

Activation volumes for intramolecular oxidative C–X (X = H, F, Cl or Br) addition to platinum(II) imine complexes as a proof of the intimate mechanism*

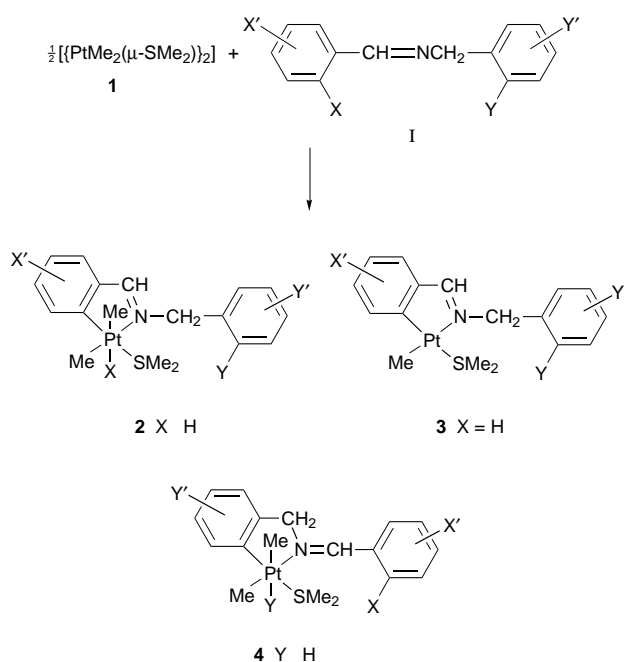
Margarita Crespo, Manuel Martinez and Esther de Pablo

Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Spain

The kinetics of C–X (X = H, F, Cl or Br) bond activation of ring-substituted, PhCHNCH₂Ph, type imines *via* intramolecular oxidative addition to platinum(II) complexes has been studied in acetone and toluene solution at different temperatures and pressures. Although the activation parameters determined are within the range expected, the latter is extremely large (ΔH^\ddagger from 25 to 70 kJ mol⁻¹, ΔS^\ddagger from -220 to -45 J K⁻¹ mol⁻¹, ΔV^\ddagger from -31.2 to -9.5 cm³ mol⁻¹). No differences were found for the reactions carried out in acetone or toluene, indicating that no polar transition state is formed during the reaction and that a common highly ordered three-centred C–Pt–X interaction is present for all the imines used. A good correlation was also obtained for the ΔS^\ddagger and ΔV^\ddagger values, independently of the solvent used, confirming the non-polarity of the transition state. A deviation from this pattern is observed only for fluorinated imines both in acetone and toluene solutions; this result is interpreted by considering an earlier transition state for the oxidative addition of C–F that has not yet produced an important volume contraction of the platinum centre despite the important spacial organization of the ligand, as shown by the very negative values of ΔS^\ddagger .

Cyclometallation reactions are well established procedures for C–X bond activation in many mononuclear co-ordination compounds of d⁸ metal centres.¹ Such reactions for dinuclear rhodium(II) complexes have also been studied, and the results seem to be in good agreement.² The mechanisms involved are fairly well studied and understood.^{1d,3} Electrophilic substitution on the carbon or oxidative addition of the C–X bond to the metal centre is operative, depending on the nature of the metal centre and/or the ligands present.⁴ We have been interested in studies of cyclometallation reactions of platinum(II) complexes by imines as shown in Scheme 1. In these cases the reactions occur *via* an oxidative addition of the C–X bond to the platinum(II) centre producing a platinum(IV) complex.⁵ Surprisingly, although the thermal activation parameters are found to be very sensitive to the nature of the activated C–X bond (X = H, F, Cl or Br)^{5b} and its position (*endo versus exo* metalacycles, products **2** or **4**),^{5a} no important differences in the oxidative-addition mechanisms are apparent. Despite the fact that extremely large differences exist in the nature of the activated C–X bonds, for all the reactions studied, a good isokinetic relationship is obtained, indicating that the mechanisms operating are the same.^{5c} The above-mentioned differences in the C–X bonds would normally preclude such uniformity in the intimate mechanism for the addition.

To our knowledge, no activation volumes have been determined for this type of intramolecular oxidative-addition reactions. This fact together with the well established importance of the determination of such parameters as a tool for elucidation of the mechanisms involved in any reaction,⁶ and the large errors normally involved in the determination of ΔS^\ddagger values,⁷ led us to measure a series of activation volumes, ΔV^\ddagger , for the reactions depicted in Scheme 1 in acetone and toluene solution. The aim was to establish possible difference in the oxidative-addition processes, taking place in the cyclometallation reactions, which have not been detected in our previous work. In



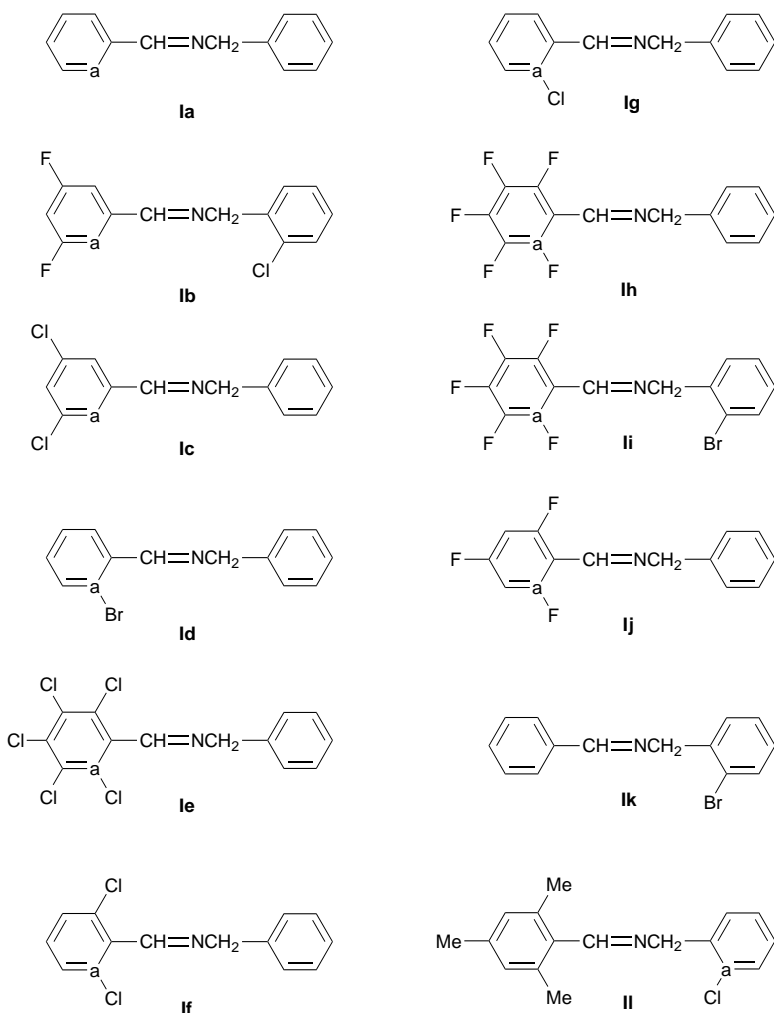
this respect we have also remeasured some of the previously determined activation parameters for the reactions in toluene solution, in order to establish further differences in the oxidative-addition mechanism. It is well established that differences in solvent polarity can tune a change in the oxidative-addition mechanism,⁸ as easily as steric hindrance⁹ or electronic changes¹⁰ in any other types of reactions.

Results and Discussion

Compounds

Reaction of the imines, prepared *via* condensation of corresponding amines and aldehydes, with the dinuclear platinum(II)

* Supplementary data available (No. SUP 57218, 11 pp.): observed and first-order rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.



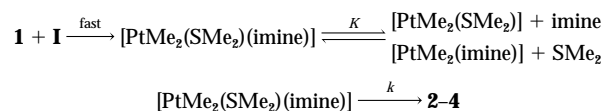
a denotes the activated proton

complex produces very cleanly the corresponding platinum(IV) complexes **2** and **4**. In cases where the activated bond is C–H the *endo* compounds **2** undergo rapid reductive elimination of methane to produce the final platinum(II) *endo* compounds **3**. All complexes, except those derived from imines **Ia** and **Ie** have been described;^{5,11} those derived from **Ia** and **Ie** have been prepared and characterized for the first time. Their structures have been assigned on the basis of the previously known data as well as their ¹H NMR spectra and coupling constants.

Even for the bulky imine **Ie**, no stable non-metallated co-ordination complexes have been detected; the subsequent metallation reaction prevents such detection, which has been achieved for the 2,4,6-Me₃C₆H₂CHNCH₂Ph imine complexes that do not undergo any C–H bond activation.^{5a} This is consistent, as found for imine **Ic**,¹¹ with the fact that, in spite of the steric hindrance that enables the detection of the 1:1 non-metallated co-ordination complex under synthetic conditions, the presence of substituents with electron-withdrawing characteristics in the *ortho* or *meta* positions of the activated bond does facilitate the oxidative-addition process. In fact the activation of C–F bonds has been achieved only for the imines having 2,4,6-F₃C₆H₂ and 2,3,6-F₃C₆H₂ moieties, while no activation has been detected for the analogous 2,6-F₂C₆H₃-CHNCH₂Ph imine ligand.^{5c}

Mechanism

The reaction of [Pt₂Me₄(μ-SMe₂)₂] with several imines was studied kinetically in acetone and toluene solution by means of UV/VIS spectroscopy. The details of the spectroscopy involved have been described.⁵ A series of experiments at different imine con-



Scheme 2

centrations, temperatures and pressures has been carried out in order to determine the kinetic and activation parameters. The observed pseudo-first-order rate constants were [imine]-dependent and, when pseudo-first-order conditions were used ($[\mathbf{I}] \gg 20[\mathbf{1}]$), well-behaved first-order absorbance *versus* time traces were obtained. No dependence on the platinum complex concentration was observed in the range ($5\text{--}10 \times 10^{-4}$ mol dm⁻³). The k_{obs} values obtained as a function of imine concentration, temperature and pressure for each imine have been deposited as SUP 57218. A rate equation such as $k_{\text{obs}} = k[\text{imine}]/(K + [\text{imine}]$),^{7b} or the corresponding double-reciprocal expression $(1/k_{\text{obs}}) = (1/k) + (K/k)[\text{imine}]^{-1}$, has been associated^{5,10} with these reactions. Fig. 1 shows typical direct and double-reciprocal, plots from which the rate constants, k , as well as the equilibrium constants, K (SUP) can be derived.

The accepted sequence for the process involves a fast reaction of compound **1** with the imine ligand to yield a monomeric platinum(II) complex that is further involved in an equilibrium with a three-co-ordinated species, K (Scheme 2). These fast processes are followed by the rate-determining, k , oxidative-addition reaction.⁵ The nature of the equilibrium constant K is not simple and further equilibria involving the co-ordinated SMe₂ have also been shown to be operative in the overall pro-

Table 1 First-order rate constants and activation parameters for the imine bond-activation reactions studied in acetone and toluene solution. Acetone solution thermal activation parameters from ref. 5 except for imines **Ia**, **Ic** and **Ie**

Imine	Activated bond	$10^3 k$ (1 MPa, 298 K)/s ⁻¹		ΔH^\ddagger /kJ mol ⁻¹		ΔS^\ddagger /J K ⁻¹ mol ⁻¹		ΔV^\ddagger /cm ³ mol ⁻¹ (77K)	
		Acetone	Toluene	Acetone	Toluene	Acetone	Toluene	Acetone	Toluene
Ia	C-H (<i>endo</i>)	3.4	5.4	60 ± 5	70 ± 5	-100 ± 10	-65 ± 15	-16.5 ± 0.6 (288)	-15.4 ± 0.5 (288)
Ib	C-H (<i>endo</i>)	3.4	5.0	45 ± 5	40 ± 1	-155 ± 5	-160 ± 10	-21.3 ± 0.9 (288)	-19.7 ± 0.9 (288)
Ic	C-H (<i>endo</i>)	2.4	4.2	75 ± 5	75 ± 5	-55 ± 20	-45 ± 5	-14.4 ± 0.1 (288)	-15.9 ± 0.2 (293)
Id	C-Br (<i>endo</i>)	5.9	—	50 ± 10	—	-125 ± 30	—	-22.1 ± 1.1 (298)	—
Ie	C-Cl (<i>endo</i>)	3.9	2.0	70 ± 5	70 ± 5	-70 ± 5	-70 ± 5	-11.9 ± 0.7 (293)	-14.7 ± 0.2 (293)
If	C-Cl (<i>endo</i>)	5.4	4.9	70 ± 10	65 ± 5	-70 ± 30	-80 ± 5	-13.1 ± 0.6 (288)	-18.3 ± 1 (293)
Ig	C-Cl (<i>endo</i>)	2.1	—	60 ± 10	—	-90 ± 30	—	-20.3 ± 0.7 (298)	—
Ih	C-F (<i>endo</i>)	3.4	1.9	30 ± 5	45 ± 5	-195 ± 15	-160 ± 20	-14.0 ± 0.6 (293)	-12.9 ± 1.0 (293)
Ii	C-F (<i>endo</i>)	1.3	—	35 ± 8	—	-189 ± 25	—	-9.5 ± 1.4 (298)	—
Ij	C-F (<i>endo</i>)	1.1	—	54 ± 1	—	-129 ± 4	—	-12.4 ± 0.2 (298)	—
Ik	C-Br (<i>exo</i>)	2.6	—	25 ± 5	—	-220 ± 5	—	-31.2 ± 0.7 (288)	—
Il	C-Cl (<i>exo</i>)	3.6	4.2	34 ± 2	60 ± 5	-179 ± 7	-95 ± 20	-24.6 ± 2.0 (298)	-18.3 ± 1.1 (293)

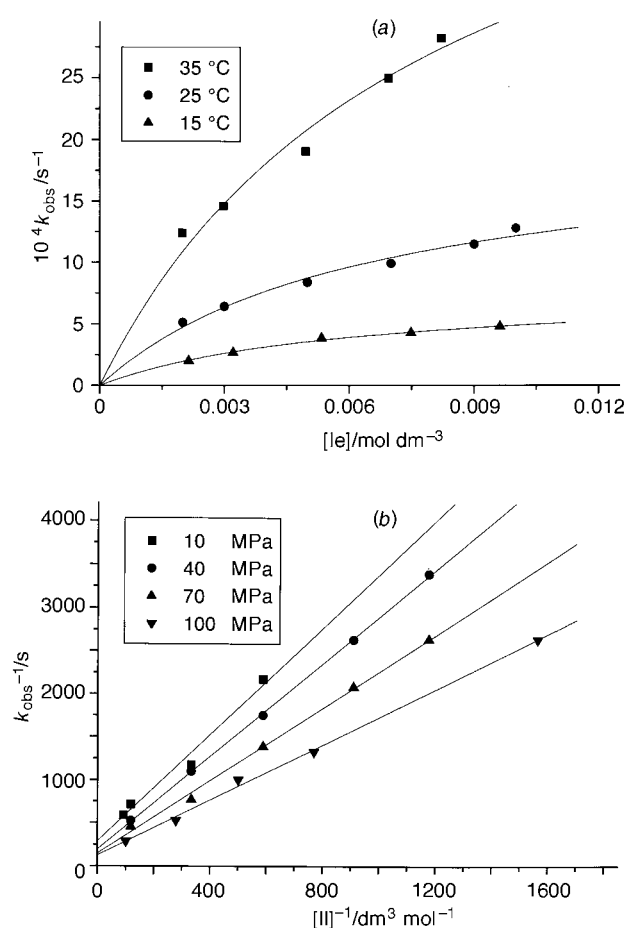


Fig. 1 Plots of (a) k_{obs} versus [imine] for the reaction of complex **1** with imine **Ie** at different temperatures in toluene solution ($P = 1$ MPa), (b) $1/k_{\text{obs}}$ versus $1/[\text{imine}]$ for the reaction of **1** with **II** at different pressures in acetone solution (25 °C)

cess;⁵ therefore the values of K [generally in the range $(4\text{--}13) \times 10^{-3}$ mol dm⁻³] have been used only in order to establish the validity of the good correlation between the direct, k_{obs} versus [imine], and the corresponding double-reciprocal plots and are not further discussed. Table 1 collects the kinetic, and thermal and pressure activation, parameters, together with previously available data, for the reactions of the imines included in this study. For some of the systems no data in toluene were calculated due in part to the fact that toluene solutions tend to be much less stable and to the fact that no meaningful differences were detected.

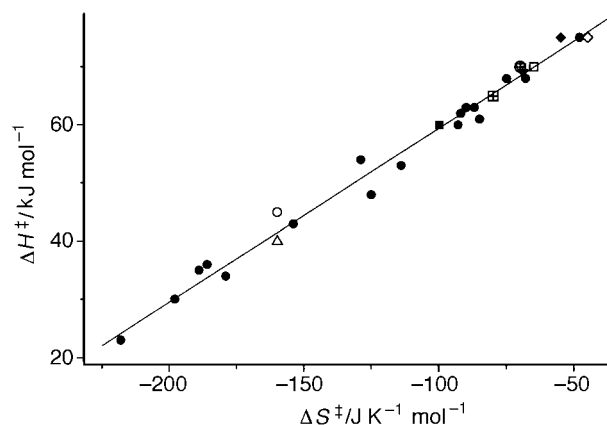


Fig. 2 Isokinetic plot for the reactions studied: ●, in acetone solution, data from ref. 5; ■ (**Ia**), ◆ (**Ic**), ▼ (**Ie**), in acetone: □ (**Ia**), △ (**Ib**), ◇ (**Ic**), ○ (**Ih**), ▽ (**Ie**), ⊕ (**If**), ⊕ (**Il**), in toluene

The values found for the enthalpy, entropy and volume of activation are in the same ranges for all the systems studied, indicating a possible common mechanism.⁵ All the entropies and volumes of activation are clearly negative, in agreement with a highly ordered transition state.^{12,13} In this sense, the existence of a very good isokinetic relationship covering a very large span of thermal activation parameters including all the C–X bond activation points to the existence of a common mechanism with a transition state having a three-centred C–Pt–X interaction.^{7b,9a} The inclusion in this plot (Fig. 2) of the values found for the systems studied in toluene solution further validates the existence of this mechanism.^{8,14} Intersection of the Eyring plots for $1/T$ values close to those used for the activation parameter determination (the isokinetic temperature derived from Fig. 2 being 20 °C) does not seem a good approach in our case. Furthermore, extrapolation to $1/T$ values dramatically out of the range in which the thermal activation parameters have been determined involves an error due to the dependence of the ΔH^\ddagger and ΔS^\ddagger values on the temperature.¹⁵

In this respect the plot shown in Fig. 3 seems much more revealing. Although there is no mathematical relationship between the ΔS^\ddagger and ΔV^\ddagger parameters it is clear that they have to be related in some way.^{6,7} In order to avoid the large errors in ΔS^\ddagger , and given the extremely good linearity of the isokinetic plot in Fig. 2, a plot of ΔV^\ddagger versus ΔH^\ddagger has been used instead to visualize the existence of a common mechanism for this series of reaction. If no important differences take place in inner or solvent rearrangement in a series of similar reactions, parallel trends should be observed for the activation enthalpy and volume of activation for the same set of reactions. This

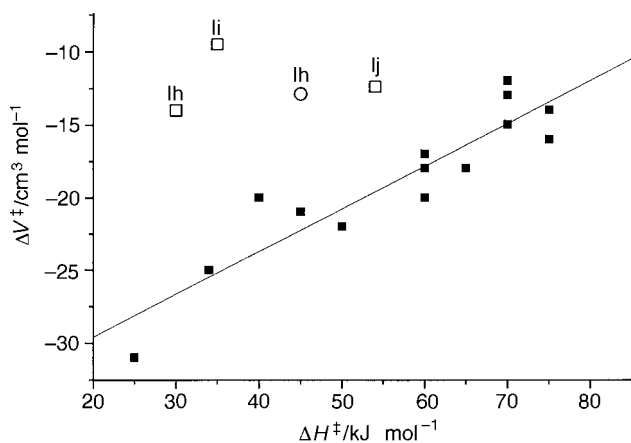


Fig. 3 Plot of ΔV^\ddagger versus ΔH^\ddagger for the reactions studied. The values for amines **lh–lj** in acetone (\square) and toluene (\circ) have not been included in the regression-zone estimation

approach has been used for series of similar substitution reactions in organometallic compounds.¹⁶ Furthermore, more recently the lack of a parallel trend has been associated with the existence of a different kind of complex–solvent interaction during outer-sphere redox reactions of cobalt(III) complexes.¹⁰

It is clear from the data plotted in Fig. 2 that no differences due to solvent polarity exist in the thermal activation parameters despite the small random changes found in the values of k , as seen in Table 1 and SUP 57218. This fact points to the existence of a common concerted mechanism, with a three-centred C–Pt–X transition state, operating for all the series of reactions studied. Although no solvent scan has been carried out¹³ (acetone and toluene relative permittivity 20.7 and 3.379 at 25 °C, respectively),¹⁷ it is clear that if a difference in mechanism that could involve a more polar, or ionic, intermediate is present, it would be perfectly evident from the activation parameters. In this respect the values found for the activation volumes are much more indicative; there is a clear parallel trend between the values of ΔH^\ddagger and ΔV^\ddagger indicating that the differences in organization (paralleled by ΔH^\ddagger , see Fig. 2) on going to the transition state are accompanied by important changes in the activation volume. The only compounds that deviate from the trend are those derived from imines leading to C–F bond activation (Fig. 3). Furthermore, the values found for ΔV^\ddagger in acetone and toluene are the same within experimental error (Table 1), again indicating that the existence of a polar, or ionic, intermediate can be disregarded.^{8,12,14,18}

The differences found for the compounds involved in C–F bond activation have to be considered in the following context. A less negative activation volume could be associated with a smaller increase in electrostriction and/or an earlier transition state in the $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^{\text{IV}}$ reaction coordinate despite a high spacial organization in the three-centred C–Pt–F interaction in the above-mentioned transition state. Since no differences are detected on changing the solvent, the first reason has to be discarded. Nevertheless, it is surprising that the parallel trend between the entropy and volumes of activation is maintained for much less electronegative X substituents (**ld** and **lk** where X = Br). As pointed out previously for these imines, the symmetry of the fluorinated benzyl ring probably plays an important role in this process;^{5c} the existence of fluorine substituents in the ring seems to produce an increase in electron density in the C–X bond which creates a transition state in which the oxidation of Pt^{II} is not as advanced as for the other complexes with the same spatial organization. In this respect, the fact that the π -donating ability of the fluorine substituent increases the strength of the C–F bond, together with the low values found for the enthalpy of activation, also points to a

transition state very much closer to the initial state than for the other systems.

Summarizing, the first study of the activation volumes of the series of intramolecular reactions depicted in Scheme 1 has proved a very interesting and powerful tool for the confirmation of the existence of a common mechanism for C–X (X = H, F, Cl or Br) bond activation *via* an oxidative-addition reaction at the platinum(II) centre. The surprising inclusion of the C–F activation reaction in the three-centred C–Pt–X mechanism is explained by the activation volumes being less negative than expected, derived from an increase in the electron density in the carbon atom which enables the transition state to occur at an earlier stage on the platinum(–II) to (–IV) oxidation coordinate.

Experimental

All UV/VIS spectra were recorded on an HP 8452A instrument equipped with a multicell holder thermostatted (± 0.2 °C) by an external circulator; NMR spectra by using Varian Gemini 200 (200 MHz) spectrometers respectively and referenced to SiMe_4 . All kinetic runs were monitored at 340 nm where the differences in absorbance between the initial and final species were large enough, and no interference from the solvent (acetone) was important. Pseudo-first-order conditions (at least a 20-fold excess of imine over the platinum dimer concentration) were used for all runs and absorbance *versus* time traces were fitted by an exponential form using the Marquardt algorithm. For runs at elevated pressure a pressurizing system and high-pressure cell, fitted on a Beckman UV5230 instrument, as described¹⁰ were used. All the k_{obs} errors were in the range of 3–5% of the actual value obtained, indicating a very good fit up to three to four half-lives. The platinum concentration was $(2\text{--}13) \times 10^{-4}$ mol dm^{-3} , achieved by the addition of small quantities (0.1–0.2 cm^3) of a concentrated stock solution (kept at -10 °C) to a previously thermostatted solution of the imine. The double reciprocal, $1/k_{\text{obs}}$ *versus* $1/[\text{imine}]$, plots were fitted by unweighted least squares. Thermal and pressure activation parameters were derived from standard Eyring and $\ln k$ *versus* P plots by the same method.^{7b}

Platinum complexes **1**, **2f–j**, **3b,c** and **4k,l** have previously been prepared and characterized; **1a–d**, **1f–l** have also been reported.^{5,11,19} The procedures were repeated when necessary. Solvents were distilled under nitrogen and stored over molecular sieves.

Compound **1e** was prepared by reaction of the corresponding aldehyde (5 mmol)† with an equimolar amount of the benzylamine in ethanol. The mixture was refluxed for 2 h and then the solvent was removed under vacuum to yield a white solid. Yield 70%; m.p. 96 °C (decomp.). ¹H NMR (CDCl_3): δ 4.94 (d, CH_2), 7.34 (m, C_6H_5) and 8.44 (t, CH).

Compounds **3a** and **2e** have been prepared for the first time by reaction of **1** (0.1 g, 0.17 mmol) and the corresponding imines, **1a** and **1e** (0.35 mmol) in acetone. The mixture was stirred for 24 h and the solvent removed under vacuum. The residue was washed and recrystallized from hexane giving light yellow compounds.

$[\text{PtMe}(\text{SMMe}_2)(\text{C}_6\text{H}_4\text{CH}=\text{NCH}_2\text{Ph})]$ **3a**: yield 60%; m.p. 110 °C (decomp.) [Found (Calc.): C, 44.3 (43.8); H, 4.7 (4.55); N, 3.0 (3.0)]. ¹H NMR [$(\text{CD}_3)_2\text{CO}$]: δ 0.84 [s, $J(\text{PtH}) = 83$, CH_3], 5.18 [s, $J(\text{PtH}) = 14$, CH_2], 7.30 (m, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$) and 8.78 [s, $J(\text{PtH}) = 56$ Hz, CH].

$[\text{PtMe}_2\text{Cl}(\text{SMMe}_2)(\text{C}_6\text{Cl}_4\text{CH}=\text{NCH}_2\text{Ph})]$ **2e**: yield 25%; m.p.

† The compound $\text{C}_6\text{Cl}_5\text{CHO}$ was prepared by reaction of $\text{Mg}(\text{C}_6\text{Cl}_5)\text{Cl}$ with CH_2O in tetrahydrofuran followed by hydrolysis and oxidation with pyridinium chlorochromate in CH_2Cl_2 .²⁰ The crude product was recrystallized from toluene after filtering through Celite. ¹H NMR (CDCl_3): δ 10.33 (s).

93 °C (decomp.) [Found (Calc.): C, 33.8 (33.1); H, 3.4 (3.1); N, 2.0 (2.1)%]. ¹H NMR [(CD₃)₂CO]: δ 1.03 [s, J(PtH) = 69.5, axial CH₃], 1.72 [s, J(PtH) = 66.5, equatorial CH₃], 2.12 [s, J(PtH) = 13.5, SMe₂], 5.29 and 5.48 [dd, AB pattern, J(HH) = 14.6, CH₂], 7.45 (m, C₆H₅) and 9.26 [s, J(PtH) = 44.0 Hz, CH].

Acknowledgements

We acknowledge financial support from Dirección General de Investigación Científica y Técnica.

References

- (a) R. R. Schrock and G. W. Parshall, *Chem. Rev.*, 1976, **42**, 243; (b) I. Omae, *Chem. Rev.*, 1979, **79**, 287; (c) I. Omae, *Coord. Chem. Rev.*, 1988, **83**, 137; (d) A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403.
- G. González, P. Lahuerta, M. Martínez, E. Peris and M. Sanaú, *J. Chem. Soc., Dalton Trans.*, 1994, 545; F. Estevan, P. Lahuerta, E. Peris, M. A. Ubeda, S. García-Granda, F. Gomez-Beltrán, E. Pérez Carreño, G. González and M. Martínez, *Inorg. Chim. Acta*, 1994, **218**, 189; F. Estevan, G. González, P. Lahuerta, M. Martínez, E. Peris and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, 1996, 1045.
- M. R. Díaz, F. Estevan, A. García-Bernabé, G. González, S. García-Granda, P. Lahuerta, M. Martínez, E. Peris, B. Tejerina and M. A. Ubeda, *New J. Chem.*, 1996, **20**, 83.
- A. J. Canty and G. van Koten, *Acc. Chem. Res.*, 1995, **28**, 406.
- M. Crespo, M. Martínez and J. Sales, (a) *Organometallics*, 1992, **11**, 1288; (b) *J. Chem. Soc., Chem. Commun.*, 1992, 822; (c) *Organometallics*, 1993, **12**, 4297.
- R. van Eldik, T. Asano and W. J. Le Noble, *Chem. Rev.*, 1989, **89**, 549.
- (a) R. van Eldik, *Inorganic High Pressure Chemistry: Kinetics and Mechanisms*, Elsevier, Amsterdam, 1986; (b) R. G. Wilkins, *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, VCH, Weinheim, 1991.
- J. A. Venter, J. G. Leipoldt and R. van Eldik, *Inorg. Chem.*, 1991, **30**, 2207.
- (a) G. González, M. Martínez, X. Solans and M. Font-Bardía, *Inorg. Chim. Acta*, 1993, **203**, 229; (b) G. González, M. Martínez, A. E. Merbach and B. Moullet, *Inorg. Chem.*, 1994, **33**, 2330; (c) G. González, M. Martínez and E. Rodríguez, *J. Chem. Soc., Dalton Trans.*, 1995, 891.
- M. Martínez, M. A. Pitarque and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, 1994, 3159; M. Martínez and M. A. Pitarque, *J. Chem. Soc., Dalton Trans.*, 1995, 4107; M. Martínez, M. A. Pitarque and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, 1996, 2665; *Inorg. Chim. Acta*, in the press.
- M. Crespo, X. Solans and M. Font-Bardía, *J. Organomet. Chem.*, 1996, **518**, 105.
- P. K. Byers, A. J. Canty, M. Crespo, R. Puddephatt and J. D. Scott, *Organometallics*, 1988, **7**, 1363.
- R. Pipoh, R. van Eldik and G. Henkel, *Organometallics*, 1993, **12**, 2236; *Organometallics*, 1993, **12**, 2668.
- H. Stieger and H. Kelm, *J. Phys. Chem.*, 1973, **77**, 290.
- W. Linert, *Chem. Soc. Rev.*, 1994, 429; A. D. Selmeczy, W. D. Jones, R. Osman and R. N. Perutz, *Organometallics*, 1995, **14**, 5677.
- S. Wieland and R. van Eldik, *Organometallics*, 1991, **10**, 3110; A. Neubrand, A. J. Poë and R. van Eldik, *Organometallics*, 1995, **14**, 3249.
- CRC Handbook of Chemistry and Physics*, 75th edn., ed. D. R. Lide, CRC, Boca Raton, FL, 1994.
- C. Dücker-Benfer, R. van Eldik and A. J. Canty, *Organometallics*, 1994, **13**, 2414.
- J. D. Scott and R. Puddephatt, *Organometallics*, 1983, **2**, 1643.
- A. I. Vogel, *Textbook of Practical Organic Chemistry*, 5th edn., Longman, Harlow, 1989, pp. 534, 590.

Received 7th October 1996; Paper 6/06872C