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Synthesis and reactivity of cyclometallated platinum (II) compounds containing [C,N,N′] terdentate ligands: Crystal structures of $[PtCl\{(CH_3)_2N(CH_2)_3NCH(4\text{-}ClC_6H_3)\}]$, $[PtCl\{(CH_3)_2N(CH_2)_3NCH(2\text{-}ClC_6H_3)\}]$ and $[PtCl\{(CH_3)_2N(CH_2)_3NCH(3\text{-}(CH_3)C_6H_3)\}]$

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Abstract

The reaction of compound *cis*-$[PtCl_2(dmso)_2]$ with ligands $RCHN(CH_2)_3NMe_2$ (**1a**–**1h**) in which R is a phenyl group containing substituents such as Cl, F, Me, NO_2 and MeO produced compounds $[PtCl_2\{(CH_3)_2N(CH_2)_3NCHR\}]$ (**2**), as mixtures of *Z* and *E* isomers. When treated with an equimolar amount of sodium acetate in refluxing methanol compounds **2** gave cyclometallated platinum compounds **3** containing a terdentate [C,N,N′] ligand. The obtained compounds were fully characterized including structure determinations for compounds **3a**, **3b** and **3e**. The effects of the substituents in the regioselectivity of the cyclometallation reaction and the reactivity of **3a** and **3b** with mono and bidentate phosphines were also studied.

Keywords: Platinum; Cyclometallation; Nitrogen ligands

1. Introduction

Cyclometallated compounds, in particular those derived from nitrogen ligands, have been a topic of interest in the last years as a consequence of the wide range of their potential applications in many areas [1]. Although this field has been widely studied for bidentate [C,N] ligands, there are less examples of the cyclometallation of potentially terdentate [C,N,N′] ligands, which benefit from a second N-donor atom [2].

In this work, the reactions of ligands $RCHN(CH_2)_3NMe_2$ (R being a substituted aryl ring) with *cis*-$[PtCl_2(dmso)_2]$ are reported. Analogous potentially terdentate imines $RCHN(CH_2)_2NMe_2$ have been reported to produce intramolecular C–H bond activation via oxidative addition at platinum substrates such as $[Pt(dba)_2]$ [3], $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ [4] or $[PtMe_2(cod)]$ [5]. Compound $[Pt(\mu\text{-}Cl)(\eta^3\text{-}2Me\text{-}C_3H_4)]_2$ has also been used for the synthesis of terdentate cycloplatinated derivatives [6]. The recent progress in using the platinum (II) complex *cis*-$[PtCl_2(dmso)_2]$ as an electrophilic cyclometalating agent [7] can be attributed to its easy synthesis and high stability. In addition, [N,N′] coordination compounds can be isolated as a prior step to the

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cyclometallation process, thus improving the overall yield. As reported in the literature, [7d,7e] such coordination compounds can be readily converted into cycloplatinated derivatives via C–H activation when refluxed for several hours in a donor solvent in the presence of an external base such as sodium acetate.

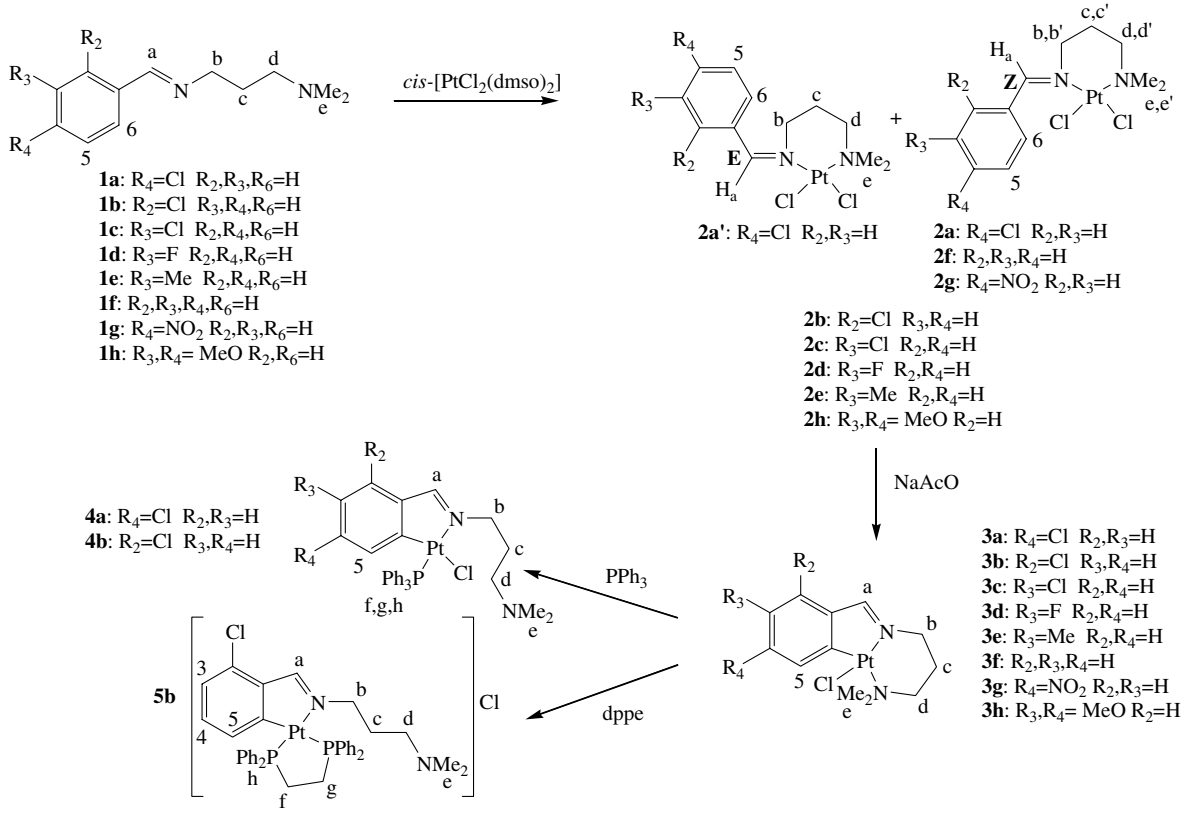
The ligands selected in the present study contain substituents of different nature in the aryl group (Cl, F, Me, NO_2, MeO) and thus should allow us to clarify the influence of stereo-electronic effects of the substituents in both the reactivity and the regioselectivity of the C–H bond activation at platinum.

2. Results and discussion

2.1. Reactions of the imines with cis-$[PtCl_2(dmso)_2]$

The *N*-(substituted benzylidene)-*N*′,*N*′-dimethyl-1,3-propanediamines $RCHN(CH_2)_3NMe_2$ (**1a**–**h**) were obtained from the condensation reaction between $Me_2N(CH_2)_3NH_2$ and the corresponding aldehyde under the usual conditions [3,8–10]. In the ^1H NMR spectra a signal (ca. 8–9 ppm) corresponding to the imine proton is displayed. IR data are consistent with the formation of a C=N bond, showing intense peaks around 1650 cm^{-1}.

The reaction of the imines with *cis*-$[PtCl_2(dmso)_2]$ in refluxing methanol gave the corresponding coordination compounds $[PtCl_2\{(CH_3)_2N(CH_2)_3NCHR\}]$ (**2**). As noted in Scheme 1, a mixture of two isomers corresponding to the two possible conformations (*Z* and *E*) around the C=N bond was obtained. Generally, the *Z* isomer was the most abundant (for imines **1f** and **1g** it was the only which could be isolated and characterised) and in the specific case of imine **1a** the two isomers could be obtained separately. These isomers display striking differences in their spectral features. The ^1H NMR shows among other peculiarities an anisotropic effect in both the methylene and NMe_2 protons in the *Z* isomer, and a strong deshielding effect in the imine proton of the *E* isomer ($\delta = 9.26$–9.54 ppm) caused by platinum. For both isomers evidence of coordination of the two nitrogen atoms to platinum is obtained from the fact that both methylamino and imine protons are coupled to ^{195}Pt. The *J*(H–Pt) values for the imine proton are higher for the *Z* (ca. 120 Hz) than for the *E* isomers (ca. 60 Hz). Furthermore, the nature of the compounds in which the imine acts as a bidentate [N,N′] ligand was confirmed by FAB mass spectra in all cases and elemental analysis except for **2f** and **2g** which could not be obtained in an analytically pure form. A slight decrease of the wave-numbers in the imine bond stretching peaks was observed in the IR spectra.



Scheme 1.

The terdentate [C,N,N′] cyclometallated compounds were obtained from the equimolar reaction of the coordination compounds and sodium acetate as auxiliary base in refluxing methanol. The process involves the activation of a C–H bond and the formal release of HCl which is promoted in the presence of a base. ^{1}H NMR, along with other characterisation tools, confirmed *ortho*-metallation of the imine and formation of a fused [6,5,6]-tricyclic system. In the ^{1}H NMR, J(H–Pt) values for the imine proton (ca. 140 Hz) are higher than those observed for compounds **2** and a new signal also coupled to ^{195}Pt appears next to the imine proton and is assigned to the aromatic proton adjacent to the metallated position. The ^{195}Pt NMR spectra (**3a**, **3b**, **3f** and **3h**) show only one signal, the position of which is consistent with the nature of the ligands bound to platinum [11]. The values indicate a downfield shift in the sequence **3f** < **3h** < **3b** ∼ **3a** which is consistent with increasing deshielding of the platinum nucleus on changing the substituents (MeO, H or Cl) in the aryl group. ^{13}C NMR spectra for compounds **3b**, **3f** and **3h** confirm the cyclometallation process since only three (**3b**), four (**3f**) and two (**3h**) resonances corresponding to aromatic C–H appear; in addition, for **3b** the metallated carbon C(6) appears as a downfield shifted signal with a large coupling constant to ^{195}Pt (J(C–Pt) = 1019 Hz). FAB spectra show two intense signals corresponding to M and M − X fragments, and in some cases weak signals corresponding to dinuclear species 2M and 2M − X. Following the tendency of coordination compounds, the ν(C=N) peaks in the IR spectra have smaller values than their precursors. That would be in agreement with a weakening of the imine bond due to the platinum and/or a delocalization effect within the metallacycle. All compounds were characterized by analytical and spectroscopic techniques, and **3a, 3b** and **3e** were characterized crystallographically as well. Compound **3b** was also synthesized following the previously reported procedure using [Pt(dba)$_2$] (dba = dibenzylideneacetone) as metallating agent and imine 2,6-$Cl_2C_6H_3CHN(CH_2)_3NMe_2$. Yield and purity were remarkably poorer than those observed for the method described in the present work.

The position and nature of the substituents in the aryl ring can either determine or favor the carbon position in which the electrophilic attack takes place. For example, imine with 4-chloro-substituted aryl ring was easily metallated, producing with higher yields bright red crystals that were fully characterised. Imines with 4-nitro-substituted and unsubstituted aryl rings, however, gave in comparison poor results, leading to low yields and unpurified products. All the experimental results here reported cannot be fully understood taking only into account the electronic effect of the substituents; a concerted mechanism via a tetra-centered transition state [7e], along with other factors such as the relative solubility of the cyclometallated compounds or conformational effects could play an important role.

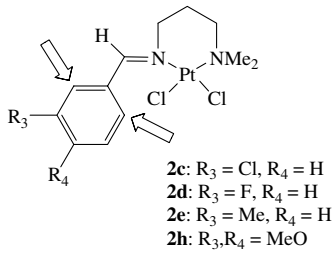


Chart 1. The two possible metallation sites for asymmetric ligands.

On the other hand, the fairly good experimental results obtained for the 2-chlorosubstituted ligand (**1b**) can be related to the N=CH···Cl interaction which reinforces the planarity of the ArC=N fragment [12] and increases the stability of the corresponding compound **3b**.

As shown in Chart 1, cyclometallation of 3-R substituted imines can give two different metallated isomers, depending whether metallation takes place at position 2 or position 6 of the phenyl ring. We performed reactions with ligands containing 3-Cl (**1c**), 3-F (**1d**), 3-Me (**1e**) and 3,4-MeO (**1h**) substituted phenyl ring in order to investigate if the steric and/or electronic effects play a significant role in the regioselectivity of the reaction. Experimental results point to a major influence of the steric hindrance of the substituents, since cycloplatination of ligands **1c**, **1e** and **1h** produced only a single isomer in which cyclometallation took place at the less hindered site (position 6) regardless of the electronic effects caused by each substituent. Only for the small fluoro substituent, activation was achieved at the two nonequivalent positions leading to a mixture of two isomers in a 2.5 : 1 ratio, the major isomer corresponding to metallation at the less hindered position. Additional evidence was obtained from the ^{19}F NMR since coupling to ^{195}Pt was observed for the signal corresponding to the minor isomer.

2.2. Reactions with phosphines

As shown in previous works [13], the reaction of cyclometallated compounds with mono or bidentate phosphines can result in the cleavage of the metallacycles, leading to bidentate [C,N] or even monodentate [C] systems. In order to analyse the reactivity of the cyclometallated compounds in front of phosphines, the reaction of **3a** and **3b** with triphenylphosphine and 1,2-bisdiphenylphosphinoethane (dppe) were studied and the results are shown in Scheme 1.

In compounds **4a** and **4b** obtained upon reaction with triphenylphosphine the imine behaves as a [C,N] bidentate ligand and the square-planar coordination of platinum (II) is completed with a phosphine and a halide

ligand. In the ^{1}H NMR spectra, no platinum satellites are observed for the dimethylamino group, thus ruling out the possibility of penta-coordination of the platinum. The *trans* arrangement of the phosphine and the imine is expected in agreement with the *transphobia* effect [14], and experimental evidence is obtained from the value of J(P–Pt) and the observed coupling of the imine to the phosphorous in *trans*.

Compound **5b** obtained upon reaction of **3b** with dppe contains the chelated diphosphine and the imine as a bidentate [C,N] ligand. The ^{31}P NMR spectrum shows two sets of resonances due to two non-equivalent phosphorus atoms, both coupled to platinum. A peak corresponding to the complex cation was obtained in the FAB mass spectrum. The formation of compound **5b** clearly shows the high stability of the metallacycle which is resistant to cleavage even when reacted with chelating diphosphine.

2.3. Crystal structures

Suitable crystals of compounds **3a**, **3b** and **3e** (Figs. 1–3, respectively) were grown from acetone solution. All crystal structures are composed of discrete molecules separated by Van der Waals distances. Selected molecular dimensions, listed in Table 1, confirm the geometries predicted from spectroscopic data.

In spite of the presence of different substituents (*para*-chloro (**3a**), *ortho*-chloro (**3b**), *meta*-methyl (**3e**)), the three structures lack of significant differences among them. The three compounds consist of a fused [6,5,6] tricyclic system containing a five-membered metallacycle, a chelate ring with two nitrogen atoms coordinated to platinum and the *ortho*-metallated phenyl group. The square-planar coordination environment of the metal, adopted by most Pt(II) compounds, is completed by a chlorine atom. For **3e**, the molecular structure provides decisive evidence of the fact that metallation takes place regioselectively at the less hindered position. As shown in Table 1, bond lengths and angles are well within the range of values obtained for analogous compounds [3,5,7]. Most bond angles at platinum are close to the ideal value of 90°, and the smallest angles correspond to the metallacycle (79.6(12)° (**3a**); 81.1(3)° (**3b**); 80.73(19)° (**3e**)). The chelate angle N(1)–Pt–N(2) is greater (95.2(8)° (**3a**); 97.3(3)° (**3b**); 95.00(18)° (**3e**)) than for analogous compounds derived from *N*,*N*-dimethylethylenediamine [3,5]. The imine C=N bond lengths lie in the usual range, and Pt–amine distances are larger than platinum–imine distances consistent with the weaker ligating ability of amines for platinum. The Pt–amine distances are greater than those observed for compounds derived from *N*,*N*-dimethylethylenediamines [3,5]. The chelate ring presents a strong deviation in its planarity caused by the propyl moiety as reported for analogous compounds [7d,10]. The metallacycle atoms adopt a practically planar arrangement, as shown by the sum of their internal bond angles which is close to 540° [15]. The metallacycle is nearly coplanar with the coordination plane, the dihedral angle between the mean planes ranging from 3.90° (**3e**) to 5.90° (**3b**).

Intramolecular distances were measured and the value obtained for N=CH···Cl in compound **3b** (3.143(10) Å) confirms the interaction suggested above.

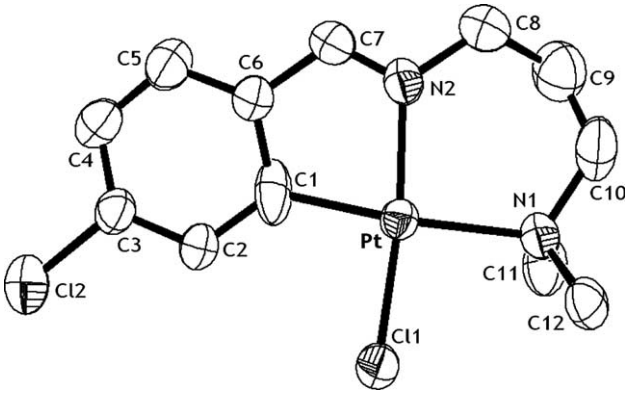


Fig. 1. Molecular structure of compound **3a**.

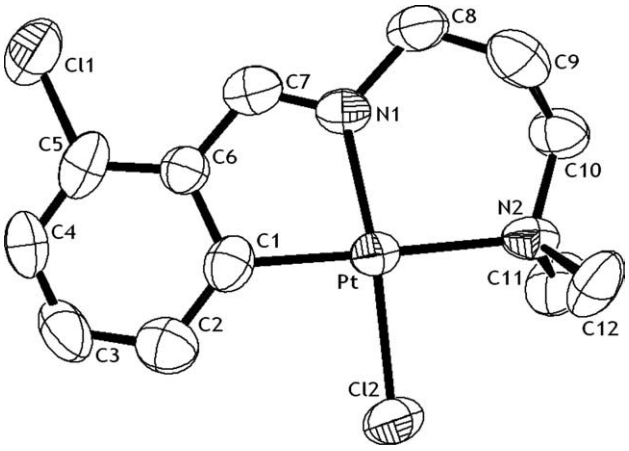


Fig. 2. Molecular structure of compound **3b**.

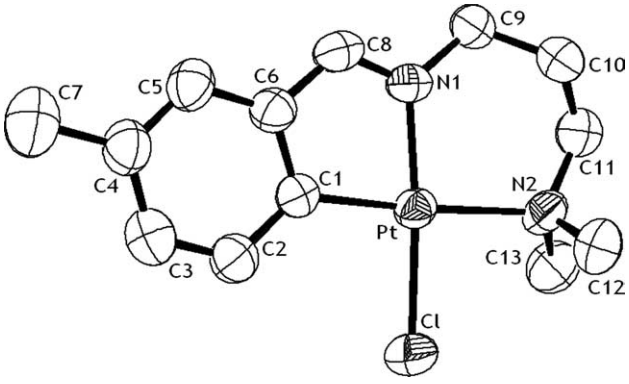


Fig. 3. Molecular structure of compound **3e**.

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

3a		**3b**		**3e**	
Pt–N(1)	2.180(9)	Pt–N(1)	1.981(7)	Pt–C(1)	1.959(5)
Pt–C(1)	1.955(15)	Pt–C(1)	1.985(8)	Pt–N(1)	1.986(4)
Pt–N(2)	2.092(13)	Pt–N(2)	2.170(8)	Pt–N(2)	2.186(5)
Pt–Cl(1)	2.240(4)	Pt–Cl(2)	2.289(2)	Pt–Cl	2.306(2)
N(2)–C(7)	1.23(2)	N(1)–C(7)	1.267(12)	N(1)–C(8)	1.282(6)
C(7)–C(6)	1.47(2)	C(7)–C(6)	1.430(12)	C(6)–C(8)	1.423(7)
C(6)–C(1)	1.47(4)	C(6)–C(1)	1.419(11)	C(1)–C(6)	1.388(6)
C(1)–Pt–N(2)	79.6(12)	N(1)–Pt–C(1)	81.1(3)	N(1)–Pt–C(1)	80.73(19)
N(2)–Pt–N(1)	95.2(8)	N(1)–Pt–N(2)	97.3(3)	N(1)–Pt–N(2)	95.00(18)
C(1)–Pt–Cl(1)	93.7(12)	C(1)–Pt–Cl(2)	92.5(3)	C(1)–Pt–Cl	93.74(16)
N(1)–Pt–Cl(1)	91.7(8)	N(2)–Pt–Cl(2)	89.02(18)	N(2)–Pt–Cl	90.40(16)
Total:[a]	360.2		359.92		359.87
N(2)–Pt–C(1)	79.6(12)	N(1)–Pt–C(1)	81.1(3)	C(1)–Pt–N(1)	80.73(19)
C(7)–N(2)–Pt	116.8(10)	C(7)–N(1)–Pt	115.9(6)	C(8)–N(1)–Pt	114.9(3)
C(7)–C(6)–C(1)	112.0(12)	C(7)–C(6)–C(1)	113.4(7)	C(6)–C(1)–Pt	114.0(3)
C(6)–C(1)–Pt	114.6(18)	C(6)–C(1)–Pt	111.6(6)	C(1)–C(6)–C(8)	112.8(4)
N(2)–C(7)–C(6)	116.9(13)	N(1)–C(7)–C(6)	117.1(7)	N(1)–C(8)–C(6)	117.4(4)
Total:[b]	539.9		539.1		539.83

[a] Sum of angles in the coordination environment of the platinum atom.
[b] Sum of internal angles of the metallacycle.

In addition, short distances C(2)-H(2)···Cl (**3a**, 3.266(15) Å; **3b**, 3.250(10) Å; **3e**, 3.26(10) Å) suggest a weak intramolecular interaction similar to those reported for analogous palladium compounds [12].

In relation to intermolecular interactions, a ca. 3.6 Å distance was observed between the aromatic rings of **3e**. That might suggest π–π interactions within the aromatic moieties, as reported previously in other works with platinum cyclometallated compounds [16].

3. Conclusions

Although several platinum substrates, such as *cis*-$[PtCl_2(dmso)_2]$, $[Pt(dba)_2]$ and $[Pt(\mu\text{-}Cl)(\eta^3\text{-}2Me\text{-}C_3H_4)]_2$ under different reaction conditions were initially investigated in order to optimize the synthesis of cyclometallated platinum compounds, the best yields and the most easily purified metallacycles were those obtained using *cis*-$[PtCl_2(dmso)_2]$. Indeed, the reaction of *cis*-$[PtCl_2(dmso)_2]$ with *N*-(substituted benzylidene)-*N*′,*N*′-dimethyl-1,3-propanediamines allows the synthesis of compounds in which the imine behaves as [N,N′] ligand which are precursors of new cyclometallated platinum (II) compounds containing a terdentate [C,N,N′] ligand. The latter react with phosphines to yield compounds in which the imine acts as a bidentate [C,N] ligand.

The general picture of the process leading to [C,N,N′] cyclometallated compounds is analogous to that described for *N*-benzylidene-*N*′,*N*′-dimethyl-ethanediamines which consists of: (i) coordination of the bidentate ligand and (ii) intramolecular C–H bond activation in the presence of a base. Isomerization of the ligand to the adequate conformation around the C=N bond has been reported to be a key step of the C–H bond activation process [7d,7e] and occurs more readily for the more flexible propyl derivatives which are obtained as a mixture of (*Z*) and (*E*) conformers than for the ethylene analogues which isomerizes only in the presence of a base [7e]. In addition a pre-equilibrium dechelation process is needed for the C–H activation to occur [8] and this should be easier for the propylene than for the ethylene amines assuming that a greater platinum–amine distance, as obtained from crystallographic data of compounds **3**, also apply to coordination compounds derived from propyleneamine. Given the advantageous features of the propyl system, a study of regioselectivity could also be realised for several 3-substituted ligands (**1c**, **1d**, **1e** and **1h**) and allow us to conclude that steric effects play a decisive role in the selectivity of the C–H bond activation.

4. Experimental

4.1. General

The solvents were purified and distilled by standard methods. Methanol (dry, max. 0.005H_2O) was purchased from Panreac.

Mass spectra were performed by the Servei d'Espectrometria de Masses de la Universitat de Barcelona.

NMR spectra were performed at the Unitat de NMR d'Alt Camp de la Universitat de Barcelona. Microanalyses were performed by the Servei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili de Tarragona.

IR spectra were recorded in Nicolet 520, Thermo-Nicolet 5700 and Thermo-Nicolet Avatar 330 spectrofotometers, using KBr pellets for solid samples and NaCl support for liquid samples.

FAB mass spectra were carried out in VG-Quattro (with a 3-nitrobenzyl alcohol matrix) and Voyager DE-RP (with a dithranol matrix) spectrometers. ^{1}H, ^{13}C, ^{31}P, ^{19}F and ^{195}Pt NMR spectra were recorded by using Varian Gemini-200 (^{1}H, 200 MHz), Bruker DRX-250 (^{1}H, 250 MHz; ^{31}P, 101 MHz; ^{195}Pt, 54 MHz), Varian Unity-300 (^{1}H, 300 MHz; NOESY; 13C, 75 MHz), Mercury-400 (^{1}H, 400 MHz; ^{13}C, 100.6 MHz; ^{19}F, 376 MHz; NOESY), Inova-500 (^{1}H, 500 MHz) and Bruker DMX-500 (^{1}H, 500 MHz; COSY) spectrometers, and referenced to $SiMe_4$ (^{1}H, ^{13}C), $P(OMe)_3$ in $(CD_3)_2CO$ (^{31}P) and H_2PtCl_6 in D_2O (^{195}Pt). δ values are given in ppm and J values in Hz (s = singulet; d = doblet; t = triplet; q = quadruplet; qi = quintuplet; m = multiplet; b = broad).

4.2. Preparation of the compounds

$[PtCl_2(dmso)_2]$ was prepared as reported elsewhere [17]. Ligands **1a**–**1h** were prepared under the usual conditions reported in the literature [3,8–10] (see supplementary material).

4.2.1. Preparation of the coordination compounds

$[PtCl_2\{(CH_3)_2N(CH_2)_3NCH(4\text{-}ClC_6H_4)\}]$ (**2a**,**2a′**) was obtained from 0.316 g (0.7 mmol) of *cis*-$[PtCl_2(dmso)_2]$ and 0.169 g (0.7 mmol) of imine **1a** which were allowed to react in refluxing methanol (30 ml) for 4 h. The solvent was removed in a rotary evaporator and the residue was treated with methanol–dichloromethane, yielding a yellow solid which was filtered in vacuum. Yield 72%. IR: ν(CH=N) = 1625.3 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): isomer *Z* δ 9.24 [d, ^{3}J(H–H) = 8.4, 2H, H^{2,6}], 8.50 [s, ^{3}J(Pt–H) = 120, 1H, H^{a}], 7.55 [d, ^{3}J(H–H) = 8.4, 2H, H^{3,5}], 4.90 [m, 1H, H^{b}], 4.15 [m, 1H, H$^{b'}$], 3.20 [m, 1H, H^{d}], 2.97 [s, ^{3}J(Pt–H) = 34.5, 3H, H^{e}], 2.83 [s, ^{3}J(Pt–H) = 28.5, 3H, H$^{e'}$], 2.73 [m, 1H, H$^{d'}$], 2.38 [m, 1H, H^{c}], 1.95 [m, 1H, H$^{c'}$]; isomer *E* δ 9.30 [s, ^{3}J(Pt–H) = 61, 1H, H^{a}], 7.56 [d, ^{3}J(H–H) = 8.6, 2H, H^{2,6}], 7.48 [d, ^{3}J(H–H) = 8.6, 2H, H^{3,5}], 4.10 [td, ^{3}J(H–H) = 5, ^{4}J(H–H) = 1.8, ^{3}J(Pt–H) = 34, 2H, H^{b}], 3.00 [s, ^{3}J(Pt–H) = 30, 6H, H^{e}], 2.63 [m, ^{3}J(H–H) = 5, ^{3}J(Pt–H) = 34, 2H, H^{d}], 2.23 [m, ^{3}J(H–H) = 5.5, 2H, H^{c}]. FAB-MS, *m*/*z*: 455 $[M - Cl]^+$, 417 $[M - 2Cl]^+$. *Anal*. Calc.: C, 30.07; H, 3.57; N, 6.14. Found: 29.5; H: 3.5; N: 5.7.

$[PtCl_2\{(CH_3)_2N(CH_2)_3NCH(2\text{-}ClC_6H_4)\}]$ (**2b**) was obtained from 0.408 g (0.97 mmol) of *cis*-$[PtCl_2(dmso)_2]$ and 0.217 g (0.97 mmol) of imine **1b**, using the procedure reported for **2a**. Yield 43%. IR: ν(CH=N) = 1626.7, 1619.3, 1611.8 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): isomer *Z* δ 10.79 [m, H^{6}], 9.04 [s, ^{3}J(Pt–H) = 117.2, 1H, H^{a}], 7.58 [m, 2H, H^{3,5}], 7.46 [m, 2H, H^{4}], 4.99 [m, 1H, H^{b}], 4.25 [m, 1H, H$^{b'}$], 3.20 [m, 1H, H^{d}], 2.99 [s, 3H, H^{e}], 2.90 [s, 3H, H$^{e'}$], 2.76 [m, 1H, H$^{d'}$], 2.41 [m, 1H, H^{c}], 2.00 [m, 1H, H$^{c'}$]; isomer *E* δ 9.38 [s, ^{3}J(Pt–H) = 59.9, 1H, H^{a}], 7.48 [dd ^{4}J(H–H) = 1.75, ^{3}J(H–H) = 6.4, H^{8}], 7.47 [m, 1H, H$^{4\text{ or }5}$], 7.39 [td, ^{4}J(H–H) = 2.4, ^{3}J(H–H) = 7, 1H, H$^{4\text{ or }5}$], 7.29 [d, ^{3}J(H–H) = 7.2, 1H, H^{3}], 3.92 [td, ^{4}J(H–H) =1.5, ^{3}J(H–H) = 6.75, ^{3}J(Pt–H) = 35, 2H, H^{b}], 3.01 [s, ^{3}J(Pt–H) = 33.2, H^{e}], 2.70 [m, 2H, H^{d}], 2.14 [m, 2H, H^{c}]. FAB-MS, *m*/*z*: 532.90 $[M - Cl + dmso]^+$, 455 $[M - Cl]^+$, 419 $[M - 2Cl]^+$. *Anal*. Calc.: C, 29.36; H, 3.68; N, 5.62. Found: C, 29.5; H: 3.5; N: 5.7.

$[PtCl_2\{(CH_3)_2N(CH_2)_3NCH(3\text{-}ClC_6H_4)\}]$ (**2c**) was obtained from 0.320 g (0.75 mmol) of *cis*-$[PtCl_2(dmso)_2]$ and 0.168 g (0.75 mmol) of imine **1c**, using the procedure reported for **2a**. Yield 34%. IR: ν(CH=N) = 1629.3 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): isomer *Z* δ 9.94 [d, ^{3}J(H–H) = 7.6, 1H, H^{6}], 8.50 [s, ^{3}J(Pt–H) = 107, 1H, H^{a}], 8.47 [t, ^{4}J(H–H) = 1.8, 1H, H^{2}], 7.6–7.4 [m, 2H, H^{4,5}], 4.99 [m, 1H, H^{b}], 4.17 [m, 1H, H$^{b'}$], 3.20 [bm, 1H, H^{d}], 2.98 [s, 3H, H^{e}], 2.96 [s, 3H, H$^{e'}$], 2.69 [m, 1H, H$^{d'}$], 2.40 [m, 1H, H^{c}], 1.96 [m, 1H, H$^{c'}$]; isomer *E* δ 9.31 [s, ^{3}J(Pt–H) = 60, 1H, H^{a}], 7.64 [dt, ^{3}J(H–H) = 8.8, ^{4}J(H–H) = 1.2, 1H, H^{6}], 7.42 [t, ^{4}J(H–H) = 1.75, 1H, H^{2}], 4.11 [td, ^{3}J(H–H) = 6.5, ^{4}J(H–H) = 1.6, ^{3}J(Pt–H) = 56.0, 2H, H^{b}], 3.01 [s, 6H, H^{e}], 2.66 [m, 2H, H^{d}], 2.23 [m, 2H, H^{c}]; non-assigned protons: 7.64 [d, ^{3}J(H–H) = 8.8, 1H, H$^{4Z\text{ or }4E}$], 7.57 [t, ^{3}J(H–H) = 8.0, 1H, H$^{5Z\text{ or }5E}$], 7.54 [d, ^{3}J(H–H) = 8.8, 1H, H$^{4Z\text{ or }4E}$], 7.46 [t, ^{3}J(H–H) = 8.0, 1H, H$^{5Z\text{ or }5E}$].

FAB-MS, *m*/*z*: 568.96 $[M - 2Cl + 2dmso]^+$, 532.97 $[M - Cl + dmso]^+$, 452.97 $[M - Cl]^+$, 418.01 $[M - 2Cl]^+$. *Anal*. Calc.: C, 29.25; H, 3.73; N, 5.56. Found: C, 29.5; H, 3.73; N, 5.7.

$[PtCl_2\{(CH_3)_2N(CH_2)_3NCH(3\text{-}FC_6H_4)\}]$ (**2d**) was obtained from 0.353 g (0.84 mmol) of *cis*-$[PtCl_2(dmso)_2]$ and 0.174 g (0.84 mmol) of imine **1d**, using the procedure reported for **2a**. Yield 85%. IR: ν(CH=N) = 1632.1 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): isomer *Z* δ 9.25 [d, ^{3}J(H–H) = 7.6, 1H, H^{6}], 8.79 [dt, ^{3}J(F–H) = 9.2, ^{4}J(H–H) = 1.75, 1H, H^{2}], 8.53 [s, ^{3}J(Pt–H) = 112, 1H, H^{a}], 7.58 [dt, ^{3}J(H–H) = 8, ^{4}J(F–H) = 5.6, 1H, H^{4}], 7.38 [dt, ^{3}J(H–H) = 8.2, ^{4}J(F–H) = 2.54, 1H, H^{5}], 4.96 [m, 1H, H^{b}], 4.11 [m, 1H, H$^{b'}$], 3.20 [m, 1H, H^{8}], 3.01 [m, 1H, H^{9}], 2.98 [m, 1H, H$^{9'}$], 2.72 [m, 1H, H$^{8'}$], 2.40 [m, 1H, H^{7}], 1.96 [m, 1H, H$^{7'}$]; isomer *E* δ 9.54 [s, ^{3}J(Pt–H) = 45.3, 1H, H^{5}], 7.54-7.48 [m, 3H, H^{1,2,3}], 7.15 [dt, ^{3}J(F–H) = 9, ^{4}J(H–H) = 1.75, 1H, H^{4}], 4.49 [td, ^{3}J(H–H) = 6.4, ^{4}J(H–H) = 1.2, 2H, H^{6}], 2.86 [s, 6H, H^{9}], 2.72 [m, 2H, H^{8}], 2.24 [m, 2H, H^{7}]. ^{19}F NMR (376.481 MHz, $CDCl_3$); isomer *Z*: −110.06 [dd, ^{3}J(F–H) = 8.0, ^{3}J(F–H) = 14.6],

−110.83 [dd, ^3J(F–H) = 8.0, ^3J(F–H) = 14.6]; isomer *E*: −117.77 [m], −121.27 [m]. FAB-MS, *m/z*: 516.07 $[M - Cl + dmso]^+$, 439.04 $[M - Cl]^+$, 401.04 $[M - 2Cl]^+$. *Anal*. Calc.: C, 27.92; H, 3.42; N, 5.56. Found: C, 27.5; H, 3.4; N, 4.8.

$[PtCl_2\{(CH_3)_2N(CH_2)_3NCH(3\text{-}(CH_3)C_6H_4)\}]$ (**2e**) was obtained from 0.363 g (0.86 mmol) of *cis*-$[PtCl_2(dmso)_2]$ and 0.176 g (0.86 mmol) of imine **1e**, using the procedure reported for **2a**. Yield 39%. IR: ν(CH=N) = 1621.6 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): isomer *Z* δ 9.64 [d, ^3J(H–H) = 7.2, 1H, H^6], 8.55 [s, 1H, H^2], 8.49 [s, ^3J(Pt–H) = 120, 1H, H^a], 7.55–7.45 [m, 2H, $H^{4,5}$], 4.92 [m, 1H, H^b], 4.15 [m, 1H, $H^{b'}$], 3.60 [m, 1H, H^d], 3.21 [m, 1H, $H^{d'}$], 3.01 [s, 3H, H^e], 2.71 [m, 1H, H^c], 2.41 [s, 3H, H^3], 1.94 [m, 1H, $H^{c'}$]; isomer *E* δ 9.26 [s, ^3J(Pt–H) = 60, 1H, H^a], 8.90 [s, 1H, H^2], 7.40-7.30 [m, 2H, $H^{4,5,6}$], 4.13 [td, ^3J(H–H) = 6.4, ^4J(H–H) = 1.6, 2H, H^b], 2.65 [m, 2H, H^d], 2.41 [s, 3H, H^3], 2.22 [m, 2H, H^c]; non-assigned protons: 2.97 [s, 3H, $H^{e'Z \text{ or } eE}$], 2.84 [s, 3H, $H^{e'Z \text{ or } eE}$]. FAB-MS, *m/z*: 549.11 $[M - 2Cl + 2dmso]^+$, 513.10 $[M - Cl + dmso]^+$, 434.04 $[M - Cl]^+$, 397.06 $[M - 2Cl]^+$. *Anal*. Calc.: C, 30.28; H, 3.99; N, 5.04. Found: C, 30.0; H, 4.2; N, 5.1.

$[PtCl_2\{(CH_3)_2N(CH_2)_3NCH(C_6H_5)\}]$ (**2f**) was obtained from 0.391 g (0.93 mmol) of *cis*-$[PtCl_2(dmso)_2]$ and 0.177 g (0.93 mmol) of imine **1f**, using the procedure reported for **2a**. Yield 50%. IR: ν(CH=N) = 1625.6 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.28 [d, ^3J(H–H) = 7.3, 2H, $H^{2,6}$], 8.52 [s, ^3J(Pt–H) = 120, 1H, H^a], 7.68 [t, ^3J(H–H) = 7.75, 1H, H^4], 7.58 [t, ^3J(H–H) = 7.5, 2H, $H^{3,5}$], 4.94 [m, 1H, H^b], 4.13 [m, 1H, $H^{b'}$], 2.97 [s, 3H, H^e], 2.83 [s, 3H, $H^{e'}$], 3.3-2.7 [m, 2H, $H^{d,d'}$], 2.40 [m, 1H, H^c], 1.95 [m, 1H, $H^{c'}$]. FAB-MS, *m/z*: 535.08 $[M - 2Cl + 2dmso]$ 499.08 $[M - Cl + dmso]^+$, 420.03 $[M - Cl]^+$, 383.02 $[M - 2Cl]^+$.

$[PtCl_2\{(CH_3)_2N(CH_2)_3NCH(4\text{-}(NO_2)C_6H_4)\}]$ (**2g**) was obtained from 0.250 g (0.59 mmol) of *cis*-$[PtCl_2(dmso)_2]$ and 0.140 g (0.59 mmol) of imine **1g**, using the procedure reported for **2a**. Yield 49%. IR: ν(CH=N) = 1625.3 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.42 [d, ^3J(H–H) = 8.7, 2H, $H^{2,6}$], 8.77 [s, ^3J(Pt–H) = 117, 1H, H^a], 8.39 [d, ^3J(H–H) = 8.8, 2H, $H^{3,5}$], 4.98 [m, ^3J(H–H) = 7.3, 1H, H^b], 4.29 [m, ^3J(H–H) = 7.25, 1H, $H^{b'}$], 3.24 [m, 1H, H^d], 4.29 [m, 1H, $H^{d'}$], 2.99 [s, 3H, H^e], 2.89 [s, 3H, $H^{e'}$], 2.42 [m, 1H, H^c], 1.98 [m, 1H, $H^{c'}$]. FAB-MS, *m/z*: 465.04 $[M - Cl]^+$, 428.02 $[M - 2Cl]^+$. *Anal*. Calc. for $C_{12}H_{17}N_3Cl_2O_2Pt \cdot H_2O$: C, 27.75; H, 3.68; N, 8.09. Found: C, 27.6; H, 3.4; N, 7.9.

$[PtCl_2\{(CH_3)_2N(CH_2)_3NCH(3,4\text{-}(MeO)_2C_6H_3)\}]$ (**2h**) was obtained from 0.259 g (0.61 mmol) of $[PtCl_2(dmso)_2]$ and 0.154 g (0.61 mmol) of imine **1g**, using the procedure reported for **2a**. Yield 49%. IR: ν(CH=N) = 1611.6 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 10.42 [d, ^4J(H–H) = 1.6, 1H, H^2], 8.33 [s, ^3J(Pt–H) = 119.4, 1H, H^a], 7.83 [dd, ^3J(H–H) = 8.4, ^4J(H–H) = 2, 1H, H^6], 6.95 [d, ^3J(H–H) = 8.4, 1H, H^5], 4.80 [m, 1H, H^b], 4.16 [s, 3H, H^3], 3.97 [s, 3H, H^4], 2.97 [s, 3H, H^e], 2.80 [s, 3H, $H^{e'}$], 2.69 [m, 1H, H^d] 2.44 [m, 1H, H^c], 1.94 [m, 1H, $H^{c'}$]. FAB-MS, *m/z*: 559.14 $[M - Cl + dmso]^+$, 479.07 $[M - Cl]^+$, 443.09 $[M - 2Cl]^+$. *Anal*. Calc. for $C_{14}H_{22}N_2Cl_2O_2Pt \cdot H_2O$: C, 31.47; H, 4.53; N, 5.24. Found: C, 31.4; H, 4.5; N, 4.6.

4.2.2. Preparation of cyclometallated compounds

$[PtCl\{(CH_3)_2N(CH_2)_3NCH(4\text{-}ClC_6H_3)\}]$ (**3a**) was obtained from 0.100 g (0.2 mmol) of compound **2a** and 0.017 g (0.2 mmol) of sodium acetate which were allowed to react in refluxing methanol for 12 h. The solvent was removed using a rotary evaporator, and the residue was treated with dichloromethane–methanol. The precipitated red crystals were washed with diethyl ether and filtered in vacuum. Yield 50%. IR: ν(CH=N) = 1598.8 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 [s, ^3J(Pt–H) = 142.5, 1H, H^a], 7.98 [d, ^4J(H–H) = 2, ^3J(Pt–H) = 44, 1H, H^5], 7.02 [d, ^3J(H–H) = 8.4, 1H, H^2], 6.98 [d, ^3J(H–H) = 8.4, 1H, H^3], 3.85 [td, ^3J(H–H) = 5, ^3J(Pt–H) = 35, ^4J(H–H) = 1.5, 2H, H^b], 2.82 [m, 2H, H^d], 2.81 [s, ^3J(Pt–H) = 14.5, 6H, H^e], 2.02 [qi, ^3J(H–H) = 5, 2H, H^c]. ^{195}Pt NMR (54 MHz, $CDCl_3$): −3510.97 [s]. MALDI-MS, *m/z*: 454.53 $[M]^+$, 416.58 $[M - Cl]^+$. *Anal*. Calc.: C, 31.78; H, 3.56; N, 6.18. Found: C, 31.0; H, 3.8; N, 6.2.

$[PtCl\{(CH_3)_2N(CH_2)_3NCH(2\text{-}ClC_6H_3)\}]$ (**3b**) was obtained from 0.072 g (0.15 mmol) of compound **2b** and 0.013 g (0.15 mmol) of sodium acetate using the procedure reported for **3a**. Yield 66%. IR: ν(CH=N) = 1589.8 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.79 [t, ^4J(H–H) = 1.5, ^3J(Pt–H) = 140, 1H, H^a], 7.93 [dd, ^3J(H–H) = 7.75, ^4J(H–H) = 0.75, ^3J(Pt–H) = 44, 1H, H^5], 7.10 [t, ^3J(H–H) = 7.75, 1H, H^4], 6.93 [dd, ^3J(H–H) = 7.75, ^4J(H–H) = 0.75, 1H, H^3], 3.91 [td, ^3J(H–H) = 5, ^3J(Pt–H) = 35, ^4J(H–H) = 1.5, 2H, H^b], 2.88 [m, 2H, H^d], 2.84 [s, ^3J(Pt–H) = 14.5, 6 H, H^e], 2.03 [qi, ^3J(H–H) = 5, 2H, H^c]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.19 [^2J(C–Pt) = 93, C^a], 144.26 [^1J(C–Pt) = 1019, C^6], 141.93 [C^2], 133.01 [^2J(C–Pt) = 56.5, C^5], 132.52 [^2J(C–Pt) = 51.0, C^4], 131.30 [^2J(C–Pt) = 50.0, C^1], 123.68 [C^3], {64.00, 58.28 [J(C–Pt) = 39.0], 50.13, C^b, C^c, C^d}, 27.18 [^2J(C–Pt) = 30.8, C^e]. ^{195}Pt NMR (54 MHz, $CDCl_3$): −3519.10 [s]. MALDI-MS, *m/z*: 453.9 $[M]^+$, 418 $[M - Cl]^+$. *Anal*. Calc.: C, 31.78; H, 3.56; N, 6.18. Found: C, 31.2; H, 3.6; N, 6.1.

$[PtCl\{(CH_3)_2N(CH_2)_3NCH(3\text{-}ClC_6H_3)\}]$ (**3c**) was obtained from 0.045 g (0.1 mmol) of compound **2c** and 0.007 g (0.1 mmol) of sodium acetate using the procedure reported for **3a**. Yield 52%. IR: ν(CH=N) = 1593.9 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.38 [s, ^3J(Pt–H) = 141.2, 1H, H^a], 7.99 [d, ^3J(H–H) = 8.4, ^3J(Pt–H) = 39, 1H, H^5], 7.23 [s, 1H, H^2], 7.17 [m, H^4], 3.92 [t, ^3J(H–H) = 4.8, ^3J(Pt–H) = 35,

2H, H^b], 2.97 [m, 2H, H^d], 2.85 [m, 6H, H^e], 2.05 [m, 1H, H^c]. *Anal*. Calc.: for $C_{12}H_{16}N_2Cl_2Pt{\cdot}CH_2Cl_2$: C, 28.95; H, 3.36; N, 5.19. Found: C, 28.6; H, 3.5; N, 4.2.

[PtCl{$(CH_3)_2N(CH_2)_3NCH(3\text{-}FC_6H_3)$}] (**3d**) was obtained from 0.100 g (0.21 mmol) of compound **2d** and 0.017 g (0.21 mmol) of sodium acetate using the procedure reported for **3a**. Yield 25%. IR: ν(CH=N) = 1595.8 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): major isomer: δ 8.37 [s, ^3J(Pt–H) = 141.5, 1H, H^a], 7.98 [dd ^3J(H–H) = 8, ^4J(H–F) = 6, ^3J(Pt–H) = 39, 1H, H^5], 7.0-6.9 [m, 1H, $H^{2,4}$], 3.92 [t, ^3J(H–H) = 4.5, ^3J(Pt–H) = 37, 2H, H^b], 2.86 [m, 2H, H^d], 2.85 [s, ^3J(Pt–H) = 14.5, 6H, H^e], 2.02 [qi, ^3J(H–H) = 5.0, 2H, H^c]; minor isomer: δ 8.46 [d, ^4J(H–H) = 1.37, ^3J(Pt–H) = 137, 1H, H^a], 7.16 [d, ^3J(H–H) = 7.23, 1H, H^2], 6.9 [m, 1H, H^3], 6.81 [dd, ^3J(H–H) = 8.4, ^3J(H–F) = 10, 1H, H^4], 3.86 [m, 2H, H^b] 2.96 [s, 6H, H^e], 2.86 [m, 2H, H^d], 2.0 [m, H^c]. ^{19}F NMR (376.481 MHz, $CDCl_3$): major isomer: −121.25 [dd, ^3J(F–H) = 8.66, ^3J(F–H) = 9.06]; minor isomer: −93.91 [dd, ^3J(F–H) = 10, ^4J(F–H) = 5.9, ^3J(Pt–F) = 75]. Anal. Calc.: C, 32.92; H, 3.68; N, 6.40. Found: C, 32.6; H, 2.5; N, 6.2.

[PtCl{$(CH_3)_2N(CH_2)_3NCH(3\text{-}(CH_3)C_6H_3)$}] (**3e**) was obtained from 0.100 g (0.21 mmol) of compound **2e** and 0.017 g (0.21 mmol) of sodium acetate using the procedure reported for **3a**. Yield 22%. IR: ν(CH=N) = 1601.8 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): 8.24 [s, ^3J(Pt–H) = 143.6, 1H, H^a], 7.85 [d, ^3J(H–H) = 8, ^3J(Pt–H) = 38, 1H, H^5], 7.05 [s, 1H, H^2], 6.98, [d, ^3J(H–H) = 7, 1H, H^4], 3.84 [t, ^3J(H–H) = 5, ^3J(Pt–H) = 36, 2H, H^b], 2.8 [bm, 8H, $H^{d,e}$], 2.23 [s, 3H, H^3], 1.98 [m, 2H, H^c].

[PtCl{$(CH_3)_2N(CH_2)_3NCHC_6H_4$}] (**3f**) was obtained from 0.100 g (0.22 mmol) of compound **2f** and 0.020 g (0.22 mmol) of sodium acetate using the procedure reported for **3a**. Yield 37%. IR: ν(CH=N) = 1593.5 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 8.34 [t, ^4J(H–H) = 1.25, ^3J(Pt–H) = 142, 1H, H^a], 7.60 [d, ^3J(H–H) = 7.45, ^3J(Pt–H) = 40,1H, H^5], 7.25 [dd, ^3J(H–H) = 7.2, ^4J(H–H) = 1.25, 1H, H^2], 7.16 [td, ^3J(H–H) = 7.5, ^4J(H–H) = 1.2, 1H, $H^{3\,or\,4}$], 6.98 [td, ^3J(H–H) = 7.4, ^4J(H–H) = 1.25, 1H, $H^{3\ or\ 4}$], 3.88 [td, ^3J(H–H) = 5, ^4J(H–H) = 1.5, ^3J(Pt–H) = 35.2, 2H, H^b], 2.86 [m, 2H, H^d], 2.84 [s, ^3J(Pt–H) = 14, 6H, H^e], 2.01 [q, ^3J(H–H) = 5.2, 2H, H^c]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 176.60 [C^a], 144.66 [C^6], 141.96 [C^1], 134.70 [C^4], 131.09 [^2J(Pt–C) = 44.1, C^5], 127.15 [^3J(Pt–C) = 32.0, C^2], 123.50 [C^3], {64.17, 57.96 [^2J(Pt–C) = 39.0], 50.06, C^b, C^c, C^d}, 27.32 [C^e]. ^{195}Pt NMR (54 MHz, $CDCl_3$): −3581.21 [s]. FAB-MS, *m/z*: 419.33 $[M]^+$, 383.35 $[M - Cl]^+$. Anal. Calc. for $C_{12}H_{17}N_2ClPt \cdot H_2O$: C, 32.91; H, 4.37; N, 6.40. Found: C, 33.2; H, 4.4; N, 6.7.

[PtCl{$(CH_3)_2N(CH_2)_3NCH(4\text{-}(NO_2)C_6H_3)$}] (**3g**) was obtained from 0.050 g (0.1 mmol) of compound **2g** and 0.009 g (0.1 mmol) of sodium acetate using the procedure reported for **3a**. Yield 44%. IR: ν(CH=N) = 1595.3 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 8.83 [d, ^4J(H–H) = 2.25, ^3J(Pt–H) = 42.3, 1H, H^5], 8.58 [s, ^3J(Pt–H) = 140, 1H, H^a], 7.85 [dd, ^3J(H–H) = 8.5, ^4J(H–H) = 2.25, 1H, H^3], 7.40 [d, ^3J(H–H) = 8.25, 1H, H^2], 4.00 [td, ^3J(H–H) = 5.50, ^4J(H–H) = 1.75, ^3J(Pt–H) = 17.3, 2H, H^b], 2.98 [m, 2H, H^d], 2.86 [s, ^3J(Pt–H) = 15, 6H, H^e], 2.08 [m, ^3J(H–H) = 4.75, 2H, H^c]. FAB-MS, *m/z*: 466.08 $[M]^+$, 428.05 $[M - Cl]^+$. Anal. Calc. for $C_{12}H_{16}N_3ClO_2Pt \cdot H_2O$: C, 29.86; H, 3.75; N, 8.70. Found: C, 29.7; H, 3.4; N, 8.5.

[PtCl{$(CH_3)_2N(CH_2)_3NCH(3,4\text{-}(MeO)_2C_6H_2)$}] (**3h**) was obtained from 0.124 g (0.24 mmol) of compound **2h** and 0.020 g (0.24 mmol) of sodium acetate using the procedure reported for **3a**. Yield 32%. IR: ν(CH=N) = 1592.6 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.17[t, ^4J(H–H) = 1.2, ^3J(Pt–H) = 142.4, 1H, H^a], 7.59[s, ^3J(Pt–H) = 44, 1H, H^5], 6.84 [s, ^4J(Pt–H) = 6.2, 1H, H^2], 3.97 [s, 3H, H^3], 3.83 [m, 2H, H^b], 3.80 [s 3H, H^4], 2.84 [s, ^3J(Pt–H) = 14.4, 6H, H^e], 2.85 [m, 2H, H^d], 1.99 [q, ^3J(H–H) = 5.2, 2H, H^c]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 175.46 [C^a], 151.10 [C^4], 145.72 [C^3], 136.90 [C^6], 136.02 [C^1], 116.71 [^2J(Pt–C) = 67.4, C^5], 110.04 [^3J(Pt–C) = 40.4, C^2], {56.06, 55.99, C^{MeO}}, {64.25, 57.40 [^2J(Pt–C) = 37.4], 50.11, C^b, C^c, C^d}, 27.43 [C^e]. ^{195}Pt NMR (54 MHz, $CDCl_3$): −3567.00 [s]. FAB-MS, *m/z*: 479.9 $[M]^+$, 442.9 $[M - Cl]^+$. Anal. Calc.: C, 35.04; H, 4.41; N, 5.84. Found: C, 35.3; H, 4.9; N, 5.8.

4.2.3. Preparation of phosphine derivatives

[PtCl{$(CH_3)_2N(CH_2)_3NCH(4\text{-}ClC_6H_3)$}($PPh_3$)] (**4a**) was obtained from 0.035 g (0.08 mmol) of compound **3a** and 0.020 g (0.08 mmol) of triphenylphosphine, which were allowed to react in acetone at room temperature for 4 h. The residue was washed with hexane and dried in vacuum. Yield 98%. IR: ν(CH=N) = 1618.0 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 8.84 [d, ^4J(P–H) = 9.4, ^3J(Pt–H) = 100, 1H, H^a], 7.73 [m, ^3J(H–H) = 9, ^3J(P–H) = 12, 6H, H^f], 7.4–7.3 [m, $H^{g,h}$], 7.18 [d, ^3J(H–H) = 7.9, 1H, H^2], 6.88 [d, ^3J(H–H) = 6.8, 1H, H^3], 6.4 [s, ^3J(Pt–H) = 56, 1H, H^5], 4.12 [m, ^3J(H–H) = 5.25, 2H, H^b], 2.42 [t, ^3J(H–H) = 6.8, 2H, H^d], 2.26 [s, 6H, H^e], 2.10 [m, ^3J(H–H) = 6.7, 2H, H^c]. ^{31}P NMR (101 MHz): δ 21.36 [s, ^1J(P–Pt) = 4132.8]. FAB-MS, *m/z*: 716.8 $[M]^+$, 681.0 $[M - Cl]^+$.

[PtCl{$(CH_3)_2N(CH_2)_3NCH(2\text{-}ClC_6H_3)$}($PPh_3$)] (**4b**) was obtained from 0.035 g (0.08 mmol) of compound **3b** and 0.020 g (0.08 mmol) of triphenylphosphine, which were allowed to react in acetone at room temperature for 4 h. The residue was washed with hexane and dried in vacuum. Yield 44%. IR: ν(CH=N) = 1610.6 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.85 [d, ^4J(P–H) = 9.5, ^3J(Pt–H) = 95, H^a], 7.72 [ddd, ^3J(H–H) = 8.2, ^4J(H–H) = 1.75, ^3J(P–H) = 11.8, 5H, H^f], 7.5-7.3 [m, $H^{g,h}$], 6.83 [dd, ^3J(H–H) = 7.75, ^4J(H–H) = 1.25, 1H, H^3], 6.48 [t, ^3J(H–H) = 7.6, H^4], 6.37

Table 2
Crystallographic and refinement data

	Compound **3a**	Compound **3b**	Compound **3e**
Empirical formula	$C_{12}H_{16}Cl_2N_2Pt$	$C_{12}H_{16}Cl_2N_2Pt$	$C_{13}H_{19}ClN_2Pt$
Molecular weight	454.26	454.26	433.84
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1/n$	Orthorhombic, *Pbca*
Unit cell dimensions			
a (Å)	6.231(5)	6.4940(10)	10.670(10)
b (Å)	11.603(3)	11.398(10)	11.282(18)
c (Å)	9.721(3)	18.7880(10)	22.96(4)
α (°)	90	90	90
β (°)	94.3(10)	100.640(10)	90
γ (°)	90	90	90
Volume (Å^3)	701.1(6)	1366.8(12)	2764(7)
Z; calculated density (Mg m^{-3})	2; 2.152	4; 2.208	8; 2.085
Absorption coefficient (mm^{-1})	10.368	10.636	10.326
F(000)	428	856	1648
Crystal size (mm)	$0.1 \times 0.1 \times 0.2$	$0.1 \times 0.1 \times 0.2$	$0.1 \times 0.1 \times 0.2$
Θ range for data collection (°)	2.10–29.96	3.65–35.90	2.61–33.48
Limiting indices	$-8 \leqslant h \leqslant 8.0 \leqslant k \leqslant 16.0 \leqslant l \leqslant 13$	$-8 \leqslant h \leqslant 8.0 \leqslant k \leqslant 15.0 \leqslant l \leqslant 27$	$0 \leqslant h \leqslant 16.0 \leqslant k \leqslant 17.0 \leqslant l \leqslant 35$
Reflections collected/unique [R(int)]	2085/2085 [0.0918]	6801/2699 [0.0453]	4327/4327 [0.0825]
Completeness to θ	97.7% ($\theta = 29.99$)	–	–
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2085/1/148	2699/0/154	4327/0/155
Goodness-of-fit on F^2	1.057	1.144	1.212
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0482$, $wR_2 = 0.1171$	$R_1 = 0.0436$, $wR_2 = 0.1352$	$R_1 = 0.0348$, $wR_2 = 0.0885$
R indices (all data)	$R_1 = 0.0566$, $wR_2 = 0.1217$	$R_1 = 0.0497$, $wR_2 = 0.1494$	$R_1 = 0.0452$, $wR_2 = 0.0959$
Absolute structure parameter	0.08(3)	–	0.00019(11)
Largest diff. peak and hole (e Å^{-3})	0.989 and −0.868	0.884 and −0.765	0.832 and −0.818

[dd, ^3J(H–H) = 8.0, ^4J(H–H) = 2.4, ^3J(Pt–H) = 49, 1H, H^5], 4.15 [m, ^3J(H–H) = 4.5, 2H, H^b], 2.50 [t, ^3J(H–H) = 6.25, 2H, H^d], 2.34 [s, 6H, H^e], 2.17 [m, 2H, H^c]. ^{31}P NMR (101 MHz): δ 21.36 [s, ^1J(P–Pt) = 4132.8]. FAB-MS, m/z: 717.6 [M]$^+$, 681.6 [M − Cl]$^+$.

[Pt{$(CH_3)_2N(CH_2)_3NCH$(2-ClC_6H_3)}{$PPh_2(CH_2)_2$-PPh_2}]Cl (**5b**) was obtained from 0.030 g (0.07 mmol) of compound **3b** and 0.026 g (0.07 mmol) of triphenylphosphine, which were allowed to react in acetone at room temperature for 4 h. The residue was washed with hexane and filtered in vacuum. Yield 44%. IR: ν(CH=N) = 1600.9 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 [d, ^3J(P–H) = 7.6, ^3J(Pt–H) = 90, 4H, H^a], 7.89 [d, ^3J(P–H) = 12.0, ^3J(H–H) = 7.0, 4H, H^h], 6.98 [d, ^3J(H–H) = 7.6, H^4], 6.79 [td, ^3J(H–H) = 8.0, ^4J(H–H) = 1.76, 1H, H^3], 6.67 [m, H^5], 3.75 [bm, 2H, H^b]. ^{31}P NMR (101 MHz): δ 46.68 [s, ^1J(P–Pt) = 1906.21, P_A], 39.96 [s, ^1J(P–Pt) = 3605.95, P_B]. FAB-MS, m/z: 816.86 [M − Cl]$^+$.

4.3. X-ray structure analysis

4.3.1. Data Collection, structure solution and refinement for *3a*

A prismatic crystal was selected and mounted on an Enraf-Nonious CAD4 four circle diffractometer. Intensities were collected with graphite monochromatized Mo Kα radiation. The structures were solved by using SHELXS program [18], and refined by full-matrix least-squares method with SHELX 97 computer program using 2085 reflections (very negative intensities were not assumed). Further details are given in Table 2.

4.3.2. Data Collection, structure solution and refinement for *3b* and *3e*

Prismatic crystals were selected and mounted on a MAR345 diffractometer with an image plate detector. Intensities were collected with graphite monochromatized Mo Kα radiation. The structures were solved using SHELXS program [18], and refined by full-matrix least-squares method with SHELX97 computer program using 2699 (**3b**) and 4327 (**3e**) reflections (very negative intensities were not assumed). Further details are given in Table 2.

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Appendix A. Supplementary data

The preparation and spectroscopic data (IR, ^{1}H NMR) of compounds **1a**–**1h** (3 pages).

The crystallographic data of compounds **3a**, **3b** and**3e** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 268978, 268979 and 268980, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.06.038.

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