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Effects of chlorine substituents upon the formation, reactivity and electrochemical properties of platinum(II) and platinum(IV) metallacycles

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Abstract

The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with chlorinated ligands $Me_2NCH_2CH_2N{=}CHAr$ (Ar = C_6Cl_5 (**2a**); 2,3,6-$C_6H_2Cl_3$ (**2b**); 2,3,5-$C_6H_2Cl_3$ (**2c**); 2,4-$C_6H_3Cl_2$ (**2d**); 3,5-$C_6H_3Cl_2$ (**2e**) and 3-C_6H_4Cl (**2f**)) yield either cyclometallated [C,N,N′] platinum(IV) complexes $[PtMe_2Cl(Me_2NCH_2CH_2N{=}CHR{-}C,N,N')]$, arising from C–Cl bond activation, or cyclometallated [C,N,N′] platinum(II) complexes $[PtMe(Me_2NCH_2CH_2N{=}CHR{-}C,N,N')]$, arising from C–H bond activation, followed by methane elimination. These processes occur at room temperature except for the formation of compound $[PtMe\{Me_2NCH_2CH_2N{=}CH(3,5\text{-}C_6H_2Cl_2)\}]$ (**4e**) which is produced in refluxing toluene, since at room temperature cyclometallation of ligand **2e** is not achieved. Compound $[PtMe_2\{Me_2NCH_2CH_2N{=}CH(3,5\text{-}C_6H_3Cl_2){-}N,N')\}]$ (**3e**), arising from coordination of the ligand to the platinum center, is obtained at room temperature. The reactions of **1** with ligands $PhCH_2N{=}CHAr$ (Ar = 2,3,6-$C_6H_2Cl_3$ (**2g**) and 2,3,5-$C_6H_2Cl_3$ (**2h**)) produce cyclometallated [C,N] platinum(IV) complexes. The reactivities of the platinum complexes towards phosphines and methyl iodide have been studied. All complexes have been characterized by NMR spectroscopy and the X-ray crystal structure of $[PtMe_2Cl\{Me_2NCH_2CH_2N{=}CH(3,5\text{-}C_6H_2Cl_2){-}C,N,N'\}]$ (**4c**) has been determined. The electrochemical properties of the compounds based on cyclic voltammetry have also been studied. While the first reduction step is nearly reversible for cyclometallated platinum(II) compounds, coordination complex **3e** and cyclometallated platinum(IV) compounds exhibit an irreversible reduction wave. In all cases oxidation occurs in an irreversible manner. The processes involved and the influence of the chlorine substituents are discussed.

Keywords: Crystal structure; Cyclometallation; Electrochemistry; N-donor ligands; Platinum complexes

1. Introduction

The rapid growth of the chemistry of cyclometallated complexes is due to their successful application in organic synthesis, catalysis, and asymmetric synthesis. Moreover, cyclometallated platinum complexes showing interesting photochemical, photophysical or electrochemical properties have been reported [1].

Following our interest in cyclometallated platinum(II) and platinum(IV) complexes, containing terdentate [C,N,N′] [2–4] or bidentate [C,N] [5,6] ligands, we now report the synthesis, reactivity and electrochemical properties of new compounds obtained by the reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and chlorosubstituted imines derived from *N*,*N*-dimethylethylenediamine and *N*-benzylideneamine.

The stereo-electronic effects of chlorine substituents, involved in the regioselectivity of the C–H bond activation at platinum, have already been reported [7]. The iminic ligands selected in the present study should allow us to carry out a parallel study for C–Cl bond activation.

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Electrochemical measurements should reflect the reactivity of the compounds and provide insight into the electronic properties of the cyclometallated compounds. Cyclic voltammetry experiments were carried out on the platinum complexes and the corresponding free ligands.

2. Results and discussion

The ligands $Me_2NCH_2CH_2N{=}CHAr$ and $C_6H_5CH_2N{=}CHAr$ were prepared by reaction of the corresponding aldehyde and *N*,*N*-dimethylethylenediamine or benzylamine in toluene and characterized by ^{1}H-NMR spectra and CI mass spectra.

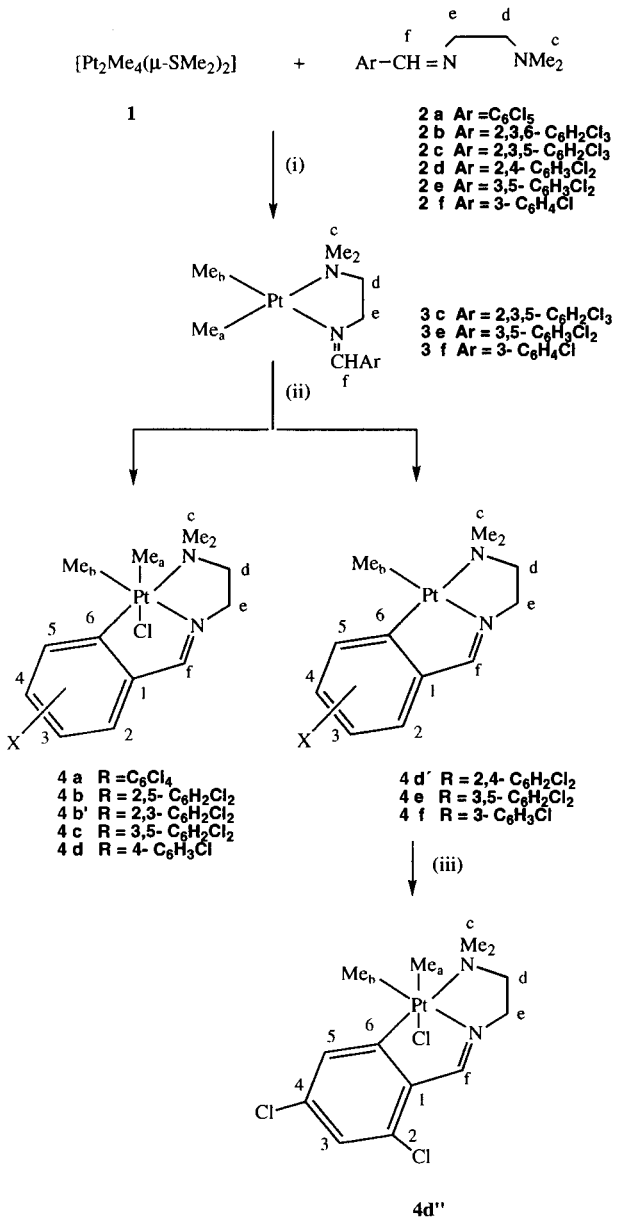
2.1. Cyclometallation reactions

The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with ligands $Me_2NCH_2CH_2N{=}CHAr$ ($Ar = C_6Cl_5$ (**2a**); 2,3,6-$C_6H_2Cl_3$ (**2b**); 2,3,5-$C_6H_2Cl_3$ (**2c**); 2,4-$C_6H_3Cl_2$ (**2d**); 3,5-$C_6H_3Cl_2$ (**2e**) and 3-C_6H_4Cl (**2f**) are summarized in Scheme 1.

For ligands **2a**, **2b** and **2c**, platinum(IV) cyclometallated compounds were obtained by oxidative addition of the *ortho* C–Cl bonds. Ligand **2b** gave an approximately equimolar mixture of cyclometallated platinum(IV) compounds **4b** and **4b′**, from which separation of the two isomers was not attempted. These arise from activation of the two non-equivalent *ortho* C–Cl bonds and, thus, the presence of a chlorine atom in the position adjacent to the C–Cl bond to be activated does not affect the metallation process.

Ligands **2c** and **2d** could in principle afford two different metallacycles, arising from the intramolecular activation of either an *ortho* C–Cl or an *ortho* C–H bond. Examples on the activation of C–H bonds at platinum in the presence of the weaker C–Cl bonds have been reported [5,7,8]. While exclusive activation of the C–Cl bond occurred for **2c**, an approximately equimolar mixture of a platinum(IV) and a platinum(II) cyclometallated compounds was obtained for **2d**. These arose, respectively, from activation of a C–Cl bond or activation of a C–H bond followed by the elimination of methane. Reductive elimination of C–H bonds from alkylhydridoplatinum(IV) compounds is well documented [9]. The elution on a SiO_2 column, using $CHCl_3/CH_3OH$ (100:1) as eluent of the reaction mixture obtained from **2d** allowed the isolation of a pure sample of $[PtMe_2Cl\{Me_2NCH_2CH_2N{=}CH(4\text{-}C_6H_3Cl)\text{-}C,N,N'\}]$ (**4d**) and of $[PtMe_2Cl\{Me_2NCH_2CH_2N{=}CH(2,4\text{-}C_6H_2Cl_2)\text{-}C,N,N'\}]$ (**4d″**) a derivative of **4d′** produced in the column.

In the same experimental conditions, ligand **2e** produced compound $[PtMe_2\{Me_2NCH_2CH_2N{=}CH(3,5\text{-}C_6H_3Cl_2)\text{-}N,N'\}]$ (**3e**) from which cyclometallated compound **4e** could only be obtained in refluxing toluene. Attempts to obtain several other compounds $[PtMe_2\{Me_2NCH_2CH_2N{=}CHR\text{-}N,N'\}]$ were carried out for R = 2,3,5-$C_6H_2Cl_3$ (**3c**) and 3-C_6H_4Cl (**3f**); these complexes were detected by ^{1}H-NMR in acetone solution but could not be isolated in a pure form since subsequent metallation took place. For instance, cyclometallated compound **4f** was formed readily at room temperature and consists of a single isomer which is assumed to result from C–H bond activation at the less hindered position. This result, together with the more



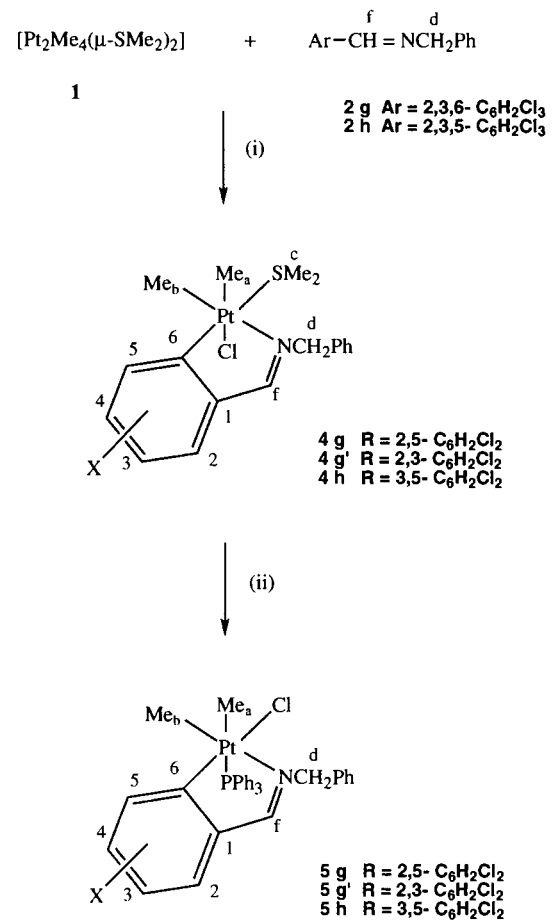
Scheme 1. (i) Acetone, r.t., 30 min; (ii) acetone or toluene r.t., 16 h, except for 4e, refluxing toluene, 2 h; (iii) elution of the reaction mixture from ligand 2d on a SiO_2 column using $CHCl_3$/MeOH (100/1).

drastic conditions required to produce C–H bond activation at ligand **2e** suggests that the stereo–electronic effects of a chlorine substituent in an adjacent position, though irrelevant in C–Cl bond activation as observed for **2b**, may be decisive in the regioselectivity of C–H bond activation.

Moreover, the presence of a chlorine substituent, adjacent to the *ortho* C–H in **2c**, may be responsible for the exclusive C–Cl bond activation observed for this ligand, in contrast to the competition between C–H and C–Cl bond activation observed for **2d**.

It has been previously shown that a concerted mechanism with a transition state having a three-centered C–Pt–X interaction operates for intramolecular activation of both C–Cl and C–H bonds at platinum [2,10]. It seems, however, that the factors governing these processes are not entirely similar and activation of C–H bonds is more sensitive to the stereo–electronic effects of an adjacent chlorine substituent than activation of a C–Cl bond. Therefore, both regio- and chemoselectivity can be tuned on these grounds. We tentatively suggest that the chlorine atom Cl(5) hinders C–H bond activation, since reductive elimination of methane, the driving force of C–H bond activation, would be inhibited by the presence of a chlorine atom in such position.

In order to compare potentially bidentate [C,N] and terdentate [C,N,N′] systems, the reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with ligands bearing a single nitrogen donor atom such as $PhCH_2N{=}CHAr$ ($Ar = 2,3,6\text{-}C_6H_2Cl_3$ (**2g**) and $2,3,5\text{-}C_6H_2Cl_3$ (**2h**)) were also studied, as summarized in Scheme 2.



Scheme 2. (i) Acetone, r.t., 16 h; (ii) $+PPh_3$, toluene, 30 min.

Ligand **2g** produced an approximately equimolar mixture of cyclometallated compounds **4g** and **4g′** arising from activation of the two non-equivalent *ortho* C–Cl bonds, while a single compound **4h**, arising from exclusive C–Cl bond activation, was formed for **2h**.

These results, together with those previously reported for ligands $PhCH_2N{=}CHAr$ ($R = 2,4\text{-}C_6H_3Cl_2$; $3,5\text{-}C_6H_3Cl_2$ and $3\text{-}C_6H_4Cl$) [7], indicate that the regio- and chemoselectivity of the reaction are unaffected by the presence of one or two nitrogen donor atoms in the ligand. However, for sterically crowded aryl groups such as $3,5\text{-}C_6H_3Cl_2$, the metallation requires more drastic conditions for the terdentate than for the bidentate ligand system, since vacant sites are necessary for bond activation to occur, consistent with the proposed mechanism for related processes [2].

Elemental analysis and FAB mass spectra of compound **3e** and compounds **4** are consistent with the proposed formulae. Selected ^{1}H-NMR data are given in Table 1.

For compounds **3**, two methylplatinum resonances were observed with ^2J(HPt) values of ca. 92 Hz for methyl *trans* to NMe_2 and ca. 85 Hz for methyl *trans* to imine. The NMe_2 and the imine protons are also coupled with ^{195}Pt, thus showing the coordination of both nitrogen atoms to the metal center.

The coupling constants for both methylplatinum and imine protons in cyclometallated platinum(IV) compounds were lower than in compounds **3**. One single methylplatinum resonance, coupled to ^{195}Pt, appears in the ^{1}H-NMR spectra of cyclometallated platinum(II) compounds. A reduction in J(CPt) for methyl and iminic carbon atoms is also observed when comparing ^{13}C-NMR data for platinum(IV) and platinum(II) compounds.

The ^{1}H-NMR data for cyclometallated compounds (Table 1) show a downfield shift for the methylplatinum resonances when a chlorine atom is present at C(5). Similarly, a chlorine atom at C(2) produces a downfield shift of the imine resonance. As previously reported [7], this indicates CH…Cl interactions between methyl groups and Cl(5), and between the imine proton and Cl(2). This result allows the assignment of the resonances due to compounds **4b** and **4b′**, and those due to compounds **4g** and **4g′**. A similar effect has been reported for fluorinated derivatives [11].

Table 1
Selected ^{1}H-NMR data[a]

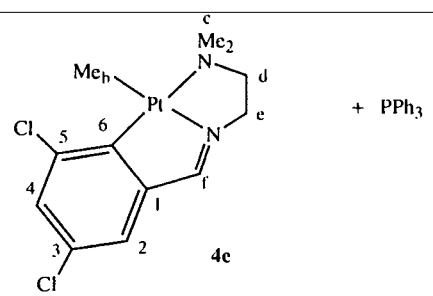
	$\delta(Me_a)[^2J(HPt)]$	$\delta(Me_b)[^2J(HPt)]$	$\delta(CH{=}N)[^3J(HPt)]$
$[PtMe_2\{Me_2NCH_2CH_2N{=}CHAr\}]$[b]			
R = 2,3,5-$C_6H_2Cl_3$ (**3c**)	−0.12 (92)	0.45 (86)	9.41 (43)
R = 3,5-$C_6H_3Cl_2$ (**3e**)	0.02 (92)	0.45 (86)	9.19 (44)
R = 3-C_6H_4Cl (**3f**)	0.06 (92)	0.45 (85)	9.17 (45)
$[PtMe_2Cl\{Me_2NCH_2CH_2N{=}CHR\}]$[c]			
R = C_6Cl_4 (**4a**)	0.79 (73)	1.39 (61)	9.41 (44)
R = 2,5-$C_6H_2Cl_2$ (**4b**)	0.74 (74)	1.38 (62)	9.26 (43)
R = 2,3-$C_6H_2Cl_2$ (**4b′**)	0.56 (73)	0.92 (63)	9.15 (43)
R = 3,5-$C_6H_2Cl_2$ (**4c**)	0.72 (74)	1.38 (62)	8.89 (43)
R = 4-C_6H_3Cl (**4d**)	0.56 (73)	0.94 (64)	8.74 (47)
R = 2,4-$C_6H_2Cl_2$ (**4d″**)	0.57 (73)	0.92 (63)	9.08 (43)
$[PtMe\{Me_2NCH_2CH_2N{=}CHR\}]$			
R = 2,4-$C_6H_2Cl_2$ (**4d′**)		−0.83 (79)	9.13 (64)
R = 3,5-$C_6H_2Cl_2$ (**4e**)		−1.15 (78)	8.93 (55)
R = 3-C_6H_3Cl (**4f**)		−0.82 (80)	8.77 (61)
$[PtMe_2I\{Me_2NCH_2CH_2N{=}CHR\}]$[c]			
R = 3-C_6H_3Cl (**7f**)	0.75 (72)	1.15 (65)	8.71 (49)
$[PtMe_2Cl\{PhCH_2N{=}CHR\}(SMe_2)]$[c]			
R = 2,5-$C_6H_2Cl_2$ (**4g**)	1.04 (70)	1.75 (67)	9.17 (43)[d]
R = 2,3-$C_6H_2Cl_2$ (**4g′**)	0.83 (70)	1.19 (67)	9.12 (48)[d]
R = 3,5-$C_6H_2Cl_2$ (**4h**)	1.01 (70)	1.75 (67)	8.84 (42)

[a] δ in parts per million, J in Hertz, solvent acetone-d^6.
[b] Me_a *trans* to NMe_2, Me_b *trans* to imine.
[c] Me_a *trans* to Cl or I, Me_b *trans* to imine.
[d] Imine resonances for compounds **4g** and **4g′** could not be unambiguously assigned.

2.2. Crystal structure of *4c*

The structure consists of the packing of four independent molecules in the asymmetric unit separated by van der Waals interactions. Molecule 1, shown in Fig. 1, corresponds to one enantiomer and molecules 2, 3 and 4 correspond to the opposite.

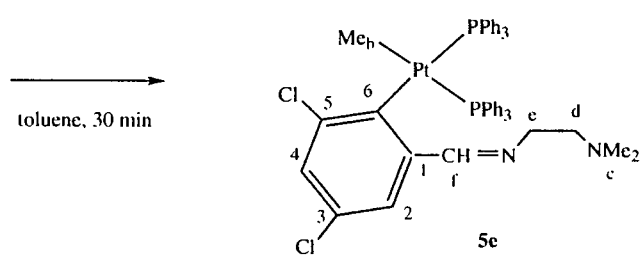
In all four molecules, the coordination around the platinum atom is essentially octahedral, with three carbon atoms in *fac* geometry and the terdentate ligand in *mer* geometry. The quasi-planarity of the metallacycle is limited to atoms N(2), C(3), C(4) and C(9), with platinum lying at a distance between 0.180 (molecule 2) and 0.298 Å (molecule 4) from the plane defined by those atoms. In the PtN(1)C(1)C(2)N(2) ring, C(1) lies between 0.550 (molecule 2) and 0.629 Å (molecule 4) from the plane defined by the remaining four atoms.



Selected bond parameters for molecule 1, equal within experimental error [3σ] to those for the remaining three molecules, are given in Table 2 and are within the expected range. However, the previously reported structure of compound $[PtMe_2Cl\{Me_2NCH_2CH_2CH{=}N(2\text{-}C_6H_3Cl)\text{–}C,N,N'\}]$ consists of a single enantiomer [2].

2.3. Reactivity of cyclometallated compounds

As shown below, the reaction of compound **4e** with triphenylphosphine in a 1:2 molar ratio in toluene solution gave compound **5e**, in which both nitrogen atoms were displaced by two equivalents of PPh_3.



Attempts to obtain a cyclometallated compound containing only one equivalent of PPh_3 were unsuccessful. In contrast, the reaction of compound **4f** with triphenylphosphine, in the same reaction conditions,

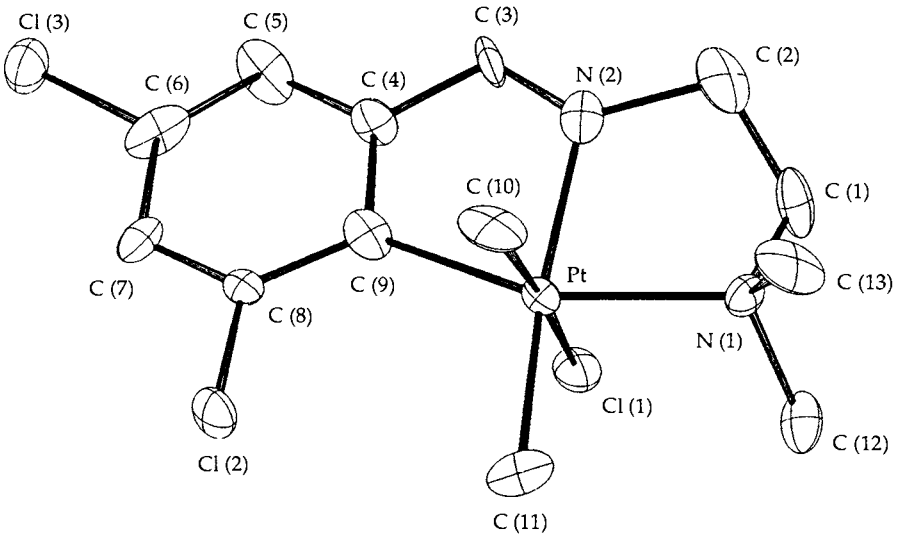


Fig. 1. Molecular structure of compound **4c**.

gave cyclometallated compound **5f**, in which only the NMe_2 moiety is displaced by PPh_3, as shown in Scheme 3.

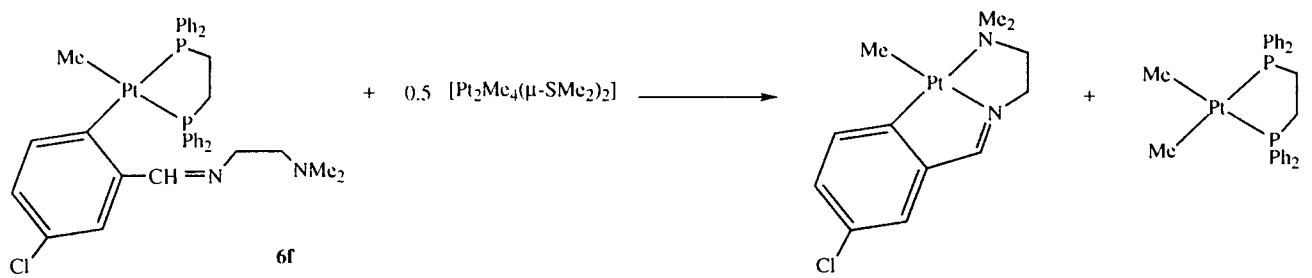
The differences in reactivity towards triphenylphosphine can be attributed to the presence of a chlorine atom in the position adjacent to the Pt–C_{aryl} bond in **4e**. The cleavage of the metallacycle would relieve the steric repulsion between the methyl group and Cl(5) in the coordination sphere of platinum. Analogous results have been reported for fluorinated derivatives [4,11]. However, in spite of the presence of a chlorine substituent at position 5, PPh_3 did not produce the cleavage of the metallacycle for platinum(IV) compounds **4h** and **4g**/**4g′** (see Scheme 2), and this is likely due to the harder nature of platinum(IV) when compared with platinum(II).

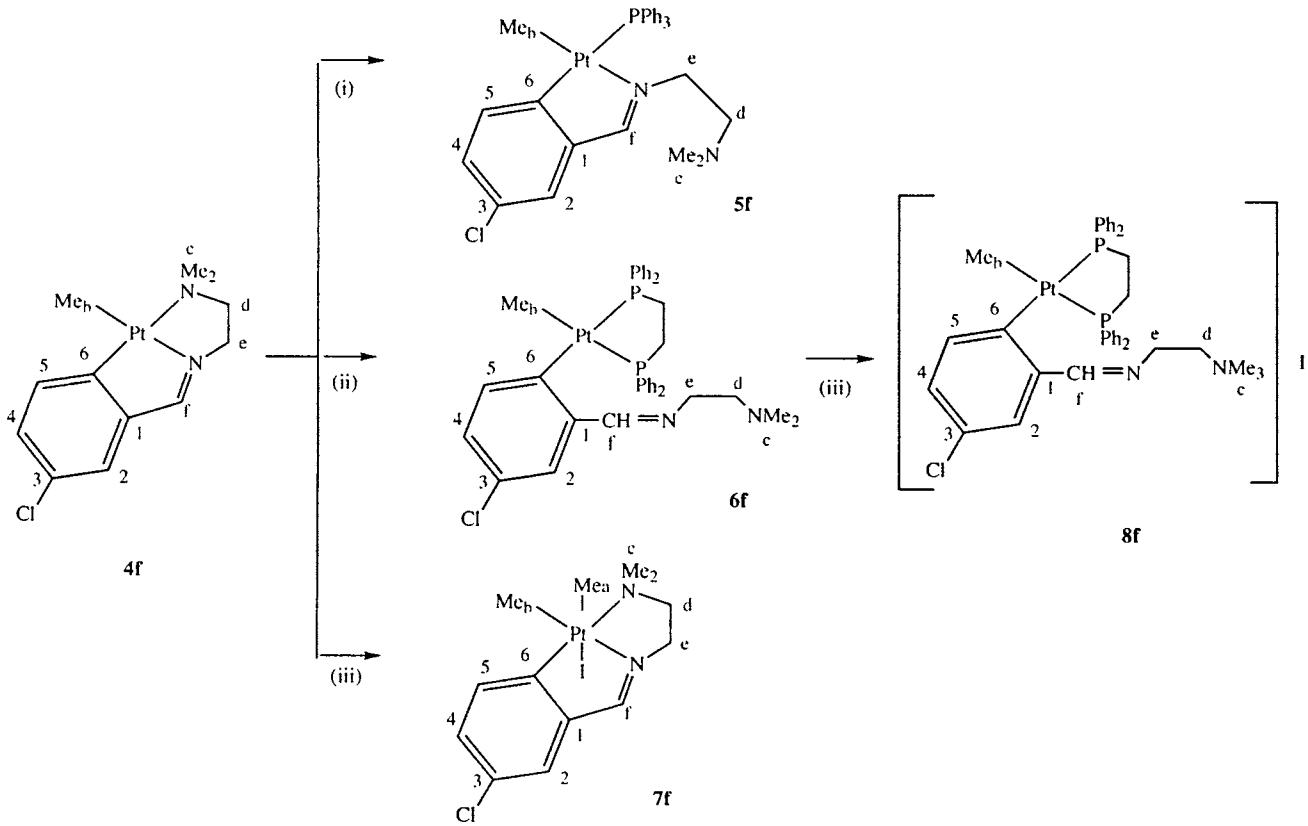
Both NMe_2 and iminic nitrogen in **4f** were readily displaced upon reaction with a chelating phosphine such as bis(diphenylphosphino)ethane (dppe) in a (1:1) molar ratio in toluene to yield compound **6f** (see Scheme 3). Displacement of the phosphine and recoordination of both nitrogen atoms was achieved by reaction with **1**, as shown below:

As shown in Scheme 3, reactions of **4f** and **6f** with an excess of methyl iodide gave, respectively, cyclometallated platinum(IV), compound **7f** and ionic platinum(II), compound **8f**. It is well known that the nitrogen

Table 2
Selected bond lengths (Å) and angles (°) for Compound 4c (molecule 1)

Pt–C(11)	2.04(3)	N(1)–C(1)	1.47(5)
Pt–C(9)	2.04(4)	N(2)–C(3)	1.26(4)
Pt–C(10)	2.06(4)	N(2)–C(2)	1.52(5)
Pt–N(2)	2.09(3)	C(1)–C(2)	1.50(6)
Pt–N(1)	2.23(3)	C(3)–C(4)	1.38(4)
Pt–Cl(1)	2.469(8)	C(4)–C(9)	1.38(4)
C(11)–Pt–C(9)	107(2)	C(10)–Pt–Cl(1)	173.8(14)
C(11)–Pt–C(10)	89(2)	N(2)–Pt–Cl(1)	87.5(8)
C(9)–Pt–C(10)	86(2)	N(1)–Pt–Cl(1)	91.0(8)
C(11)–Pt–N(2)	174(2)	C(1)–C(2)–N(2)	107(3)
C(9)–Pt–N(2)	78.6(12)	C(1)–N(1)–Pt	103(2)
C(10)–Pt–N(2)	91(2)	C(3)–N(2)–Pt	113(2)
C(11)–Pt–N(1)	93(2)	C(2)–N(2)–Pt	114(3)
C(9)–Pt–N(1)	159.6(11)	N(1)–C(1)–C(2)	114(4)
C(10)–Pt–N(1)	95(2)	N(2)–C(3)–C(4)	120(3)
N(2)–Pt–N(1)	80.9(11)	C(3)–C(4)–C(9)	116(3)
C(11)–Pt–Cl(1)	93.7(10)	C(4)–C(9)–Pt	112(3)
C(9)–Pt–Cl(1)	88.2(9)		





Scheme 3. (i) $+PPh_3$, toluene, r.t., 30 min; (ii) + dppe, toluene, r.t., 30 min; (iii) $+CH_3I$, acetone, r.t., 2 h.

donor atoms enhance the nucleophilic nature of the platinum center [12] and, thus, oxidative addition at the metal occurs readily at **4f** but does not take place for the phosphine derivative **6f**. On the other hand, addition of methyl iodide to the dangling NMe_2 group, yielding a trimethylammonia compound, occurs for **6f** but is prevented when this group is coordinated to the platinum center. It is worth pointing out that dissociation and alkylation of the amine arm has been reported for analogous reactions at cyclometallated platinum compounds [13].

Elemental analysis and FAB mass spectra of compounds **5**, **6**, **7**, and **8** are consistent with the proposed formulae. Selected ^1H and ^{31}P-NMR data are given in Table 3.

Table 3
Selected ^1H and ^{31}P-NMR data for the phosphine derivatives[a]

	δ(Me)[^2J(HPt)][^3J(HP)]	δ(CH=N) [^3J(HPt)]	δ(P)[^1J(PPt)][^2J(PP)]
[PtMe{$Me_2NCH_2CH_2N$=CH(3,5-$C_6H_2Cl_2$)}(PPh_3)$_2$] (**5e**)	0.29 (66) (6)	9.50 (10)	25.76 (2165) (14), 25.51 (2020) (14)
[PtMe{$Me_2NCH_2CH_2N$=CH(3-C_6H_3Cl)}(PPh_3)] (**5f**)	0.76 (82) (7)	8.54 (55)	30.50 (2226)
[PtMe{$Me_2NCH_2CH_2N$=CH(3-C_6H_3Cl)}(dppe)] (**6f**)	0.55 (70) (8)	8.67 (10)	45.38 (1722), 46.46 (1883)
[PtMe{$Me_2NCH_2CH_2N$ = CH(3-C_6H_3Cl)}(dppe)]I (**8f**)	0.47 (70) (7)	8.60 (10)	45.58 (1721), 46.97 (1905)
[$PtMe_2Cl$\{$PhCH_2N$=CH(3,5-$C_6H_2Cl_2$)}(PPh_3)] (**5h**)	1.08 (59) (8)[b], 2.04 (68) (8)[c]	7.71 (41)	−5.32 (982)
[$PtMe_2Cl$\{$PhCH_2N$=CH(2,5-$C_6H_2Cl_2$)}(PPh_3)] (**5g**)	1.08 (59) (8)[b], 1.90 (66) (8)[c]	8.34 (45)[d]	−5.40 (972)[d]
[$PtMe_2Cl$\{$PhCH_2N$=CH(2,3-$C_6H_2Cl_2$)}(PPh_3)] (**5g′**)	0.89 (55) (8)[b] 1.36 (68) (8)[c]	8.20 (52)[d]	−5.85 (991)[d]

[a] δ in parts per million, J in Hertz, solvent $CDCl_3$ (**5f, 6f**, **8f**, **5h**) or acetone-d^6 (**5e**).[b] Me *trans* to PPh_3.[c] Me *trans* to imine.[d] Resonances for compounds **5g** and **5g′** could not be unambiguously assigned.

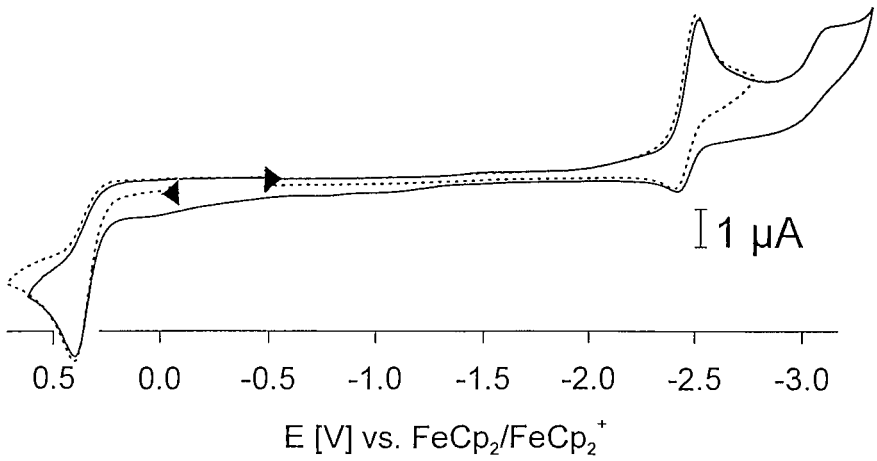


Fig. 2. Cyclic voltammogram of **4f** in THF/0.1M Bu_4NPF_6 at 100 mV s^{-1} scan rate.

The methylplatinum resonance is coupled with one phosphorus atom for compound **5f**, and with two non-equivalent phosphorus atoms for compounds **5e**, **6f** and **8f**. For the latter compounds, the value of the coupling constant to platinum is smaller than for **5f** since the *trans* influence of the phosphine is greater than that of the imine. The small value (ca. 10Hz) of the coupling of the iminic hydrogen to ^{195}Pt can be taken as evidence for the decoordination of the imine group. For compound **5h**, two methylplatinum resonances, coupled with the phosphorus atom, were observed and the decrease in the coupling constant of the axial methyl with platinum suggests that the PPh_3 is *trans* to this group.

One single resonance appears in the ^{31}P-NMR spectra of compounds **5f** and **5h**, and the value of the coupling to ^{195}Pt for the platinum(IV) is lower than that for the platinum(II) compounds. Resonances due to two non-equivalent phosphorus atoms, both coupled to platinum, appear for compounds **5e**, **6f** and **8f**, and J(PP) coupling is observed for **5e**.

2.4. Electrochemical measurements

The ability of the complexes to gain or lose electrons was studied by cyclic voltammetry at various temperatures. Previously reported compounds $Me_2NCH_2CH_2N{=}CHPh$ (**2i**) and [PtMe{$Me_2NCH_2CH_2N{=}C$-HC_6H_4-C,N,N'}] (**4i**) [2] were also included in this study. Fig. 2 shows a typical cyclic voltammogramm for the cyclometallated platinum(II) complexes, Fig. 3 shows an example of the experiments at variable temperature and Tables 5 and 6 contain the electrochemical data.

At low scan rates, the first reduction wave of the cyclometallated platinum(II) complexes **4e**, **4f** and **4i** display only partial chemical reversibility. At 100 mV s^{-1}, the measured peak current ratios (i_{pc}/i_{pa}) vary from 0.7 to 0.9. The peak-to-peak separation (ΔE_{pp}) lies in all three cases in the same range as for an added equimolar amount of ferrocene. At higher scan rates (>500 mV s^{-1}) the peak current ratios are always higher than 0.95. The first electrochemical reduction process involves one

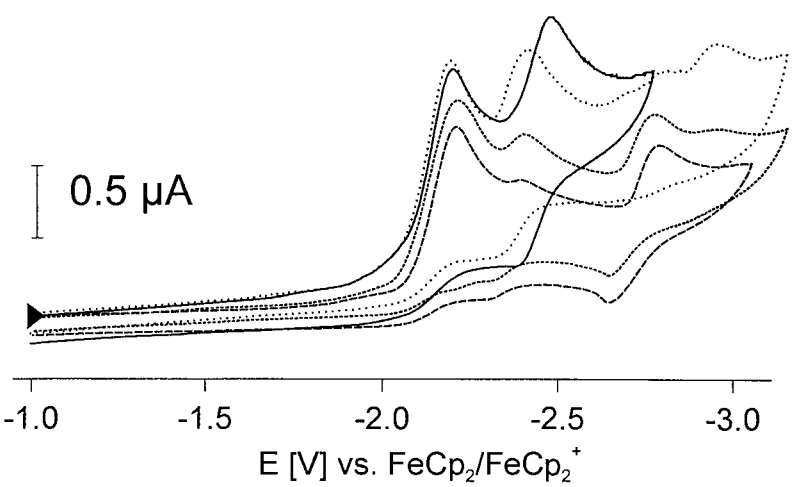


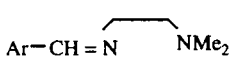
Fig. 3. Cyclic voltammogram of **4c** in THF/0.1M Bu_4NPF_6 at 100 mV s^{-1} scan rate, at 25°C (—), at −10°C (· · · · · ·), at −30°C (-----) and at −50°C (– – – –).

Table 4
Crystallographic data and details of the refinements for Compounds 4c

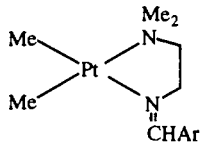
Formula	$C_{13}H_{19}Cl_3N_2Pt$
FW	504.74
Crystal System	Orthorhombic
Space group	$Pbc2_1$
a, b, c (Å)	7.372(7), 27.951(11), 31.344(4)
α, β, γ (°)	90
V (Å^3)	6459(7)
D_c (g cm^{-3})	2.076
Z	16
$F(000)$	3840
Crystal size (mm^3)	$0.1 \times 0.1 \times 0.2$
λ(Mo–K$_\alpha$) (Å)	0.71069
T (K)	293(2)
No. of reflections collected	9687
R	0.067
$Rw(F^2)$	0.159
No. of refined parameters	687
Max. shift /esd	0.1
Max./min. difference peaks (e Å^{-3})	0.716/−0.374

electron as confirmed by comparison of the peak currents of equimolar amounts of ferrocene. The first reduction wave is followed by an irreversible second reduction wave. On the anodic side, an irreversible oxidation wave occurs in all cases. The first reduction potentials are markedly less negative than those of the corresponding free ligands and decrease in the order **4e** > **4f** > **4i** according to the decreasing number of chlorine substituents, thus reflecting their inductive electron-withdrawing ability. The oxidation potentials follow the same trend, although variations are smaller. The comparison between dimethylplatinum complex **3e** and its cyclometallated analog **4e** reveals that the oxidation potential of the former is much lower and comparable to that of the complex [$PtMe_2$(tmeda)] (tmeda = N,N,N′,N′-tetramethylethylenediamine), which lies at 0.19 V [14], whereas the reduction potential lies higher and turns out to be irreversible, most probably due to a fast chemical reaction following the reduction. Interestingly, **3e** exhibits quasi-reversible reduction processes at lower temperature. The peak-to-peak separation (ΔE_{pp}) are markedly higher than those of an added ferrocene sample. At 20°C, **3e** exhibits a second reversible reduction, that could be attributed to the product of the chemical process following the first reduction. At 10°C, anodic return waves were detected for both cathodic waves. The ratio of anodic and cathodic peak currents ($i_{pa}/i_{pc} = 0.73$) for the first wave indicates that, under these conditions, the chemical reaction following the electrode process is still operative. Upon cooling to −20°C, the chemical reaction is

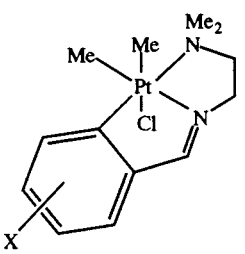
Table 5
Electrochemical data of free ligands and platinum complexes[a]



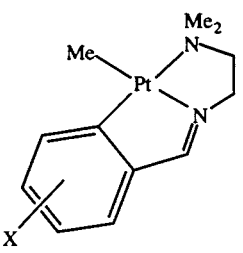
2 a Ar = C_6Cl_5
2 c Ar = 2,3,5- $C_6H_2Cl_3$
2 e Ar = 3,5- $C_6H_3Cl_2$
2 f Ar = 3- C_6H_4Cl
2 i Ar = C_6H_5



3 e Ar = 3,5- $C_6H_3Cl_2$



4 a R = C_6Cl_4
4 c R = 3,5- $C_6H_2Cl_2$



4 e R = 3,5- $C_6H_2Cl_2$
4 f R = 3- C_6H_3Cl
4 i R = C_6H_4

Compound	E^b_{pa}Ox1	$E_{1/2}$Red1 (ΔE_{pp})[c]	$E_{1/2}$Red2 (ΔE_{pp})	E^d_{pc}Red3
2a	0.49	−2.31 irr.[d]	−2.47 irr.[d]	−2.68
2c	0.47	−2.25 irr.[d]	−2.47 irr.[d]	−2.67
2e	0.65	−2.71 irr.[d]	−2.96 irr.[d]	−3.19
2f	0.48	−2.67 irr.[d]	−2.81 (75)	−3.41
2I	0.55	−3.04 irr.[d]		
3e	0.20	−2.42 irr.[d]	−2.59 irr.[d]	
4a	0.38	−2.00 irr.[d]	−2.36 irr.[d]	−2.47
4c	0.44	−2.11 irr.[d]	−2.32 (78)	−2.67
4e	0.47	−2.39 (91)	−3.12 irr.[d]	
4f	0.43	−2.45 (92)	−3.15 irr.[d]	
4I	0.35	−2.68 (73)	−3.45 irr.[d]	

[a] From cyclic voltammetry in THF/0.1M Bu_4NPF_6 at ambient temperature, potentials in V versus $FeCp_2^{0/+}$, scan rate 100 mV s^{-1}. [b] Anodic peak potential for irreversible oxidation.[c] Peak-to-peak separation $\Delta E_{pp} = E_{pc} - E_{pa}$ (mV).[d] Cathodic peak potential for irreversible reduction.

Table 6
Electrochemical data of platinum complexes at variable temperature[a]

Compound	$E_{1/2}$Red1 (ΔE_{pp})[b]	$E_{1/2}$Red2(ΔE_{pp})	E^{c}_{pc}Red3	E^{c}_{pc}Red4	ΔE_{pp} $FeCp_2^{+/0}$	T (°C)
3e	−2.42 irr.[c]	−2.59 irr.[c]			92	25
3e	−2.31 irr.[c]	−2.40 (108)	−3.02		99	20
3e	−2.24 (168)	−2.42 (135)	−3.09		87	10
3e	−2.26 (132)	−2.42 (135)	−2.82	−3.09	87	0
3e	−2.27 (120)	−2.84	−3.12		78	−10
3e	−2.30 (102)		−2.89	−3.18	81	−20
3e	−2.34 (207)		−3.05	−3.34	195	−30
3e	−2.35 (300)		−3.08	−3.41	258	−40
3e	−2.27 (258)		−3.13	−3.52	240	−50
4a	−2.00 irr.[c]	−2.36 irr.[c]	−2.47		75	25
4a	−2.04 irr.[c]	−2.33 irr.[c]	−2.47		147	−30
4a	−2.03 (212)	−2.38 (202)			198	−50
4a	−2.07 (260)	−2.36 (243)			219	−70
4c	−2.11 irr.[c]	−2.32 (78)	−2.67		78	25
4c	−2.20 irr.[c]	−2.37 (86)	−2.76 (81)		90	−10
4c	−2.27 irr.[c]	−2.40 (93)	−2.76 (126)		102	−30
4c	−2.32 irr.[c]	Obscured	−2.78 (189)		144	−50
4c	−2.49 irr.[c]	Obscured	−2.88 (242)		243	−70

[a] From cyclic voltammetry in THF/0.1M Bu_4NPF_6, potentials in V versus $FeCp_2^{0/+}$, scan rate 100 mV s^{-1}.[b] Peak-to-peak separation $\Delta E_{pp} = E_{pc} - E_{pa}$ (mV).[c] Cathodic peak potential for irreversible reduction.

totally suppressed and only the first reduction wave is detected and found to be reversible ($i_{pa}/i_{pc} = 1$).

The platinum(IV) complexes **4c** and **4a** exhibit an irreversible first reduction step followed by a partially reversible reduction reaction in the case of **4c** and an irreversible wave in the case of the higher substituted **4a**. A comparison of the measured potentials for the platinum(II) complex **4e** and its platinum(IV) analog **4c** lets us assume that the second reduction step for the latter has its slope in the first reduction of the former and the first reduction of the platinum(IV) compound must be due to a process involving the additional axial ligands. Release of chloride after reduction as a possible source for the irreversible behaviour could be excluded by experiments using large excess of chloride in the solution. At lower temperature starting from −50°C, **4a** exhibits reversible behaviour for both the first and the second reduction, the decomposition reactions being suppressed. For **4c**, the first reduction remains irreversible down to −70°C, but a third partially reversible wave appears starting from −10°C. Although the nature of the species responsible for the reduction waves following the first irreversible one is not established, they should be defined molecules, since they show defined electrochemical behaviour.

In summary, these results suggest that the reduction of the platinum(II) complexes is mainly centered on the aromatic ring system. The cyclometallation reaction leads not only to the formation of a Pt–C_{aryl} bond but also to extension of the π system to a platina–isoindole arrangement that facilitates the stabilization of the extra electron in the enlarged aromatic system. Interestingly, the aromaticity of a five-member *endo*-metallacycle fused with an aryl ring and involving the filled metal d orbitals has been proposed as the main driving force for the formation of platinum(II) and palladium(II) *endo*-metallacycles [15]. In contrast, the first reduction of the platinum(IV) complexes leads to fast decomposition of the reduced complexes most probably due to reaction at the axial ligands.

The oxidation reactions take place mainly at the platinum center yielding very unstable platinum(III) species from platinum(II) precursors. This is evidenced by the fact that the cyclometallation reaction leads to higher oxidation potentials due to the electron-withdrawing effect of the aryl group. In the case of platinum(IV) complexes, oxidation leads more likely to cleavage of the axial Pt–Me bond than to a platinum(V) species. Oxidation potentials for platinum(IV) complexes do not show the expected higher values for the increased oxidation state of platinum. Therefore, it must be concluded that the two extra ligands compensate almost exactly for the effect of the formal higher metal oxidation state. A similar result was reported for the comparable dimethylplatinum(II) and tetramethylplatinum(IV) complexes of the diazabutadienes [14].

The results reported in this paper show that the number and position of chlorine substituents are decisive both in the formation and in the reactivity of cyclometallated compounds with chlorinated aryl rings. Moreover, for cyclometallated platinum(II) compounds, the electron-withdrawing effect of the chlorine substituents is reflected for both oxidation and reduction potentials, and the latter support the proposed electronic delocalization within the metallated system.

3. Experimental details

3.1. Instrumentation

^{1}H and ^{31}P-{^{1}H}-NMR spectra were recorded by using Varian Gemini 200 (^{1}H, 200MHz), Varian 500 (^{1}H, 500MHz) and Bruker 250 (^{31}P, 101.25 MHz) spectrometers, and referenced to $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). δ values are given in ppm and J values in Hz. IR spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Microanalyses and mass spectra (CI and FAB) were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona.

Cyclic voltammetry experiments were carried out using a three-electrode configuration (glassy carbon working electrode, platinum counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator with PAR M270/250 software. As internal standard the ferrocene/ferrocenium couple ($FeCp_2^{+/0}$) was used. Ferrocene was added in equimolar amount as to estimate the electrochemical reversibility and the effects of uncompensated resistance. The temperature was adjusted using a FRYKA FT08-64 cryostat, temperature tolerance was ± 1°C. The electrochemical experiments were carried out under argon atmosphere in dried and deaerated solvents using tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) as supporting electrolyte.

3.2. Preparation of the compounds

The compound C_6Cl_5CHO [12] and the complexes $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) [16] and [PtMe{$Me_2NCH_2CH_2N$=CHC_6H_4–C,N,N'}] (**4i**) [2] were prepared according to published procedures.

3.2.1. Synthetic procedure for Compounds 2

Compounds **2** were prepared by the reaction of 5 mmol of the corresponding aldehyde with the equimolar amount of *N*,*N*-dimethylethylenediamine or benzylamine in 10 ml of toluene. After stirring for 30 min, the reaction mixture was dried over anhydrous Na_2SO_4, and the solvent was removed in a rotary evaporator to yield yellow oils (Yield 80–85%).

3.2.2. Synthetic procedure for Compounds 3

Compound **3e** was obtained by adding a solution of 127 mg (5.2×10^{-4} mol) of the imine **2e** in toluene (10ml) to a solution of 150 mg (2.6×10^{-4} mol) of compound **1** in 10 ml of toluene. The mixture was stirred for 16 h, and the orange solid was filtered, washed with hexane and dried in vacuum. Compounds **3c** and **3f** were characterized by the following procedure: a 20.0 mg (0.035 mmol) amount of complex **1** and 0.07 mmol of the corresponding imine were dissolved in 0.6 ml of acetone-d^6, and the ^{1}H-NMR spectrum was recorded.

[$PtMe_2${$Me_2NCH_2CH_2N$=$CH(3,5\text{-}C_6H_3Cl_2)$–$N,N'$}] (**3e**). Yield 200 mg (81%). Anal. Calcd. for $C_{13}H_{20}Cl_2N_2Pt$. C, 33.20; H, 4.29; N, 5.96. Found: C, 33.3; H, 4.3; N, 6.0%.

3.2.3. Synthetic procedure for Compounds 4

Compounds **4** were obtained by adding a solution of the corresponding imine in 10 ml of acetone (181 mg (**2a**), 145 mg (**2b**, **2c**), 127 mg (**2d**, **2e**), 109 mg (**2f**), or 155 mg (**2g**, **2h**), 5.2×10^{-4} mol) to a solution of 150 mg (2.6×10^{-4} mol) of compound **1** in 10 ml of acetone. The mixture was stirred for 16 h, and the solvent was removed under vacuum. The residue was washed with hexane to yield pale yellow (**4a**, **4b/b′**, **4c**, **4h**, **4g/g′**) or orange (**4f**) solids which were filtered, washed with hexane and dried under vacuum.

[$PtMe_2Cl${$Me_2NCH_2CH_2N$=CHC_6Cl_4–C,N,N'}] (**4a**). Yield 200 mg (67%). Anal. Calcd. for $C_{13}H_{17}Cl_5N_2Pt$. C, 27.22; H, 2.99; N, 4.88. Found: C, 27.6; H, 3.2; N, 3.9%. FAB(+) (NBA, m/z): 574 ([M]$^+$); 559 ([M–Me]$^+$); 544 ([M–2Me]$^+$); 524 ([M–Cl–Me]$^+$); 509 ([M–Cl–2Me]$^+$), 489 ([M–2Cl–Me]$^+$).

[$PtMe_2Cl${$Me_2NCH_2CH_2N$=CHR–C,N,N'}] (R = 2,5-$C_6H_2Cl_2$ (**4b**) and R = 2,3-$C_6H_2Cl_2$ (**4b′**)). Yield 160 mg (59%). Anal. Calcd. for $C_{13}H_{19}Cl_3N_2Pt$. C, 30.93; H, 3.79; N, 5.55. Found: C, 31.2; H, 3.9; N, 5.4%. FAB(+) (NBA, m/z): 504 ([M]$^+$); 489 ([M–Me]$^+$); 469 ([M–Cl]$^+$); 453 ([M–Cl–Me]$^+$); 438 ([M–Cl–2Me]$^+$).

[$PtMe_2Cl${$Me_2NCH_2CH_2N$=$CH(3,5\text{-}C_6H_2Cl_2)$–$C,N,N'$}] (**4c**). Yield 260 mg (98%). Anal. Calcd. for $C_{13}H_{19}Cl_3N_2Pt$. C, 30.93; H, 3.79; N, 5.55. Found: C, 31.6; H, 4.0; N, 5.8%. FAB(+) (NBA, m/z): 504 ([M]$^+$); 469 ([M–Cl]$^+$); 453 ([M–Cl–Me]$^+$); 438 ([M–Cl–2Me]$^+$).

[PtMe{$Me_2NCH_2CH_2N$ = $CH(3\text{-}C_6H_3Cl)$ – C,N,N'}] (**4f**). Yield 170 mg (77%). Anal. Calcd. for $C_{12}H_{17}ClN_2Pt$. C, 34.33; H, 4.08; N, 6.67. Found: C, 33.5; H, 4.2; N, 6.2%. FAB(+) (NBA, m/z): 419 ([M]$^+$); 403 ([M–Me]$^+$). ^{13}C-NMR (acetone-d^6): δ { − 12.5 [J(CPt) = 789], Me^b}, {48.8, Me^c}, {52.2 [J(CPt) = 30], 67.8, C^{c,d}}, {127.5 [J(CPt) = 46]; 129.6; 130.8 [J(CPt) = 74]; 134.7 [J(CPt) = 101]; 140.5 [J(CPt) = 1160]; 152.2, C^{Ar}}; 166.6 [J(CPt) = 94, C^f].

[$PtMe_2Cl${$PhCH_2N$=CHR–C,N}(SMe_2)] (R = 2,5-$C_6H_2Cl_2$ (**4g**) and R = 2,3-$C_6H_2Cl_2$ (**4g′**)). Yield 170 mg (57%). Anal. Calcd. for $C_{18}H_{22}Cl_3NSPt$. C, 36.90; H, 3.79; N, 2.39. Found: C, 36.9; H, 3.8; N, 2.7%. FAB(+) (NBA, m/z): 594 ([M]$^+$); 579 ([M–Me]$^+$); 534 ([M–Cl–Me]$^+$); 520 ([M–Cl–2Me]$^+$).

[$PtMe_2Cl${$PhCH_2N$=$CH(3,5\text{-}C_6H_2Cl_2)$–$C,N$}($SMe_2$)] (**4h**). Yield 200 mg (67%). Anal. Calcd. for $C_{18}H_{22}Cl_3NSPt$. C, 36.90; H, 3.79; N, 2.39. Found: C, 36.6; H, 3.8; N, 2.7%. FAB(+) (NBA, m/z): 594

([M]$^+$); 579 ([M−Me]$^+$); 533 ([M−Cl−Me]$^+$); 520 ([M−Cl−2Me]$^+$).

The same procedure yielded an approximately equimolar mixture of **4d**/**4d′** (190 mg). Crystallization in acetone of the reaction mixture gave a sample of pure **4d** (50 mg) and of slightly impure **4d′** (40 mg). Alternatively, elution of the reaction mixture on a SiO_2 column using $CHCl_3$/MeOH (100/1) as eluent yielded **4d** (90 mg) and **4d″** (50 mg) which were obtained by concentration under vacuum of the first and last fractions eluted, respectively.

[$PtMe_2Cl\{Me_2NCH_2CH_2N{=}CH(4\text{-}C_6H_3Cl)-C,N,N'\}$] (**4d**). Anal. Calcd. for $C_{13}H_{20}Cl_2N_2Pt$: C, 33.20; H, 4.29; N, 5.96. Found: C, 33.9; H, 4.4; N, 6.1%. FAB(+) (NBA, *m*/*z*): 470 ([M]$^+$); 455 ([M−Me]$^+$); 440 ([M−2Me]$^+$); 435 ([M−Cl]$^+$); 420 ([M−Cl−Me]$^+$); 405 ([M−Cl−2Me]$^+$). ^{13}C-NMR (acetone-d^6): δ {−3.0 [J(CPt) = 639], −3.0 [J(CPt) = 677], Me^{a,b}}, {47.4, 49.5 Me^c}, {52.4 [J(CPt) = 15], 67.1, C^{c,d}}, {124.4; 130.4 [J(CPt) = 46]; 131.2 [J(CPt) = 39]; 136.4; 143.3; 147.7, C^{Ar}}; 168.4 [J(CPt) = 49, C^f].

[$PtMe_2Cl\{Me_2NCH_2CH_2N{=}CH(2,4\text{-}C_6H_2Cl_2)-C,N,N'\}$] (**4d″**) Anal. Calcd. for $C_{13}H_{19}Cl_3N_2Pt$: C, 30.93; H, 3.79; N, 5.55. Found: C, 31.6; H, 3.7; N, 5.5%. FAB(+) (NBA, *m*/*z*): 504 ([M]$^+$); 489 ([M−Me]$^+$); 475 ([M−2Me]$^+$); 454 ([M−Cl−Me]$^+$); 437 ([M−Cl−2Me]$^+$).

[$PtMe\{Me_2NCH_2CH_2N{=}CH(3,5\text{-}C_6H_2Cl_2)-C,N,N'\}$] (**4e**) was obtained by heating under reflux for two hours a solution of 150 mg of **3e** in 10 ml of toluene. The red crystals formed after cooling to room temperature were filtered and washed with hexane. Yield 120 mg (83%). Anal. Calcd. for $C_{12}H_{16}Cl_2N_2Pt$: C, 31.73; H, 3.55; N, 6.17. Found: C, 32.2; H, 3.8; N, 6.0. FAB(+) (NBA, *m*/*z*): 439 ([M−Me]$^+$); 383 ([M−2Cl]$^+$).

3.2.4. Synthetic procedure for Compounds 5 and 6

Compounds **5** and **6** were obtained by adding one equiv. (**5f**, **5g/5g′**, **5h**) or two equiv (**5e**) of PPh_3 or one equiv. of dppe (**6f**) to a solution of 50 mg of the corresponding compound **4** in 10 ml of toluene. The mixture was stirred for 30 min, and the solvent was removed under vacuum. The residue was washed with hexane to yield orange (**5f**) or pale yellow (**5e**, **5g/5g′**, **5h**, **6f**) solids, which were filtered, washed with hexane, and dried under vacuum.

[$PtMe\{Me_2NCH_2CH_2N{=}CH(3,5\text{-}C_6H_2Cl_2)-C\}(PPh_3)_2$] (**5e**). Yield 95 mg (88%). Anal. Calcd. for $C_{48}H_{46}Cl_2N_2P_2Pt$: C, 58.90; H, 4.74; N, 2.86. Found: C, 57.9; H, 4.7; N, 2.9%.

[$PtMe\{Me_2NCH_2CH_2NCH(3\text{-}C_6H_3Cl)-C,N\}(PPh_3)$] (**5f**). Yield 73 mg (90%). Anal. Calcd. for $C_{30}H_{32}ClN_2PPt$: C, 52.83; H, 4.73; N, 4.11. Found: C, 52.1; H, 4.8; N, 4.2%. FAB(+) (NBA, *m*/*z*): 682 ([M]$^+$); 666 ([M−Me]$^+$); 455 ([M−PPh_3]$^+$).

[$PtMe_2Cl\{PhCH_2N{=}CHR-C,N\}(PPh_3)$] (R = 2,5-$C_6H_2Cl_2$ (**5g**) and R = 2,3-$C_6H_2Cl_2$ (**5g′**)). Yield 41 mg (61%). Anal. Calcd. for $C_{34}H_{31}Cl_3NPPt$: C, 51.95; H, 3.98; N, 1.78. Found: C, 52.9; H, 4.2; N, 1.8%. FAB(+) (NBA, *m*/*z*): 784 ([M]$^+$); 769 ([M−Me]$^+$); 754 ([M−2Me]$^+$); 734 ([M−Cl−Me]$^+$); 719 ([M−Cl−2Me]$^+$); 471 ([M−Cl−Me−PPh_3]$^+$).

[$PtMe_2Cl\{PhCH_2N{=}CH(3,5\text{-}C_6H_2Cl_2)-C,N\}(PPh_3)$] (**5h**). Yield 33 mg (50%). Anal. Calcd. for $C_{34}H_{31}Cl_3NPPt$: C, 51.95; H, 3.98; N, 1.78. Found: C, 51.1; H, 4.0; N, 1.9%. FAB(+) (NBA, *m*/*z*): 784 ([M]$^+$); 769 ([M−Me]$^+$); 750 ([M−Cl]$^+$); 735 ([M−Cl−Me]$^+$); 719 ([M−Cl−2Me]$^+$); 472 ([M−Cl−Me−PPh_3]$^+$); 456 ([M−Cl−2Me−PPh_3]$^+$).

[$PtMe\{Me_2NCH_2CH_2N{=}CH(3\text{-}C_6H_3Cl)-C\}$(dppe)] (**6f**). Yield 64 mg (66%). Anal. Calcd. for $C_{38}H_{41}ClN_2P_2Pt$: C, 55.12; H, 5.13; N, 3.47. Found: C, 54.2; H, 5.0; N, 3.2%. FAB(+) (NBA, *m*/*z*): 818 ([M]$^+$); 803 ([M−Me]$^+$); 592 ([Pt(ddpe)]$^+$).

3.2.5. Synthetic procedure for Compounds 7 and 8

Compounds **7f** and **8f** were prepared by adding an excess of methyl iodide (0.1 ml) to a solution of 50 mg (0.068 mmol) of the compound **4f** or **6f**, respectively, in 10 ml of acetone. The mixture was stirred for 2 h and the solvent was removed under vacuum to yield light yellow (**7f**) or white (**8f**) solids.

[$PtMe_2I\{Me_2NCH_2CH_2N{=}CH(3\text{-}C_6H_3Cl)-C,N,N'\}$] (**7f**). Yield 50 mg (75%). Anal. Calcd. for $C_{13}H_{20}ClIN_2Pt$: C, 27.80; H, 3.59; N, 4.99. Found: C, 28.2; H, 3.7; N, 5.1%. FAB(+) (NBA, *m*/*z*): 562 ([M]$^+$); 548 ([M−Me]$^+$); 532 ([M−2Me]$^+$); 510 ([M−Me−Cl]$^+$); 495 ([M−2Me−Cl]$^+$); 434 ([M−I]$^+$); 419 ([M−I−Me]$^+$); 404 ([M−I−2Me]$^+$).

[$PtMe\{Me_3NCH_2CH_2N{=}CH(3\text{-}C_6H_3Cl)-C\}$(dppe)]I (**8f**). Yield 40 mg (68%). $\Lambda_M = 105\ \Omega^{-1}\,cm^2\,mol^{-1}$ (10^{-3} M in acetone). Anal. Calcd. for $C_{39}H_{44}ClIN_2P_2Pt$: C, 48.78; H, 4.62; N, 2.91. Found: C, 48.6; H, 4.6; N, 2.6%. FAB(+) (NBA, *m*/*z*): 832 ([M−I]$^+$); 773 ([M−NMe_3]$^+$); 758 ([M−NMe_3−Me]$^+$); 733 ([M−$CH_2CH_2NMe_3$−Me]$^+$).

3.3. X-Ray structure analysis

3.3.1. Data collection

A prismatic crystal was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($12° < \theta < 21°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo–K_α radiation, using $\omega/2\theta$ scan-technique. 9687 reflections were measured in the range $2.43° < \theta < 29.95°$; 9552 were non-equivalent by symmetry and 5898 were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz polarization and absorption corrections were made. Further details are given in Table 4.

3.3.2. Structure solution and refinement

The structure was solved by Patterson synthesis, using SHELXS computer program [17], and refined by the full-matrix least-squares method, with the SHELX93 computer program [18]. The function minimized was $\sum w = ||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.1066\ P)^2 + 115.91\ P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$.$f$, f' and f'' were taken from International Tables of X-Ray Crystallography [19]. The chirality of the structure was defined from the Flack coefficient [20], which is equal to 0.10(2) for the given results. All hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. Further details are given in Table 4.

4. Supplementary material

Full data for the spectroscopic characterization of compounds **2**, **3**, **4**, **5**, **6**, **7** and **8** (5 pages). Tables of atomic coordinates, complete list of bond lengths and angles and anisotropic thermal parameters U_{ij} for **4c** (16 pages).

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