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Cyclometallation on platinum(II) complexes; the role of the solvent and added base donor capability on the reaction mechanisms†

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The reaction of $PhCH{=}NCH_2CH_2NMe_2$ with $[PtCl_2S_2]$ (S = SMe_2 or dmso) produces $[PtCl_2(PhCH{=}NCH_2CH_2NMe_2)]$ (**1**) in which the imine acts as a bidentate [N,N′] ligand. The cyclometallated [C,N,N′] platinum(II) complex $[PtCl(C_6H_4CH{=}NCH_2CH_2NMe_2)]$ (**2**) has been obtained by refluxing a methanol solution of complex **1** in the presence of base; both complexes **1** and **2** have been characterized crystallographically. The cyclometallation process has been studied kinetically at variable temperature and pressure as a function of the base added in methanol and ethanol solutions. In all cases, the actual C–H bond activation is preceded by the *Z* to *E* isomerization of the imine; detection of this species by proton NMR has also been achieved. The kinetic, thermal and baric activation parameters associated with the two processes are indicative of a different reaction mechanism operating for the reactions when the *"external"* base added ($NaCH_3CO_2$) can, in fact, react with the starting material to form a new acetato complex which allows for the reactions to be intramolecular.

Introduction

The reaction mechanisms leading to electrophilic cyclometallation reactions on Pd(II) complexes have been extensively studied.[1–5] Comparison with similar mechanisms for cyclometallation reactions on Rh(II) has also been reported,[6–8] and the conclusions drawn from the results obtained for both systems have been found equivalent. On the other hand, the study of the reaction mechanisms operating for metallations on Pt(II) complexes is dominated by oxidative addition–reductive elimination processes.[9–11] In this respect, we have been involved in the full mechanistic study of such reactions.[12–14]

Recent reports on cycloplatination reactions proved that *cis*-$[PtCl_2(dmso)_2]$ is a reasonable metalating agent leading to higher yields and cleaner reactions than the more classical $K_2[PtCl_4]$ starting material. Successful reactions have been reported for the synthesis of mono- and bis-cycloplatinated complexes containing aryl or ferrocenyl [C,N] ligands,[15–21] while in some cases deoxygenation of dimethyl sulfoxide affords platinum(IV) dimethyl sulfide complexes as final products.[22,23] Cycloplatination of aryl oximes using *cis*-$[PtCl_2(dmso)_2]$ as well as $[PtCl_2(SMe_2)_2]$ has been recently reported.[24]

Following our interest in cycloplatination of potentially terdentate ligands [C,N,N′][25–28] we now report the results obtained for the reactions of bis-sulfoxide and -sulfide dichloroplatinum(II) complexes with $PhCH{=}NCH_2CH_2NMe_2$. An additional interest in this system arises from the fact that the presence of two nitrogen atoms would facilitate the isolation of a coordination compound $[PtCl_2(PhCH{=}NCH_2CH_2NMe_2)]$ analogous to N-coordinated compounds *trans*-$[PtCl_2L(dmso)]$[15–21] which have been proposed as intermediates from starting materials to cyclometallated complexes. This would allow the investigation at variable temperatures and pressures of the reaction mechanism operating for the intramolecular C–H bond activation process. Given the important charge separation involved in the metallation process, the study of the mechanism of the C–H bond activation on these complexes has been monitored as a function of the polarity of the solvent used.[29] Furthermore, the study of the differences between the processes carried out in the presence of coordinating and non-coordinating bases has also been pursued.[8] In all cases the C–H bond activation process is always preceded by a relatively fast isomerisation reaction of the imine ligand from an unreactive *Z* conformation to a better oriented *E* conformation.[30] The presence of acetate ions in the reaction medium has been shown to lead to the formation of a much more reactive acetato complex that enables a complete intramolecular reaction process.

Results

Compounds

Ligand $PhCH{=}NCH_2CH_2NMe_2$ (**L**) was prepared as previously reported[28] and characterized by ^1H NMR in $CDCl_3$. According to NMR data only one isomer was present in solution and the expected *E* conformation was confirmed by a NOESY experiment in which cross-peak signals between imine and methylene protons (δ 8.32 and 3.75 ppm respectively) were observed. When the ligand was treated with $[PtCl_2(SMe_2)_2]$, obtained as a mixture of *cis* and *trans* isomers, in refluxing methanol, complex *cis*-$[PtCl_2(PhCH{=}NCH_2CH_2NMe_2)]$ (**1**), depicted in Chart 1, was formed as a white solid. For comparison, *cis*-$[PtCl_2(dmso)_2]$ was also tested as platinum substrate and analogous results were obtained. In spite of the fact that sulfides are better ligands for platinum(II) than sulfoxides,[22,23] and that the dimethyl sulfide complex consists of a mixture of isomers,[5] the replacement of the sulfide ligands by both nitrogen atoms of ligand **L** is easily achieved.

Our next goal was to test whether it is possible to obtain the cyclometallated complex $[PtCl(C_6H_4CH{=}NCH_2CH_2NMe_2)]$ (**2**) from complex **1**. The process involves the activation of a C–H bond and the release of HCl *via* an electrophilic substitution on the aromatic carbon. The most widely used conditions for

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† Electronic supplementary information (ESI) available: Listings of selected bond lengths (Å) and angles (°) for complex **2** with estimated standard deviations, crystallographic and refinement data for complex **2** and listing of observed rate constants for the cyclometallation reaction of complex **1**. Plot of the molecular structure of complex **2** and that of the observed rate constants corresponding to the first reaction step determined when proton sponge or neat solvent were used. ^1H NMR spectra of the mixture of *Z* and *E* isomers of complex **1**. See http://www.rsc.org/suppdata/dt/b3/b306243k/

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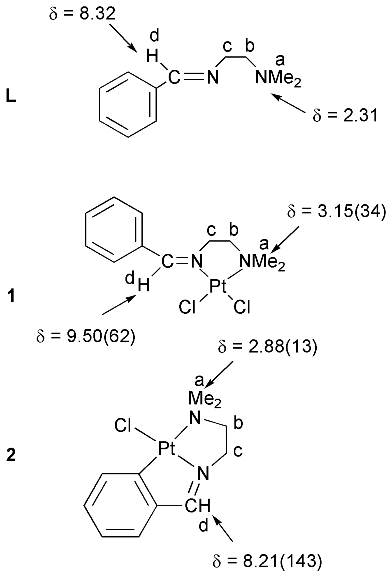


Chart 1 NMR data for the reported complexes; *δ* values in ppm, ^3J(H–Pt), in parenthesis, in Hz.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1** with estimated standard deviations

Pt–N(1)	2.014(7)	C(1)–C(2)	1.281(13)
Pt–N(2)	2.084(8)	C(1)–C(6)	1.421(13)
Pt–Cl(2)	2.288(4)	C(2)–C(3)	1.396(15)
Pt–Cl(1)	2.305(4)	C(3)–C(4)	1.352(14)
N(1)–C(7)	1.196(10)	C(4)–C(5)	1.478(13)
N(1)–C(8)	1.559(12)	C(5)–C(6)	1.343(13)
N(2)–C(10)	1.246(17)	C(6)–C(7)	1.550(12)
N(2)–C(11)	1.423(14)	C(8)–C(9)	1.529(14)
N(2)–C(9)	1.482(11)		
N(1)–Pt–N(2)	87.0(3)	N(1)–Pt–Cl(1)	179.4(2)
N(1)–Pt–Cl(2)	90.1(3)	N(2)–Pt–Cl(1)	93.0(2)
N(2)–Pt–Cl(2)	176.3(2)	Cl(2)–Pt–Cl(1)	90.01(15)

converting complexes analogous to **1** into cycloplatinated derivatives are refluxing for several hours in either toluene or in a donor solvent such as methanol or ethanol, in some cases in the presence of an *"external"* base such as $NaCH_3CO_2$.[15–21,31,32] Several experimental conditions were tested with the aim of producing cyclometallation of the coordinated imine. Complex **1** is stable in refluxing methanol; however, treatment for 12 h in the presence of an equimolar amount of sodium acetate gave complex **2** which was isolated in 58% yield. Conversion of complex **1** to complex **2** was also achieved under analogous conditions when external bases such as 1,8-bis(dimethylamino)naphtalene, commonly used as a proton sponge, or triethylamine were used instead of sodium acetate, integration of the NMR signals (Chart 1) of the final mixtures indicate 40–60% conversion yields. Reaction in refluxing toluene, even in the presence of sodium acetate, produces the recovery of the unchanged starting complex **1** after 18 h; the extreme insolubility of the complex in this solvent could be responsible for this fact.

Attempts to achieve one-pot synthesis of cyclometallated complex **2** without prior isolation of complex **1** gave poorer results. The reaction of *cis*-[$PtCl_2(dmso)_2$] and equimolecular amounts of ligand **L** and sodium acetate in refluxing methanol produced after 18 h a mixture of complex **1** and complex **2** in low yields (13 and 20%, respectively), together with small amounts of benzaldehyde and unreacted platinum substrate. Even lower yields of complexes **1** and **2** were obtained when [$PtCl_2(SMe_2)_2$] was used as starting material in agreement with the fact that SMe_2 is a worse leaving ligand than dmso for Pt(II) centres.[24]

Complex **1** was characterized by elemental analysis, NMR and mass spectrometry. The synthesis of complex **2** following an alternative route has been reported elsewhere[25] along with characterisation of the cyclometallated complex. Crystal structure determinations were carried out for complex **1** and for previously reported complex **2**. For complex **1**, evidence of coordination of both nitrogen atoms to platinum is obtained from the fact that both methylamine and imine protons are coupled to platinum (^3J(Pt–H) = 34 and 62 Hz, respectively). The downfield shift of methylamine protons (*δ* 3.15 ppm) confirms the coordination of this group to platinum. On the other hand, the chemical shift of the imine resonance (*δ* 9.50 ppm) indicates, according to previous studies for platinum or palladium complexes with coordinated imines,[31–34] a *Z*-conformation around the C=N bond with the imine proton close to the platinum nucleus. Accordingly, a cross-peak signal between aromatic (7.51 ppm) and methylene (4.06 ppm) protons was observed in 2D-NOESY NMR experiments. Therefore, since an *E*-form is required for the metallacycle formation in complex **2**, isomerisation of the ligand should take place in order to achieve the cyclometallation process.

The ^3J(H–Pt) value for the methylamine protons decrease from **1** (^3J(H–Pt) = 34 Hz) to **2** (^3J(H–Pt) = 13 Hz) as a result of the higher *trans* influence of the phenyl *vs*. the chloro ligands. Conversely, an increase in the coupling constant of the imine proton to platinum on going from **1** (^3J(H–Pt) = 62 Hz) to **2** (^3J(H–Pt) = 143 Hz) is observed; this effect may be attributed both to the higher electron density at the metal in the cyclometallated complex, and to the formation of the structure corresponding to an *endo* metallacycle. The ^{195}Pt NMR spectrum of complex **1** shows one single resonance at (*δ* −2265 ppm), which is consistent with the presence of two nitrogen and two chloro atoms in the coordination sphere of platinum(II).[35] A comparison with the value for complex **2** (*δ* −3462 ppm) indicates a shift towards higher fields upon metallation, in agreement with an increase in ligand covalency from Cl (in **1**) to C_{aryl} (in **2**).

Suitable crystals of complexes **1** and **2** were obtained from methanol concentrated solutions on standing. The crystal structures are composed of discrete molecules separated by van der Waals distances. The structures are shown in Figs. 1 and S1 (ESI †) and selected molecular dimensions are listed in Tables 1 and S1 (ESI †). For complex **1**, the platinum atom has the expected square planar coordination with the bidentate (N,N′) ligand and two mutually *cis* chloro ligands. The Pt–Cl bonds are similar in length to those found in related complexes.[15,20]

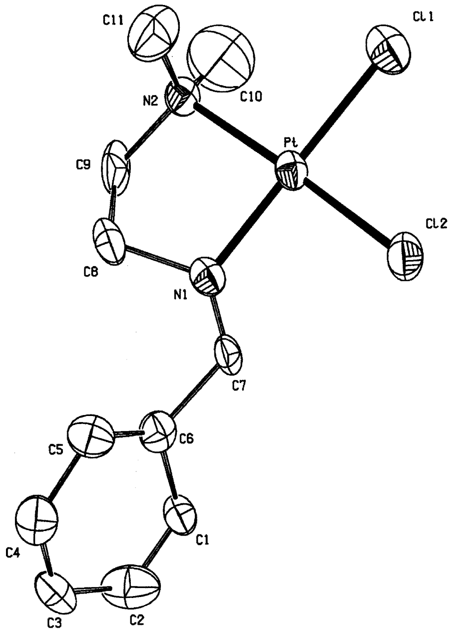


Fig. 1 Molecular structure of complex **1**.

The Pt–NMe$_2$ distance (2.084(8) Å) is longer than the Pt–NCH (2,014(7) Å), which is consistent with the relatively weak coordinating ability of tertiary amines for platinum. Bond angles at platinum are close to the ideal 90°, the smallest (87.0(3)°) corresponding to the chelate (N,N′). In agreement with the above NMR data, the conformation of the imine ligand is *Z*, the torsion angle C(6)–C(7)–N(1)–C(8) being −9.1(14)°. Description of the structure for complex **2**, which is analogous to those described for similar complexes,[28] is included in the ESI †(Fig. S1).

Mechanistic studies

When repetitive UV-Vis spectra of sodium acetate-containing methanol or ethanol solutions of the starting complex were recorded, the spectral changes indicated in Fig. 2 were obtained. As indicated in the Figure, these changes can be separated into two well-defined processes with absorbance *vs.* time traces showing a good first-order exponential behaviour on the platinum complex concentration. At low excess (1–2 fold) concentrations of sodium acetate, the magnitude of the first spectral changes appear to be dependent on the amount of sodium acetate added; nevertheless, the values found for the derived first-order rate constants are found independent on these concentrations. Practically no further changes could be observed in these cases and, consequently, further studies were carried out under pseudo-first-order conditions (20-fold minimum excess given the two possible substitution positions at the Pt centre), in order to observe the second process indicated. Even for this second process, no meaningful dependence of the observed rate constants on the concentration of sodium acetate was detected (5–20 fold margin). Although these were not the preparative conditions indicated above, proton NMR monitoring of the reaction under kinetic conditions indicated that the conversion of complex **1** to its cyclometallated derivative is quantitative without the formation of side products. As shown in Fig. 3, the value determined for the first observed reaction rate constant in methanol and ethanol solutions was found the same within error, while for the second process dramatic differences were obtained on changing the solvent. Table 2 collects all the values of the relevant kinetic and thermal and baric activation parameters derived for these processes. As stated above, in all cases ^{1}H NMR spectra of the final reaction mixture indicated that the complete process measured corresponds to the activation of the C–H bond of the coordinated imine stated above. The oxidative-addition pathway can be discarded due to the fact that platinum hydride resonances were not observed in the proton NMR spectra.

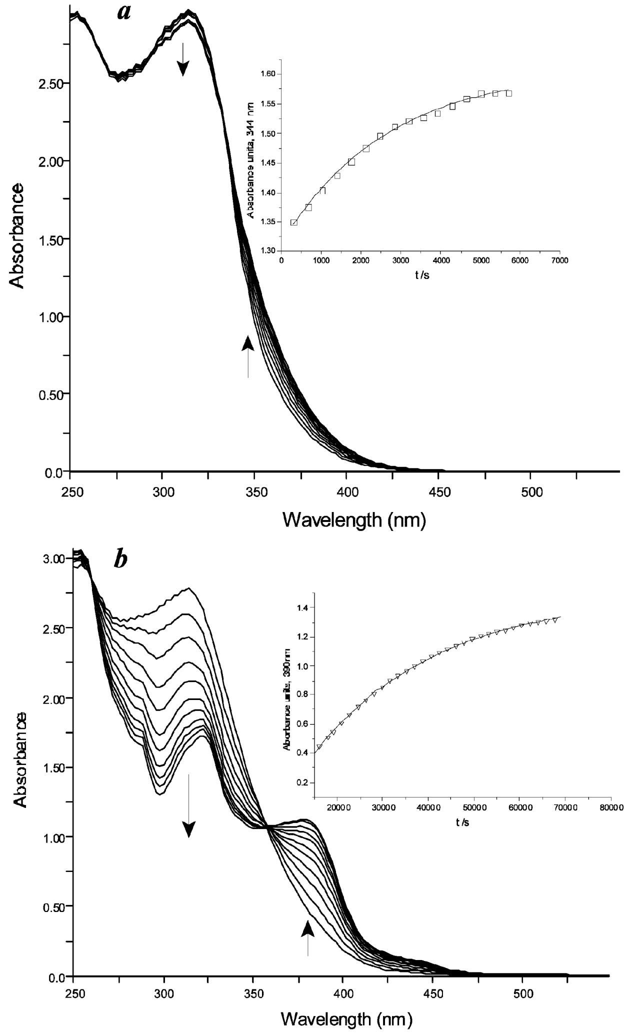


Fig. 2 Spectral changes (*a* first step, *b* second step) in the UV-Vis spectra of a solution of the starting complex, **1**, in a solution of sodium acetate (50-fold excess) in ethanol; 324 K. Symbols correspond to the experimental data, lines to the exponential fitting.

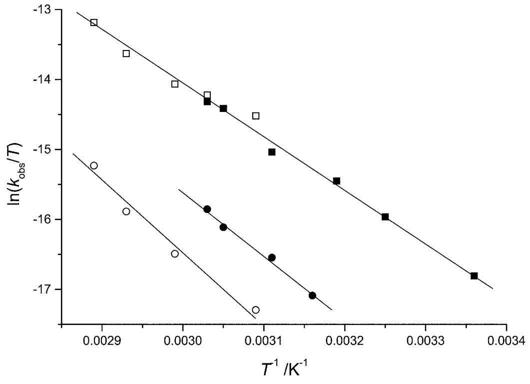


Fig. 3 Eyring plots for the rate constants corresponding to the two processes occurring on cyclometallation of complex **1** assisted by acetate in different solvents. Solid symbols correspond to methanol solution, empty symbols to ethanol solution; squares to the first step and circles to the second.

In view of the above data the cyclometallation reaction of complex **1** was monitored in the presence of other bases such as NEt$_3$, both in methanol and ethanol solutions. The same type of spectral changes than those observed for the process carried out in the presence of sodium acetate were obtained. Furthermore, the same dependences with the solvent and concentration of the base used were also made evident, Table 2 collects the relevant kinetic and activation parameters, and Fig. 4 indicates the pressure dependence of the two steps observed. When methanol or ethanol solutions of the starting material, with no sodium acetate or any base added, were monitored by UV-Vis

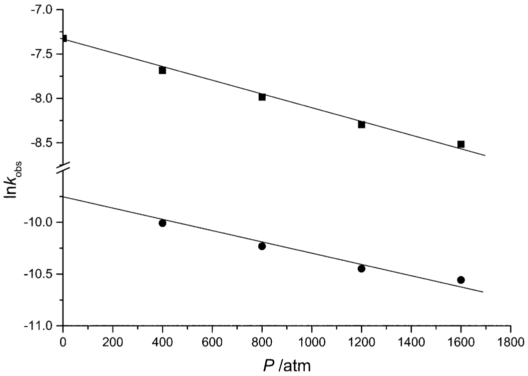


Fig. 4 Pressure dependence of the rate constants of the two processes involved in the cyclometallation reaction of complex **1** in ethanol solution in the presence of NEt$_3$. Square symbols correspond to the first step (336 K) and circles to the second (343 K).

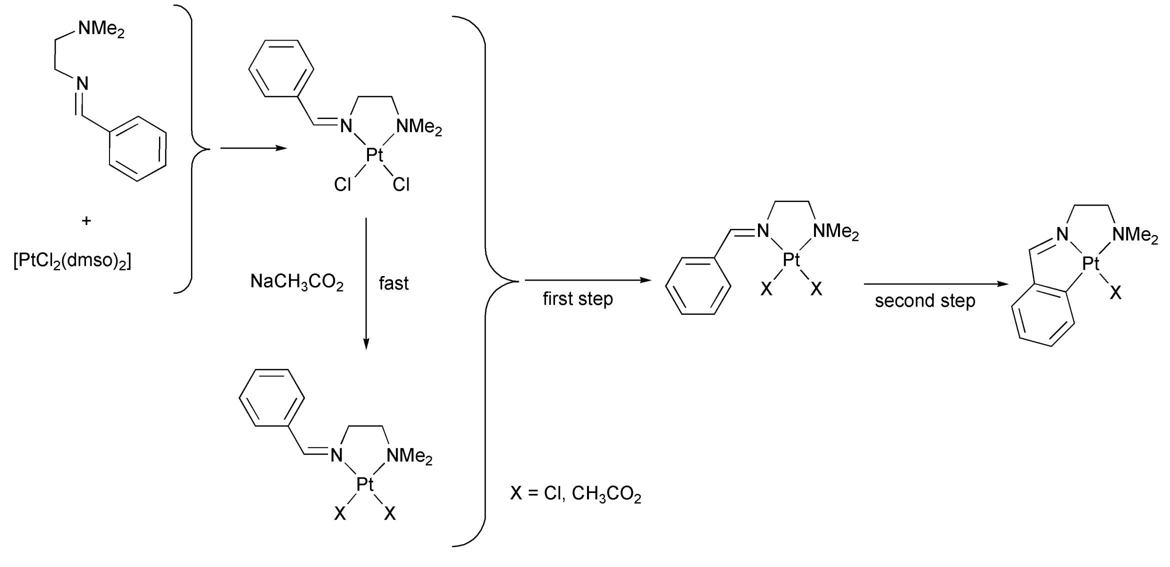
Table 2 Values of the kinetic and activation parameters for the two processes involved in the acetate- and triethylamine-assisted cyclometallation reaction of complex **1**, as a function of the solvent used.

Step	Solvent	Base	$10^5 \times {}^{323}k/\mathrm{s}^{-1}$	$\Delta H^{\neq}/\mathrm{kJ\ mol^{-1}}$	$\Delta S^{\neq}/\mathrm{J\ K^{-1}\ mol^{-1}}$	$\Delta V^{\neq}/\mathrm{cm^3\ mol^{-1}}$
First	MeOH or EtOH	$NaCH_3CO_2$	12.1	63 ± 2	−128 ± 6	−14 ± 2 (332 K, MeOH) −11 ± 2 (342 K, EtOH)
		NEt_3	8.9	109 ± 3	13 ± 11	19 ± 1 (336 K, EtOH)
Second	MeOH	$NaCH_3CO_2$	2.2	76 ± 5	−101 ± 16	−10 ± 1 (332 K)
		NEt_3	0.33	64 ± 7	−156 ± 22	−5.1 ± 1.9 (338 K)
	EtOH	$NaCH_3CO_2$	0.9	83 ± 9	−86 ± 26	−13 ± 3 (342 K)
		NEt_3	0.54	94 ± 5	−59 ± 14	13 ± 1 (343 K)

spectroscopy *vs.* time, only very small spectral changes corresponding to the first reaction step could be detected. The changes were attributed to the possible small amounts of alkoxy bases present in the solvents used, but the values derived from the absorbance *vs.* time traces agree very well with the values determined in pseudo-first-order (10-fold excess) conditions of NEt_3. In the same respect, when the base used was proton sponge, despite the dramatic interferences in the UV-Vis spectrum, the values determined for the observed rate constant corresponding to the first reaction step agree very well with the values determined when triethylamine or neat solvent were used (Fig. S2, ESI†). Unfortunately the spectral changes leading to the final cyclometallated product, **2**, could not be monitored due to interferences from the electronic spectrum of the proton sponge. Attempts to follow the cyclometallation process in other solvents with different characteristics (toluene, chloroform and acetone) were unsuccessful given the extremely low solubility of complex **1** in them (see above).

It is clear from the data obtained that the complete cyclometallation process takes place very slowly with an initial, relatively faster, formation of an intermediate species. The formation of such species takes place independly of the solvent used, but it strongly depends on the coordinating capabilities of the base added. The process switches from one having a high ordered/compressed transition state, for the reactions carried out in the presence of sodium acetate, to one having an expanded transition state where only a small increase of the ordering is apparent from the values of $\Delta S^{\neq}$. The second step leading to the final cyclometallated complex **2**, also shows dramatic differences in the activation parameters, especially in the values determined for $\Delta V^{\neq}$, depending of the coordinating capabilities of the proton abstractor used. In this case, though, even the relatively small differences in the solvent used produce changes in the energetics leading to the transition state. It seems clear that the processes taking place with $NaCH_3CO_2$ or NEt_3 present in the reaction medium depart from a different starting material. Given the UV-Vis spectral changes registered during the cyclometallation reaction studied and indicated in Fig. 2, ^{1}H NMR monitoring of the reaction under similar conditions was carried out. Effectively the NMR spectra of ethanol reaction mixtures of complex **1** with a 10-fold excess of NEt_3 showed a new series of peaks that further evolve to form the final cyclometallated complex **2**. The 2D-NOESY NMR spectrum showed a cross-peak signal, confirmed by a 1D-NOESY experiment, between the imine and the methylene resonances of a minor compound which, on these bases, was identified as the *E* isomer (Fig. S3, †).[36] As a result, the full reaction of the cyclometallation reaction of imine **L** can be interpreted as indicated in Scheme 1. The reaction times, nevertheless, are found to be extremely dependent on the solvent and coordination capability of the added base, as shown by the data in Table 2. Probably at high sodium acetate concentrations and elevated temperatures, as used in this study, complex **1** is transformed very rapidly into a mixture of acetato complexes, as expected from the known substitution processes on square-planar Pt(II) complexes (see Scheme 1).[37,38] In this respect, ^{1}H NMR spectra of freshly prepared solutions of complex **1** with a five-fold excess of sodium acetate showed three resonances corresponding to the methynic proton that can be assigned to different acetato complexes. A singlet at 9.45 ppm can be assigned to a monoacetato complex with the imine in a *Z* form, while two other singlets at 8.70 and 8.40 ppm were assigned, respectively, to mono- and bis-acetato complexes having the imine already in a *E* conformation. Accordingly in the acetate region the resonances at 2.06 and 2.07 ppm were assigned to the two monoacetato complexes (*Z* and *E* imine forms) while the two signals of equal intensity at 2.04 and 2.05 ppm were assigned to the bis-acetato complex.

Given the extreme differences observed in the mechanistic data, the discussion of the results of the reactions followed with



Scheme 1

added acetate or triethylamine has to be carried out separately. The above mentioned immediate (according to the cyclometallation timescale) formation of the acetato derivatives of **1** under the kinetic conditions used, supports this differentiation. Data in Table 2 clearly indicates that both steps of the studied process take place with a highly ordered and compressed transition state. The fact that for the first step, *Z* to *E* imine isomerisation (Scheme 1), the kinetic and activation parameters are found independent of the solvent used, indicate that the transition state has no influence from the reaction medium; insolubility of the starting complex prevented the study of the reaction in solvents with more severe differences. From Scheme 1 it is clear that the presence of an acetato ligand at the coordination sphere of the platinum centre, and in a *cis* position with respect to the iminic nitrogen, should favour an intramolecular stabilisation of the polar $\cdots CH^{(+)}–N^{(-)}–CH_2 \cdots$ form of the imine needed for the isomerisation. That is, the dangling oxygen of the monodentate acetato ligand is likely to stabilize the positive charge on the iminic carbon, allowing an easy rotation of the C–N bond to the desired *E* conformation. This process is bound to be fairly independent of the solvent, as observed, and should imply a highly ordered ($\Delta S^{\neq} = -128$ J K^{-1} mol^{-1}) and compressed ($\Delta V^{\neq} = -11/-14$ cm^3 mol^{-1}) transition state. As for the second reaction step, the activation parameters collected in Table 2, indicate that, although the activation volume results fairly independent on the solvent used, the values for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are discriminating with respect to the polarity of the solvent. In all cases the activation parameters correspond to a highly ordered and compressed transition state, with the polarity of the solvent favouring the less enthalpy demanding and more ordered one. Given the fact that this second step corresponds to the actual C–H bond activation reaction, the proton transfer from the aromatic carbon to the acetate implies an important charge separation that should be favoured in methanol, as observed. Even so, the differences in ethanol and methanol solution are not found to be very high (especially with respect to the activation volumes), which seems to indicate that the solvent participation in the transition state is small. Again the excellent positioning of the dangling oxygen of the platinum-coordinated acetate favours an intramolecular reaction *via* a tetracentered transition state involving the acetato ligand, the metal centre, the cyclometallating carbon and the hydrogen, as a whole, with charge separation being at a minimum. It this respect the known cyclometallation reactions of equivalent Pd(II) complexes[3–5] have values for the thermal and baric activation parameters very similar to the ones in this study, whilst the tetracentered transition state involved is equivalent. In those cases, the cyclometallation process is strongly accelerated by the presence of protons in the reaction medium, due to the formation of coordinated acetic acid that facilitates the exiting of the leaving ligand.[4] In this respect, all attempts to run the cyclometallation reaction from **1** to **2** in the presence of acetic acid resulted in the full recovery of the starting material; even no *Z* to *E* isomerisation of the ligand was detected. The protonation of the dangling oxygen of the acetato ligand at the platinum centre, that should destabilize the polar $\cdots CH^{(+)}–N^{(-)}–CH_2 \cdots$ form of the imine, can easily explain this fact. If the *E* form of the imine is not present the further C–H activation cannot take place.

For the full cyclometallation process carried out in the presence of a non-coordinating base, such as NEt_3, the differences observed should be related to the impossibility of an intramolecular-assisted process, both for the first and second reaction steps. Effectively, the thermal and baric activation parameters for the *Z* to *E* isomerisation, collected in Table 2, indicate a much more enthalpy demanding process, with an important expansion and little change in organization, to go to the transition state. We can speculate that the NEt_3 base should be responsible for the stabilisation of the positive charge density of the $\cdots CH^{(+)}–N^{(-)}–CH_2 \cdots$ form of the imine. The change from negative to positive activation volume has to be related to the liberation of solvent molecules from the solvated NEt_3 and the polar form of the imine occurring on going to the ion-paired transition state. As for the actual C–H bond activation process, the reaction is extremely solvent-dependent; the activation volumes having different sign and enthalpies of activation having a 1.5 fold difference (see Table 2). A very important charge separation should occur in the transition state, where a proton has to be transferred from an aromatic carbon to an external NEt_3 molecule, allowing for an anionic Cl^- to leave the Pt(II) centre. Consequently, the reaction in solvents with higher polarity should be less enthalpy demanding but having a more solvent ordered and compressed transition state, as effectively indicated by the values of Table 2.

The absolute values for the activation volumes are, nevertheless, confusing; although the trend observed is that indicated above, the values do not agree with the entropy data. These sort of opposite trends between volumes and entropies of activation have been repetitively associated with the formation of highly solvent-structured transition states in aqueous solution, where not only electrostriction is operating.[12,39–42] The solvents used in this study, nevertheless, are not prone to these type of interactions, so some other explanation should be made available. Probably some ion pairing between $NHEt_3^+$ and Cl^- is producing a less solvent-ordered and compressed transition state than expected.[29] If so, the ion pairing should be much more important in the less polar ethanol solutions[43] producing a less negative value for the entropy of activation and an important positive contribution to the volume of activation based on the intrinsic bond breaking process involved to go to the transition state.

Conclusions

It is shown in this study that the preparation of cyclometallated platinum(II) complexes containing terdentate [C,N,N′] ligands *via* electrophilic substitution is feasible using $[PtCl_2(SMe_2)_2]$ or *cis*-$[PtCl_2(dmso)_2]$ as platinum substrates. The results here described indicate the dramatic influence of the nature of the base added in the cyclometallation processes. In particular the reaction mechanism is proved to have an intramolecular character when the added base has coordination capabilities, such as sodium acetate, *vs.* the intermolecular characteristics of the process for reactions carried out in the presence of an authentic *"external"* base such as NEt_3 or proton sponge. Differences in solvent implication in the process are more difficult to quantify given the small differences between the solvents used and the insolubility of the starting material in other solvents, which prevented the monitoring of the reactions.

Experimental

Instruments

Mass and NMR spectra were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona. Microanalyses were performed by the Institut de Química Bioorgànica de Barcelona (Consejo Superior de Investigaciones Científicas)

FAB-mass spectra were carried out in a VG-Quattro spectrometer with 3-nitrobenzyl alcohol matrix. ^1H and ^{195}Pt NMR spectra were recorded by using Varian Gemini 200 (^1H, 200 MHz) and Bruker 250 (^{195}Pt, 54 MHz) spectrometers, and referenced to $SiMe_4$ (^1H) and H_2PtCl_6 in D_2O (^{195}Pt). 1D- and 2D-NOESY experiments were carried out in a Bruker 600 spectrometer; δ values are given in ppm and J values in Hz.

Compounds

Compounds *cis*-$[PtCl_2(dmso)_2]$,[44] $[PtCl_2(SMe_2)_2]$[45] and $PhCHNCH_2CH_2NMe_2$ (**L**)[28] were prepared as reported. **L** was characterized by ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.31 [s, 6H, H^a]; 2.64 [t, J(H–H) = 7, 2H, H^b]; 3.75 [t, J(H–H) = 7, 2H, H^c]; 7.41 [m, 3H, aromatics]; 7.72 [m, 2H, aromatics]; 8.32 [s, 1H, H^d].

Complex [$PtCl_2(Me_2NCH_2CH_2NCHPh)$] (**1**) was obtained from 0.100 g (2.56×10^{-4} mol) of [$PtCl_2(SMe_2)_2$] and 0.045 g (2.56×10^{-4} mol) of ligand $PhCHNCH_2CH_2NMe_2$ in 25 cm^3 of methanol. The mixture was refluxed with continous stirring during 4 h. The solvent was evaporated *in vacuo* and the remaining yellow residue was recrystallized in CH_2Cl_2–MeOH to yield white crystals. Yield 91 mg (80%). Anal. Found: C, 29.4; H, 3.7; N, 6.3. Calc. for $C_{11}H_{16}Cl_2N_2Pt$: C, 29.87; H, 3.65; N, 6.33%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.68 [t, J(H–H) = 6, 2H, H^b] 3.15 [s, J(Pt–H) = 34, 6H, H^a]; 4.06 [t, J(H–H) = 6, 2H, H^c]; 7.51 [m, 5H, aromatics]; 9.50 [s, J(H–Pt) = 62, 1H, H^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): δ −2265 [s, br]. FAB-MS, *m*/*z*: 441 [M], 406 [M − Cl], 371 [M − 2Cl].

Complex [$PtCl(Me_2NCH_2CH_2NCHC_6H_4)$] (**2**) was obtained using the following procedure: The mixture formed by 0.050 g (1.13×10^{-4} mol) of complex **1**, the equimolar amount (0.09 g) of sodium acetate and 25 cm^3 of methanol was heated under reflux during 12 h. The yellow solution was evaporated to *ca*. 10 cm^3, a small amount of complex **1** was filtered off, and the solution was allowed to crystallize at room temperature. Within several hours, red crystals of complex **2** were collected. Yield 25 mg (58%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.88 [s, J(Pt–H) = 13, 6H, H^a] 3.07 [t, J(H–H) = 6, 2H, H^b]; 3.86 [t, J(H–H) = 6, J(H–Pt) =34, 2H, H^c]; 6.99 [t, J(H–H) = 7, 1H]; 7.17 [d, J(H–H) =8, 1H]; 7.21 [t, J(H–H) = 7, 1H]; 7.69 [d, J(H–H) = 8, J(H–Pt) = 42]; 8.21 [s, J(H–Pt) = 143, 1H, H^d].

Kinetics

The reactions were followed by UV-Vis spectroscopy in the 500–300 nm range where none of the solvents absorb. Runs at room pressure were recorded on an HP8452A or Cary-50 instruments equipped with a thermostated multicell transport. For the kinetic runs at elevated pressure, a previously described pressurizing system[46] connected to the Cary-50 spectrophotometer was used. Observed rate constants were derived from absorbance *vs.* time traces at the wavelengths where a maximum increase and/or decrease of absorbance was observed. In some cases the SPECFIT[47] program was used in order to evaluate two consecutive reaction rate constants. In all cases the differences between the two observed rate constants has been found large enough (Fig. 2) to evaluate them separately. Table S2 (ESI †) collects all the obtained k_{obs} values for all the reactions studied as a function of the starting complex, added base, solvent, temperature and pressure. 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,[13,48] in all cases no dependence of the values obtained for the observed rate constant on the concentration of starting material or added base was observed; nevertheless pseudo-first-order conditions were maintained (at least 20-fold) and the platinum concentration was maintained at (2–3) × 10^{-4} M; values in Table S1 (ESI †) correspond to the average value of the data obtained under the specified conditions, in all cases errors were within 10% of the stated value. Given the very long periods during which the reactions were monitored (2–3 half lives in all cases), special care was taken to avoid solvent evaporation, plunger-stoppered or pill-box cells were used. Even for runs at temperatures close to the boiling point of the solvents used, these were carried out within the variable-pressure setup, in order to avoid lack of homogeneity in the solutions.

X-Ray structure analysis

Data collection. Prismatic crystals were selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($12 < \theta < 21°$) and refined by least-squares methods. Intensities were collected with graphite monochromated Mo-Kα radiation, using the ω–2θ scan-technique. For **1**, 3892 reflections were measured in the range $2.27 < \theta < 30.05°$; 1865 of which were assumed as observed applying the condition $I > 2\sigma(I)$. For **2**, 7009 reflections were measured in the range $2.31 < \theta < 29.96°$; 3467 of which were non-equivalent by symmetry (R_{int} = 0.069) and 1590 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls, significant decay was not observed. Lorentz polarization but not absorption corrections were made. Further details are given in Tables 3 and S3 (ESI †).

Table 3 Crystallographic and refinement data for complex **1**

Formula	$C_{11}H_{16}Cl_2N_2Pt$
M_w	442.25
T/K	293(2)
λ/Å	0.71069
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	7.919(15)
b/Å	15.528(15)
c/Å	11.099(9)
β/°	97.72(10)
V/Å^3; Z	1352(3); 4
D_c/Mg m^{-3}	2.172
μ/mm^{-1}	10.746
F(000)	832
Rflns. coll./unique (R_{int})	3892/3892 (0.0686)
Data/restraints/param.	3892 / 0 / 145
GOF on F^2	0.812
R_1 ($I > 2\sigma(I)$)	0.0356
wR_2 (all data)	0.0985
Largest peak and hole/e Å^{-3}	0.588 and −0.624

Structure solution and refinement. The structures were solved by direct methods using SHELXS computer program[49] and refined by the full-matrix least-squares method, with the SHELX97 computer program[49] using 3892 (**1**) or 3467 (**2**) reflections (very negative intensities were not assumed). The function minimised was $\Sigma w||F_o|^2 - |F_c|^2$, where $w = [\sigma^2(I) + (0.0375P)^2]^{-1}$ (**1**) and $w = [\sigma^2(I) + (0.0084P)^2]^{-1}$ (**2**) and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from International Tables of X-Ray Crystallography.[50] All hydrogen atoms were computed and refined with using a riding model with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom to which they are linked. Further details are given in Tables 3 and S3 (ESI †).

CCDC reference numbers 212048 and 212049.

See http://www.rsc.org/suppdata/dt/b3/b306243k/ for crystallographic data in CIF or other electronic format.

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References

1 A. D. Ryabov, I. K. Sakodinskaya and A. K. Yatsimirsky, *J. Chem. Soc., Dalton Trans.*, 1985, 2629.

2 A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403.

3 M. Gómez, J. Granell and M. Martínez, *Organometallics*, 1997, **16**, 2539.

4 M. Gómez, J. Granell and M. Martínez, *J. Chem. Soc., Dalton Trans.*, 1998, 37.

5 M. Gómez, J. Granell and M. Martínez, *Eur. J. Inorg. Chem.*, 2000, 217.

6 G. Gonzalez, M. Martinez, F. Estevan, Garcia, P. Lahuerta and E. Peris, *New J. Chem.*, 1996, **20**, 83.

7 G. Gonzalez, P. Lahuerta, M. Martinez, E. Peris and M. Sanau, *J. Chem. Soc., Dalton Trans.*, 1994, 545.

8 F. Estevan, G. González, P. Lahuerta, M. Martínez, E. Peris and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, 1996, 1045.

9 L. M. Rendina and R. J. Puddephatt, *Chem. Rev.*, 1997, **97**, 1735.

10 R. J. Puddephatt, *Coord. Chem. Rev.*, 2001, **219–221**, 157.

11 R. A. Gossage, A. D. Ryabov, A. L. Spek, D. J. Stufkens, J. A. M. van Beek, R. van Eldik and G. van Koten, *J. Am. Chem. Soc.*, 1999, **121**, 2488.

12 M. Crespo, M. Martínez and E. Pablo, *J. Chem. Soc., Dalton Trans.*, 1997, 1231.

13 M. Crespo, M. Martinez, J. Sales, X. Solans and M. Font-Bardía, *Organometallics*, 1992, **11**, 1288.

14 M. Crespo, M. Martinez and J. Sales, *Organometallics*, 1993, **12**, 4297.

15 Y. J. Wu, L. Ding, H. X. Wang, Y. H. Liu, H. Z. Yuan and X. A. Mao, *J. Organomet. Chem.*, 1997, **535**, 49.

16 L. Ding, D. P. Zou and Y. J. Wu, *Polyhedron*, 1998, **17**, 2511.

17 M. D. Meijer, A. W. Kleij, M. Lutz, A. L. Spek and G. van Koten, *J. Organomet. Chem.*, 2001, **640**, 166.

18 A. W. Kleij, R. J. M. K. Gebbink, M. Lutz, A. L. Spek and G. van Koten, *J. Organomet. Chem.*, 2001, **621**, 190.

19 A. D. Ryabov, I. M. Panyashkina, V. A. Polyakov and A. Fisher, *Organometallics*, 2002, **21**, 1633.

20 P. R. R. Ranatunge-Bandarage, B. H. Robinson and J. Simpson, *Organometallics*, 1994, **13**, 500.

21 P. R. R. Ranatunge-Bandarage, N. W. Duffy, S. M. Johnston, B. H. Robinson and J. Simpson, *Organometallics*, 1994, **13**, 511.

22 A. D. Ryabov, G. M. Kazankov, I. M. Panyashkina, O. V. Grozovsky, O. G. Dyachenko, V. A. Polyakov and L. G. Kuz'mina, *J. Chem. Soc., Dalton Trans.*, 1997, 4385.

23 L. Alexandrova, O. G. D'yachenko, G. M. Kazankov, V. A. Polyakov, P. V. Samuleev, E. Sansores and A. D. Ryabov, *J. Am. Chem. Soc.*, 2000, **122**, 5189.

24 A. D. Ryabov, S. Otto, P. V. Samuleev, V. A. Polyakov, L. Alexandrova, G. M. Kazankov, S. Shova, M. Revenco, J. Lipkowski and M. M. Johansson, *Inorg. Chem.*, 2002, **41**, 4286.

25 M. Crespo, J. Granell, X. Solans and M. Font-Bardía, *Organometallics*, 2002, **21**, 5140.

26 O. López, M. Crespo, M. Font-Bardía and X. Solans, *Organometallics*, 1997, **16**, 1233.

27 C. M. Anderson, M. Crespo, G. Ferguson, A. J. Lough and R. J. Puddephatt, *Organometallics*, 1992, **11**, 1177.

28 C. M. Anderson, M. Crespo, M. C. Jennings, A. J. Lough and R. J. Puddephatt, *Organometallics*, 1991, **10**, 2672.

29 F. K. Fleischmann and H. Kelm, *Tetrahedron Lett.*, 1973, **14**, 3773.

30 *Z*/*E* conformation has been assigned not taking into account the platinum coordination to the iminic nitrogen.

31 X. Riera, C. López, A. Caubet, V. Moreno, X. Solans and M. Font-Bardía, *Eur. J. Inorg. Chem.*, 2001, 2135.

32 X. Riera, A. Caubet, C. López, V. Moreno, X. Solans and M. Font-Bardía, *Organometallics*, 2000, **19**, 1384.

33 J. Albert, R. M. Ceder, M. Gómez, J. Granell and J. Sales, *Organometallics*, 1992, **11**, 1536.

34 J. Albert, M. Gómez, J. Granell, J. Sales and X. Solans, *Organometallics*, 1990, **9**, 1405.

35 P. S. Pregosin, *Coord. Chem. Rev.*, 1982, **44**, 247.

36 NMR data obtained for the *E* isomer in $CDCl_3$ (ppm, Hz): δ 3.08 [s,^3J(HPt) = 31, 6H]; 2.83 [t,^3J(HH) = 6, 2H]; 4.25 [t,^3J(HH) = 6, 2H]; 8.49 [d,^3J(HH) = 7, 1H]; 8.75 [s,^3J(HPt) = 124.1, 1H].

37 M. L. Tobe and J. Burgess, *Inorganic Reaction Mechanisms*, Addison Wesley, Edinburgh, 1999.

38 R. G. Wilkins, *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, VCH, Weinheim, 1991.

39 M. Martínez, M. A. Pitarque and R. van Eldik, *Inorg. Chim. Acta*, 1997, **256**, 51.

40 M. Martínez, M. A. Pitarque and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, 1994, 3159.

41 M. Martínez and M. A. Pitarque, *J. Chem. Soc., Dalton Trans.*, 1995, 4107.

42 P. V. Bernhardt, F. Bozoglian, B. P. Macpherson, M. Martínez, G. González and B. Sienra, *Eur. J. Inorg. Chem.*, 2003, 2512.

43 M. Albrecht, R. A. Gossage, U. Frey, A. W. Ehlers, E. J. Baerends, A. E. Merbach and G. van Koten, *Inorg. Chem.*, 2001, **40**, 850.

44 J. M. Price, A. N. Williamson, R. F. Schramm and B. B. Wayland, *Inorg. Chem.*, 1972, **11**, 1280.

45 G. S. Hill, M. J. Irwin, C. J. Levy, L. M. Rendina and R. J. Puddephatt, *Inorg. Synth.*, 1998, **32**, 149.

46 M. G. Basallote, J. Durán, M. J. Fernández-Trujillo, G. González, M. A. Máñez and M. Martínez, *J. Chem. Soc., Dalton Trans.*, 1999, 3379.

47 R. A. Binstead, A. D. Zuberbühler and B. Jung, SPECFIT version 3.0.32, Spectrum Software Associates, 2002.

48 P. V. Bernhardt, C. Gallego and M. Martínez, *Organometallics*, 2000, **19**, 4862.

49 G. M. Sheldrick, SHELXS97: A computer program for crystal structure determination, University of Göttingen, 1977.

50 *International Tables of X-Ray Crystallography*, Kynoch Press, Birmingham, UK, 1974.