PH}= 7.0 Hz);
P, -3.87 ppm (J_{PtP}= 1221 Hz)

Scheme 2 Scheme of the substitution/isomerization process studied occurring on complex **3**; indicated NMR data are at 270 K.

of the ligands. In this respect, the values of the activation volume indicated in Table 3 are a good indicative of the larger expansion expected for compound **4**, due to the proximity of the bulky and rigid Ph substituent on the nitrogen, in order to allow for the turnstile twist reorganization of the complex. As a whole, the process has to be very energetically demanding, given the high degree of rigidity existing in the system with a *fac*(Me/Me/PPh_3) geometry.

Concluding, the substitution processes of the complexes of the type indicated in Scheme 1, show a much more complicated behaviour than the simple *trans*-influence from the methyl ligands in a dissociative process. For complexes where the *trans* ligand has been changed to a phenyl ring, having a less significant *trans*-influence, the process is even faster. High electronic stabilization of the ground state due to an intramolecular SMe_2 interaction with the dangling phenyl ring of the imine ligand has to be held responsible for these facts, as proved by the displacement of the SMe_2 ligand signals in the proton NMR spectrum to lower fields. In this respect, when the sulfide is substituted by a PPh_3 ligand, the complexes isomerize to a *mer*(Me/Me/PPh_3) distribution to an extend that depends on the nature of the non-metallated imine moiety. For the 2,4,6-$Me_3C_6H_2$-containing imines the isomerization takes place during substitution from the pentacoordinated intermediate postulated in eqn. (1), producing the more stable isomer distribution in the final reaction mixture. For the remaining complexes the final reaction mixture is obtained in a process that takes place after substitution and in a reaction activated by a significant degree of dissociation of the ligands. In these cases, the rigidity of one of the two isomeric pentacoordinated intermediates has to be held responsible for the initial maintenance of the stereochemistry.

Experimental

Instruments

NMR spectra were recorded with a Bruker 250 DRX (^{1}H, ^{31}P, ^{195}Pt), Bruker DMX 500 (2D NOESY, selective 1D NOE, SIR experiments) and Bruker Advance 600 (selective 1D NOE) spectrometers. Chemical shifts (in ppm) were measured relative to $SiMe_4$ for ^{1}H, to 85% H_3PO_4 for ^{31}P and to $H_2[PtCl_6]$ for ^{195}Pt spectra; the solvents used were acetone(d_6) or chloroform(d_1). All spectra were obtained in the Unitat de RMN d'Alt Camp de la Universitat de Barcelona at room temperature unless stated.

Products

The dimethylsulfide platinum(IV) complexes **1**, **2** and **4** used in this study, were prepared according to the well established literature methods [18,28] from the corresponding imines, (2-XC_6H_4)CH_2NCH(2,4,6-$Me_3C_6H_2$) (X = Br for **1**, Cl for **2**), prepared from the condensation of the corresponding amines and mesitylaldehyde, or (2-BrC_6H_4)CHNPh for **4**, prepared from the condensation of aniline and the 2-bromobenzaldehyde, and the [{Pt(Me)$_2$(μ-SMe_2)}$_2$] dimer.[34] The ^{1}H NMR spectra of [Pt(Me)$_2$Cl{***C***$C_5H_4CH_2$***N***CH(2,4,6-$Me_3C_6H_2$)}(SMe_2)], **2**, was used for characterisation of the already prepared complex.[18]

Complex **1**, [PtBr(Me)$_2${***C***$C_5H_4CH_2$***N***CH(2,4,6-$Me_3C_6H_2$)}-(SMe_2)], has been prepared for the first time in a 59% yield, and its ^{1}H NMR spectra and elemental analysis agreed with the values expected. Anal. (%) calcd. (found) for $C_{21}H_{30}BrNPtS$: C, 42.0 (41.8); H, 5.0 (5.0); N, 2.4 (2.3). ^{1}H NMR (250 MHz, CD_3COCD_3); δ (ppm) = 0.70 (3H, ^{ax}Me, J_{HPt} = 74.0 Hz), 1.30 (3H, ^{eq}Me, J_{HPt} = 71.0 Hz), 1.82 (6H, SMe_2, J_{HPt} = 12 Hz), 5.03, 5.90 (2H, CH_2N, J_{HH} = 15 Hz), 9.38 (1H, CHN, J_{HPt} = 30 Hz). ^{195}Pt NMR (53.5 MHz, CD_3COCD_3): δ (ppm) = −2037. Its triphenylphosphine substituted derivative [PtBr(Me)$_2${***C***C_5H_4-CH_2***N***CH(2,4,6-$Me_3C_6H_2$)}(PPh_3)] was prepared *via* reaction of the dimethylsulfide starting material with the stoichiometric amount of PPh_3 in acetone solution with ocasional nitrogen stirring to favour the SMe_2 evolution. After 24 hours the solution was taken to dryness and the product was washed with hexane, analysed, and its NMR spectra collected. Yield 78%. Anal. (%) calcd. (found) for $C_{39}H_{45}BrNPPt$: C, 55.3 (55.2); H, 4.9 (5.0); N, 1.7 (1.8); ^{1}H NMR (250 MHz, CD_3COCD_3): δ (ppm) = 1.14 (3H, ^{ax}Me, J_{HPt} = 65.0 Hz, J_{HP} = 7.6 Hz), 1.26 (3H, ^{eq}Me, J_{HPt} = 74.0 Hz, J_{HP} = 9.2 Hz), 4.68, 4.88 (2H, CH_2N, J_{HH} = 14 Hz), 9.34 (1H, CHN, J_{HPt} = 31 Hz). ^{31}P NMR (101.25 MHz, CD_3COCD_3): δ (ppm) = 2.22 (J_{PPt} = 827 Hz).

Compound **3** has been prepared *via* the well established process of oxidative addition of MeI to the known [PtMe(***C***C_5-H_4CH***N***CH_2Ph)(SMe_2)] platinum(II) complex. The complex obtained after taking the solution to dryness, is insoluble in acetone or chloroform, but slowly dissolves in SMe_2 solution. ^{1}H NMR of this solution indicated the existence of two isomers in a 1 : 3 ratio; ^{1}H NMR (250 MHz, CD_3COCD_3): minor (*fac* isomer), δ (ppm) = 0.61 (3H, ^{ax}Me, J_{HPt} = 70.3 Hz), 1.29 (3H, ^{eq}Me, J_{HPt} = 68.9 Hz), 2.21 (6H, SMe_2, J_{HPt} = 11.3 Hz), 5.37 (2H, CH_2N), 8.60 (1H, CHN, J_{HPt} = 44.3 Hz; major (*mer* isomer), δ (ppm) = 1.15 (3H, ^{ax}Me, J_{HPt} = 71.3 Hz), 1.45 (3H, ^{eq}Me, J_{HPt} = 69.6 Hz), 2.03 (6H, SMe_2, J_{HPt} = 14.0 Hz), 5.72, 5.46 (2H, CH_2N, J_{HH} = 14.5), 8.64 (1H, CHN, J_{HPt} = 45.6 Hz. ^{195}Pt NMR (53.5 MHz, CD_3COCD_3): minor (*fac* isomer), δ (ppm) = −3103; major (*mer* isomer), δ (ppm) = −3001. From these solutions the

final *fac*/*mer* mixture can be precipitated by addition of hexane. Anal. (%) calcd. (found) for $C_{18}H_{24}INPtS$: C, 35.5 (35.4); H, 4.0 (3.9); N, 2.3 (2.4). Its triphenylphosphine substituted derivative $[Pt(Me)_2I(\boldsymbol{C}C_5H_4CH\boldsymbol{N}CH_2Ph)(PPh_3)]$ was prepared *in situ via* reaction of the starting material with the stoichiometric amount of PPh_3 in acetone solution. The product was characterised in solution by its ^1H and ^{31}P NMR spectra. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.24 (3H, ^{ax}Me, J_{HPt} = 59.8 Hz, J_{HP} = 7.5 Hz), 1.61 (3H, ^{eq}Me, J_{HPt} = 70.3 Hz, J_{HP} = 7.6 Hz), 4.66, 5.55 (2H, CH_2N, J_{HH} = 17.5 Hz), 7.68 (1H, CHN, J_{HPt} = 46.9 Hz). ^{31}P NMR (101.25 MHz, $CDCl_3$): δ (ppm) = −7.82 (J_{PPt} = 1009 Hz).

Complex **4**, $[PtBr(Me)_2(\boldsymbol{C}C_5H_4CH\boldsymbol{N}Ph)(SMe_2)]$, has been prepared for the first time in a 35% yield as its dimeric form $[\{Pt(Me)_2(\boldsymbol{C}C_5H_4CH\boldsymbol{N}Ph)(\mu\text{-}Br)\}_2]$. The insoluble dimer is made soluble by treatment in acetone or chloroform solutions of SMe_2. The ^1H NMR spectra of these solutions agreed with the values expected for a mixture of two isomers in a 1 : 2.5 ratio. Anal. (%) calcd. (found) for $C_{15}H_{16}BrNPt$: C, 37.1 (37.2); H, 3.3 (3.2); N, 2.9 (2.6). ^1H NMR (200 MHz, $CDCl_3$): minor (*fac* isomer), δ (ppm) = 0.80 (3H, ^{ax}Me, J_{HPt} = 70.6 Hz), 1.45 (3H, ^{eq}Me, J_{HPt} = 68.8 Hz), 2.14 (6H, SMe_2, J_{HPt} = 14.0 Hz), 8.39 (1H, CHN, J_{HPt} = 41.0 Hz; major (*mer* isomer), δ (ppm) = 1.29 (3H, ^{ax}Me, J_{HPt} = 69.6 Hz), 1.54 (3H, ^{eq}Me, J_{HPt} = 70.6 Hz), 2.03 (6H, SMe_2, J_{HPt} = 12.8 Hz), 8.51 (1H, CHN, J_{HPt} = 39.6 Hz). Its triphenylphosphine substituted derivative $[PtBr(Me)_2(\boldsymbol{C}C_5H_4CH\boldsymbol{N}Ph)(PPh_3)]$ was prepared *in situ via* reaction of the starting dimethylsulfide material with the stoichiometric amount of PPh_3 in acetone solution. The product was characterised in solution by its ^1H and ^{31}P NMR . ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.37 (3H, ^{ax}Me, J_{HPt} = 58.6 Hz, J_{HP} = 7.5 Hz), 1.61 (3H, ^{eq}Me, J_{HPt} = 72.2 Hz, J_{HP} = 8.0 Hz), 8.07 (1H, CHN, J_{HPt} = 40.6 Hz). ^{31}P NMR (101.25 MHz, $CDCl_3$): δ (ppm) = 0.80 (J_{PPt} = 1023 Hz).

Complex **5**, $[PtBr(Me)_2\{\boldsymbol{C}C_5H_4CH\boldsymbol{N}(2,4,6\text{-}Me_3C_6H_2)\}(SMe_2)]$, has been prepared for the first time *via* oxidative addition of MeBr to the new $[PtMe\{\boldsymbol{C}C_5H_4CH\boldsymbol{N}(2,4,6\text{-}Me_3C_6H_2)\}(SMe_2)]$ platinum(II) (prepared *via* the standard oxidative addition of the $PhCHN(2,4,6\text{-}Me_3C_6H_2)$ imine on the $[\{Pt(Me)_2(\mu\text{-}SMe_2)\}_2]$ dimer) complex in a 43% yield, as its dimeric form $[\{Pt(Me)_2\{\boldsymbol{C}C_5H_4CH\boldsymbol{N}(2,4,6\text{-}Me_3C_6H_2)\}(\mu\text{-}Br)\}_2]$ as for compound **4**. The insoluble dimer is made soluble by treatment in acetone or chloroform solutions of SMe_2. Its ^1H NMR spectra agreed with the values expected for a mixture of two isomers in a 1 : 1 ratio. From these solutions the final *fac*/*mer* mixture can be precipitated by addition of hexane. Anal. (%) calcd. (found) for $C_{20}H_{28}BrNPtS$: C, 40.8 (40.6); H, 4.8 (4.9); N, 2.4 (2.3). ^1H NMR (200 MHz, $CDCl_3$): *mer* isomer, δ (ppm) = 1.32 (3H, ^{ax}Me, J_{HPt} = 69.6 Hz), 1.49 (3H, ^{eq}Me, J_{HPt} = 69.6 Hz), 8.32 (1H, CHN, J_{HPt} = 40.0 Hz); *fac* isomer, δ (ppm) = 0.94 (3H, ^{ax}Me, J_{HPt} = 70.4 Hz), 1.54 (3H, ^{eq}Me, J_{HPt} = 68.8 Hz), 8.30 (1H, CHN, J_{HPt} = 41.0 Hz). Its triphenylphosphine substituted derivative $[PtBr(Me)_2\{\boldsymbol{C}C_5H_4CH\boldsymbol{N}(2,4,6\text{-}Me_3C_6H_2)\}(SMe_2)]$ was prepared *in situ via* reaction of the starting dimethylsulfide material with the stoichiometric amount of PPh_3 in acetone solution. The product was characterised in solution by its ^1H and ^{31}P NMR spectra, as a mixture of isomers in a 1 : 7.5 ratio. ^1H NMR (250 MHz, CD_3COCD_3): major (*mer* isomer), δ (ppm) = 1.35 (3H, ^{ax}Me, J_{HPt} = 58.7 Hz, J_{HP} = 7.6 Hz), 1.40 (3H, ^{eq}Me, J_{HPt} = 72.0 Hz, J_{HP} = 8.6 Hz), 8.32 (1H, CHN, J_{HPt} = 41.5 Hz); minor (*fac* isomer), δ (ppm) = 0.57 (3H, ^{ax}Me, J_{HPt} = 68.6 Hz, J_{HP} = 6.7 Hz), 1.59 (3H, ^{eq}Me, J_{HPt} = 71.3 Hz, J_{HP} = 7.3 Hz), 8.47 (1H, CHN, J_{HPt} = 42.3 Hz). ^{31}P NMR (101.25 MHz, CD_3COCD_3): major (*mer* isomer), δ (ppm) = 2.09 (J_{PPt} = 998 Hz); minor (*fac* isomer), δ (ppm) = −1.05 (J_{PPt} = 1241 Hz).

Compound **6** has been prepared, as compound **3**, from the new $[PtMe\{\boldsymbol{C}C_5H_4CH\boldsymbol{N}(2,4,6\text{-}Me_3C_6H_2)\}(SMe_2)]$ platinum(II) complex in a 32% yield, as its dimeric form $[\{Pt(Me)_2(\boldsymbol{C}C_5H_4CH\boldsymbol{N}(2,4,6\text{-}Me_3C_6H_2))(\mu\text{-}I)\}_2]$. The insoluble dimer is made soluble by treatment in acetone or chloroform solutions of SMe_2. Its ^1H NMR spectra agreed with the values expected for a mixture of two isomers in a 1 : 1.3 ratio. Anal. (%) calcd. (found) for $C_{18}H_{22}INPt$: C, 37.6 (37.6); H, 3.9 (3.9); N, 2.4 (2.3). ^1H NMR (250 MHz, $CDCl_3$): minor (*mer* isomer), δ (ppm) = 1.50 (3H, ^{ax}Me, J_{HPt} = 70.5 Hz), 1.64 (3H, ^{eq}Me, J_{HPt} = 71.5 Hz), 8.36 (1H, CHN, J_{HPt} = 39.53 Hz); major (*fac* isomer), δ (ppm) = 1.09 (3H, ^{ax}Me, J_{HPt} = 68.3 Hz), 1.69 (3H, ^{eq}Me, J_{HPt} = 69.5 Hz), 8.29 (1H, CHN, J_{HPt} = 42.5 Hz). Its triphenylphosphine substituted derivative $[Pt(Me)_2I\{\boldsymbol{C}C_5H_4CH\boldsymbol{N}(2,4,6\text{-}Me_3C_6H_2)\}(PPh_3)]$ was prepared *in situ via* reaction of the starting material with the stoichiometric amount of PPh_3 in acetone solution. The product was characterised in solution by its ^1H and ^{31}P NMR spectra, as a mixture of isomers in a 1 : 2 ratio. ^1H NMR (250 MHz, CD_3COCD_3): major (*mer* isomer), δ (ppm) = 1.47 (3H, ^{ax}Me, J_{HPt} = 55.1 Hz, J_{HP} = 8.6 Hz), 1.53 (3H, ^{eq}Me, J_{HPt} = 59.5 Hz, J_{HP} = 7.3 Hz), 8.33 (1H, CHN, J_{HPt} = 40.8 Hz); minor (*fac* isomer), δ (ppm) = 0.83 (3H, ^{ax}Me, J_{HPt} = 67.0 Hz, J_{HP} = 6.5 Hz), 1.68 (3H, ^{eq}Me, J_{HPt} = 71.8 Hz, J_{HP} = 7.3 Hz), 8.43 (1H, CHN, J_{HPt} = 41.3 Hz). ^{31}P NMR (101.25 MHz, CD_3COCD_3): major (*mer* isomer), δ (ppm) = −2.59 (J_{PPt} = 990 Hz); minor (*fac* isomer), δ (ppm) = −5.51 (J_{PPt} = 1246 Hz).

Crystallography

Good X-ray quality crystals from compounds $[Pt(Me)_2Cl\{\boldsymbol{C}C_5H_4CH_2\boldsymbol{N}CH\ (2,4,6\text{-}Me_3C_6H_2)\}(SMe_2)]$ and $[PtBr(Me)_2\{\boldsymbol{C}C_5H_4CH_2\boldsymbol{N}CH(2,4,6\text{-}Me_3C_6H_2)\}(SMe_2)]$ were obtained by cooling concentrated acetone solutions of the complexes in a refrigerator for extended periods. Selected prismatic crystals were mounted on a MAR345 with a image plate detector for **1**, or on an Enraf-Nonius CAD4 four-circle diffractometer for **2**, and using graphite monochromated Mo-Kα radiation (λ 0.71069 Å) in the ω–2θ scan mode. Unit-cell parameters were determined from automatic centering of 7164 ($3 < \theta/° < 31$) for **1**, and 25 ($12 < \theta/° < 21$) reflections for **2**, and refined by least-squares method; Lorentz-polarization and absorption corrections were made. The structure was solved by Direct methods, using the SHELXS computer program[35] and refined by full-matrix least-squares method with the SHELX-97 computer program.[36] The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.1331P)^2]^{-1}$, for **1**, and $w = [\sigma^2(I) + (0.0494P)^2]^{-1}$, for **2**, and $P = (|F_o|^2 + 2|F_c|^2)/3$, f, f' and f'' were taken from *International Tables of X-Ray Crystallography*.[37] All H atoms were computed and refined, using a riding model, with an overall isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which are linked.

CCDC reference numbers 176777 and 176778.

See http://www.rsc.org/suppdata/dt/b2/b209844j/ for crystallographic data in CIF or other electronic format.

Kinetics

The reactions were followed by UV-Vis spectroscopy in the 500–330 nm range where none of the solvents absorb. At atmospheric pressure runs with $t_{½}$ > 170 s were recorded on an HP8452A instrument equipped with a thermostated multicell transport; for runs with $t_{½}$ < 7 s an Applied-Photophysics stopped-flow instrument connected to a J&M TIDAS spectrophotometer was used. Observed rate constants were derived from absorbance *versus* time traces at the wavelengths where a maximum increase and/or decrease of absorbance was observed. In some cases the use of the SPECFIT[38] program was needed in order to separate the two exponential traces for the reactions on complexes **3** and **4**. For runs at variable pressure, a home made stopped-flow[39] connected to a J&M TIDAS spectrophotometer was used. No dependence of the observed rate constant values on the selected wavelengths was detected, as expected for reactions where a good retention of isosbestic points is observed. The general kinetic technique is that previously described,[13] in all cases pseudo-first order conditions

were maintained and the platinum concentration was maintained at (2–6) × 10^{-4} M to avoid undesired decomposition reactions. For the processes involving compounds **3** and **4** kinetic stock solutions were prepared from the dimeric platinum species prepared (see above) and SMe_2 in acetone with [SMe_2] being always 10 times that of the platinum compound; the remaining concentration conditions were established as usual. Table S1 (supporting information) collects all the obtained k_{obs} values for all the complexes studied as a function of the starting complex, entering and leaving ligands, solvent and temperature.

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