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Reactions of [C,N,N′]-cyclometallated platinum compounds with phosphines: *transphobia* and effect of the chloro substituents Crystal structure of $[PtCl(3,5\text{-}C_6H_2Cl_2CHNCH_2CH_2NMe_2)(PPh_3)_2]$

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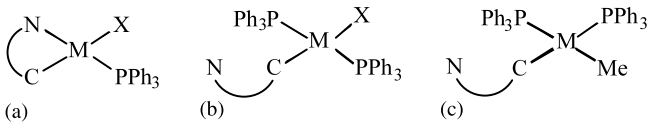
Abstract

The reaction of [C,N,N′]-cyclometallated platinum compounds $[PtX(C_6H_{4-n}Cl_nCHNCH_2CH_2NMe_2)]$ (**1a**–**1g**) with triphenylphosphine gave either [C,N]-cyclometallated compounds $[PtX(C_6H_{4-n}Cl_nCHNCH_2CH_2NMe_2)PPh_3]$ (**2**), in which PPh_3 is *trans* to the imine nitrogen, or compounds $[PtX(C_6H_{4-n}Cl_nCHNCH_2CH_2NMe_2)(PPh_3)_2]$ (**4**), with cleavage of the metallacycle. The stereochemistry of compounds **2** is the expected one according to the *transphobia* effect, while formation of compounds **4** takes place only when there is a chlorine atom adjacent to the metallated carbon. An ionic compound **3** has also been obtained using the chelate diphosphine 1,2-bis(diphenylphosphino)ethane. All compounds have been fully characterised including a structure determination for $[PtCl(3,5\text{-}C_6H_2Cl_2CHNCH_2CH_2NMe_2)(PPh_3)_2]$ (**4f**).

Keywords: Platinum; Cyclometallated compounds; Phosphines; N-donor ligands

1. Introduction

Cyclometallated compounds attract a great deal of interest due to their numerous applications in several fields, such as organic and organometallic synthesis, the design of new metallomesogens, and biologically active compounds [1]. The most widely studied examples are palladium and platinum metallacycles with nitrogen donors, which can be stabilised as monomers (Figure a of Chart I) using ligands such as tertiary phosphines [2].



The regioselectivity of the reaction between cyclometallated dinuclear complexes and Lewis bases has been extensively studied and the term *transphobia* has been proposed to explain the increasing phobia of being mutually *trans* of the following pair of ligands: X-donor/Y-donor (X,Y = halogen, N-donor, P-donor) ≃ C-donor, X-donor (X = halogen, N-donor) < C-donor/P-donor < C-donor/C-donor [3]. In addition, the *trans* choice concept has been recently proposed as the effect according to which the most stable complex is that having the softest and the hardest ligands in *trans* positions [4]. Both *transphobia* and *trans* choice concepts can be related to the previously reported antisymbiotic effect which indicates that two soft ligands in mutually *trans* positions will have a desestabilising effect when attached to a class b metal [5].

There is a lot of information available about these reactions in palladium complexes, but in contrast platinum compounds have been less studied and present some exceptions to these rules since kinetically controlled reactions are not rare in platinum chemistry [4].

On the other hand, depending on the nature of the cycle and the basicity of the nitrogen donor, cleavage of the metal–nitrogen bond may be achieved in the reaction of palladacycles with monodentate phosphines

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[6]. Moreover, steric crowding in the coordination sphere of the metal has been shown to favour the cleavage of metallacycles upon reaction with triphenylphosphine. In particular, the presence of a fluorine [7] or a chlorine [8] atom in the position adjacent to the M–C(aryl) bond seems to be decisive. In such cases, the newly entering phosphine replaces the nitrogen atom, leading either to a *trans* or a *cis* arrangement of both phosphines, as depicted in structures b and c of Chart I.

This paper analyses the reactions of triphenylphosphine with cyclometallated platinum compounds of general formula $[PtX(C_6H_{4-n}Cl_nCHNCH_2CH_2NMe_2)]$ recently reported [9]. These compounds contain a terdentate [C,N,N′] ligand and may upon reactions with phosphines, lead to either bidentate [C,N] or monodentate [C] systems. Both the influence of the chlorine substituents in the tendency of the metallacycle to open up and the stereochemistry of the obtained compounds will be analysed. It should be noted that these ligands direct the entering phosphine to a position *trans* to the carbon atom, and that this is not the most favoured arrangement according to the previously mentioned models.

2. Results and discussion

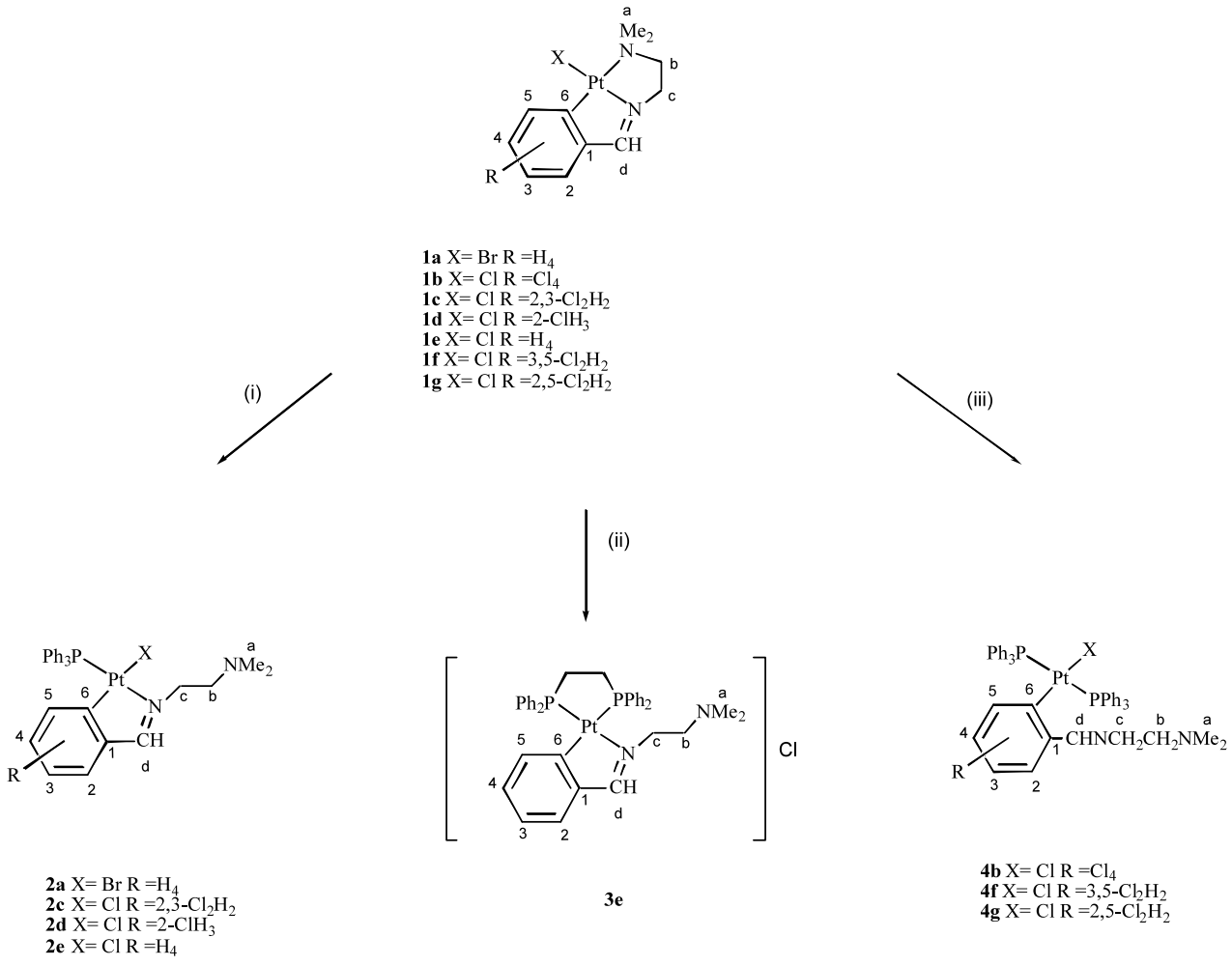
2.1. Reactions with phosphines

The reactions of **1a**–**1f** with phosphines were carried out in acetone at room temperature and produced the compounds depicted in Scheme 1.

The reactions of **1a**, **1c**, **1d** and **1e** with triphenylphosphine gave compounds **2**, in which 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. Spectral characterisation of these compounds indicates that the phosphine is *trans* to nitrogen in agreement with the *transphobia* effect described above [3]. Therefore, initial displacement of the NMe_2 moiety by the phosphine ligand is followed by isomerisation to the more stable isomer. Compounds **2** are yellow solids, which were characterised by elemental analyses, FAB-MS, and ^{1}H-, ^{31}P- and ^{195}Pt-NMR spectra. The J(P–Pt) values observed in both ^{31}P- and ^{195}Pt-NMR spectra suggest the presence of a PPh_3 coordinated to platinum and the obtained values (**2a**: 4042 Hz, **2c**: 4080 Hz, **2d**: 4120 Hz and **2e**: 4159 Hz) support the *trans* arrangement of phosphorus and nitrogen indicated above. The ^{195}Pt-NMR spectra show a doublet, due to coupling with one phosphorous atom, the position of which is consistent with the nature of the ligands bound to platinum(II) [10]. The $\delta(^{195}Pt)$ values indicate a downfield shift on increasing the chlorination of the aryl ring which is consistent with deshielding of the platinum nucleus. In the ^{1}H-NMR spectra, no platinum satellites are observed for the dimethylamino group, thus ruling out the possibility of pentacoordination of the platinum. The imine group appears as a doublet due to coupling to ^{31}P and also shows platinum satellites, which confirms both coordination of the imine nitrogen to platinum and a *trans* arrangement of this atom and the phosphine ligand. For **2a** and **2e**, the methylene resonances appear as broad unresolved signals. The ^{1}H- and ^{31}P-NMR spectra of **2e** recorded at lower temperatures showed the presence of two compounds with coordinated triphenylphosphine in nearly (1:1) ratio for which the structures in Scheme 2 are deduced [11]. The conductivity observed for compound **2e** in acetone is consistent with the proposed equilibrium between a neutral and an ionic compound. Moreover, the FAB mass spectrum of **2e** does not show the molecular peak but a peak corresponding to the loss of the chloro ligand.

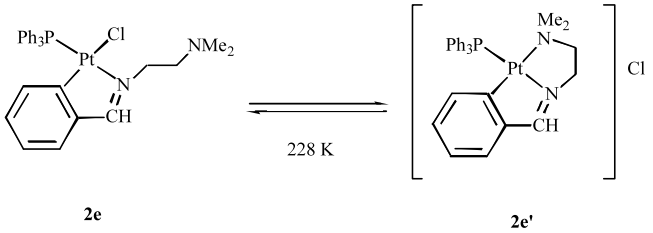
The reaction of compound **2e** with 1 mol of PPh_3 was monitored by ^{1}H- and ^{31}P-NMR, and no evidence of coordination of a second phosphine with cleavage of the metallacycle was obtained. However, several changes in the spectra took place in the presence of free phosphine. The methylene resonances appear as well-resolved triplets, the phosphorus resonance is very broad and the imine proton is now a singlet coupled to ^{195}Pt but not to phosphorus. These results are consistent with a fast exchange between coordinated and free phosphine, as proposed for analogous palladium compounds (see Scheme 3) [12].

Since both palladium(II) [13] and platinum(II) [14] metallacycles are easily cleaved with diphosphines due to the chelating nature of these ligands, the reaction of **1e** with 1,2-bis(diphenylphosphino)ethane (dppe) was also studied. Examples in which the formation of either compounds containing a bridging diphosphine [15] or ionic compounds with a chelate diphosphine [16] is favoured over cleavage of the metallacycles have also been reported in the literature. Upon reaction with dppe, compound **1e** gave a light yellow solid which was characterised by FAB-MS, ^{1}H-, ^{31}P- and ^{195}Pt-NMR spectra. The ^{1}H-NMR spectrum suggests that the imine behaves as a [C,N] ligand since no platinum satellites are observed for the dimethylamino group, while the imine resonance consists of a doublet due to coupling to the phosphorus in *trans* position and also shows platinum satellites. The ^{31}P-NMR spectrum shows two sets of resonances due to two non-equivalent phosphorus atoms, both coupled to platinum. The values of J(P–Pt) which were confirmed by ^{195}Pt-NMR are consistent with the presence of a N-donor (J(P–Pt) = 3635 Hz) and a C-donor (J(P–Pt) = 1876 Hz) *trans* to the phosphorus atoms. The spectral characterisation and the conductivity observed in acetone ($\Lambda = 98\ \Omega^{-1}\ cm^2\ mol^{-1}$) are consistent with an ionic nature for cyclometallated compound **3e** as depicted in Scheme 1. A peak



(i): + PPh_3 (1:1) in acetone ; (ii): + dppe (1:1) in acetone; (iii): + PPh_3 (2:1) in acetone

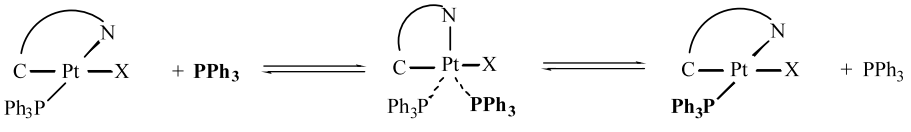
Scheme 1.



Scheme 2.

corresponding to the complex cation was obtained in the FAB mass spectrum. Compound **3e** could not be isolated in a pure form due to decomposition processes during attempted crystallisation in several solvents. The formation of an ionic compound with dissociation of the chloro ligand clearly shows the high stability of the metallacycle which is resistant to cleavage even when reacted with chelating diphosphines.

Compounds **1b**, **1f** and **1g** which contain a chloro substituent in position 5 gave under reaction conditions similar to those reported for the reactions of **1a** with triphenylphosphine, a 1:1 mixture of $[PtCl(C_6H_{4-n}Cl_nCH{=}NCH_2CH_2NMe_2)(PPh_3)_2]$ (**4**) and starting platinum material [17]. Compounds **4**, best obtained from reaction of the corresponding compound **1** with two equivalents of PPh_3, are white solids. They were characterised by elemental analyses, ^{1}H-, ^{31}P- and ^{195}Pt-NMR spectra, and compound **4f** was



Scheme 3.

also characterised by ^{13}C-NMR and X-ray crystal structure determination. Both dimethylamine and imine protons lack platinum satellites, indicating that the imine is acting as a monodentate ligand through the aryl carbon. Only one signal is observed in the ^{31}P-NMR spectra and the coupling constant J(P–Pt) deduced from both ^{31}P and ^{195}Pt spectra is in the range expected for mutually *trans* phosphines [18]. The ^{195}Pt-NMR spectra consist of a triplet due to coupling with two mutually *trans* phosphorus atom. The $\delta(^{195}\text{Pt})$ values move to high field when compared to compounds **2** in agreement with replacement of a N-donor for a P-donor in the coordination sphere of platinum [10].

2.2. Crystal structure of compound *4f*

Suitable crystals were obtained upon addition of diethylether to an acetone solution of **4f** followed by slow evaporation. The crystal structure is composed of discrete molecules separated by van der Waals interactions. A view of the molecule is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The crystal structure confirms the square-planar coordination around platinum, completed with two mutually *trans* PPh_3 ligands, a chloro and a monodentate [C] ligand, as well as the presence of a chlorine atom (Cl[5]) adjacent to the metallated carbon in the aryl group. Bond lengths and angles are well within the range of values obtained for analogous compounds [16]. As observed for square-planar aryl complexes of platinum(II), the metallated

Table 1
Selected bond lengths (Å) and angles (°) for compound **4f** with estimated standard deviations

Bond length (Å)	
Pt–C(1)	2.023(4)
Pt–P(1)	2.3092(11)
Pt–P(2)	2.3106(10)
Pt–Cl(1)	2.3767(11)
Cl(2)–C(4)	1.737(4)
Cl(3)–C(6)	1.717(4)
C(2)–C(7)	1.524(5)
N(1)–C(7)	1.191(6)
N(2)–C(10)	1.444(10)
N(2)–C(9)	1.449(9)
N(2)–C(11)	1.481(12)
N(1)–C(8)	1.474(8)
C(8)–C(9)	1.531(11)
Bond angle (°)	
C(1)–Pt–P(1)	89.66(11)
C(1)–Pt–P(2)	89.31(11)
P(1)–Pt–Cl(1)	91.14(4)
P(2)–Pt–Cl(1)	89.85(4)

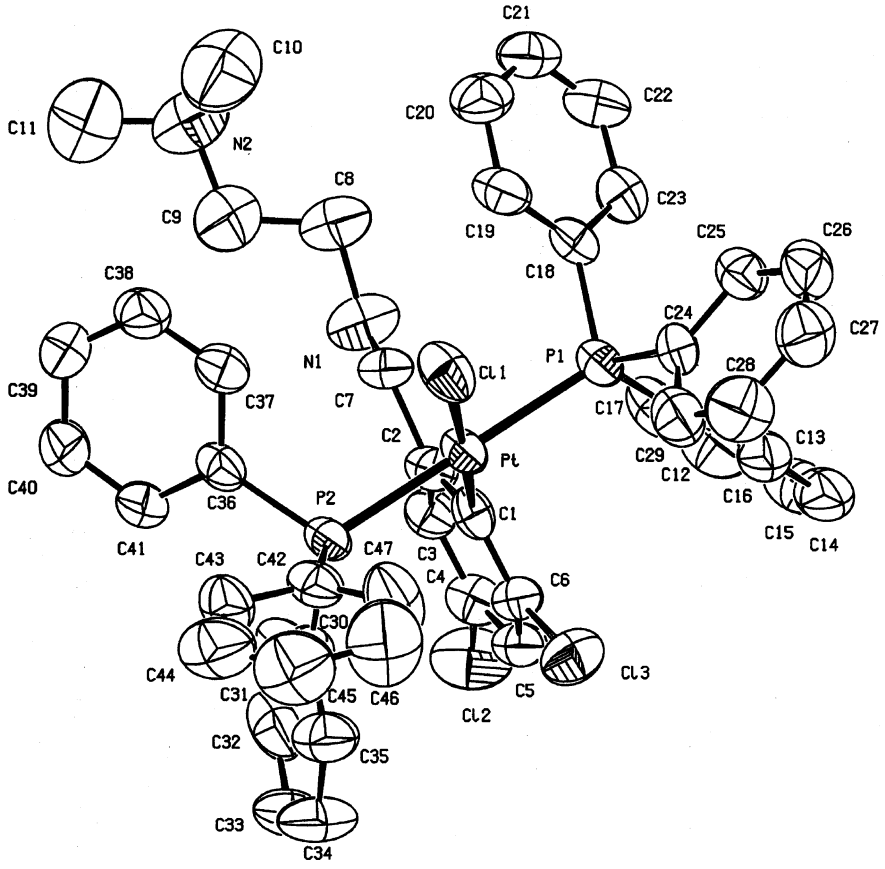


Fig. 1. Molecular structure of compound **4f**.

phenyl ring is nearly perpendicular to the coordination plane, the dihedral angle being 91.85°.

In conclusion, the five-membered *endo* platinacycles are very stable as is shown in the reaction of **1e** with dppe. However, this type of metallacycle can be easily cleaved provided that a chloro substituent is present in a position adjacent to the Pt–C bond. As previously reported for analogous systems [6,7], the cleavage of the metallacycle relieves the steric crowding in the coordination sphere of platinum. On the other hand, the stereochemistry of all the new platinum compounds containing triphenylphosphine is in agreement with the *transphobia* effect, in spite of the fact that the [C,N,N′] ligand directs the entering phosphine to a position *trans* to the carbon atom that is not the most favoured arrangement according to this model.

3. Experimental

3.1. General

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

FAB mass spectra were carried out in a VG-Quattro spectrometer with 3-nitrobenzyl alcohol matrix. ^{1}H-, ^{13}C-, ^{31}P- and ^{195}Pt-NMR spectra were recorded by using Varian Gemini 200 (^{1}H, 200 MHz), Varian XL300FT (^{13}C, 75.4 MHz) and Bruker 250 (^{31}P, 101.2 MHz; ^{195}Pt, 54 MHz) spectrometers, and referenced to $SiMe_4$ (^{1}H, ^{13}C), H_3PO_4 (^{31}P) and H_2PtCl_6 in D_2O (^{195}Pt). δ values are given in ppm and J values in Hz.

3.2. Preparation of the compounds

Compounds **1** were prepared as previously reported [9].

Compound [PtBr($C_6H_4CHNCH_2CH_2NMe_2$)PPh_3] (**2a**) was obtained from 50 mg (1.1×10^{-4} mol) of compound **1a** and 29 mg (1.1×10^{-4} mol) of PPh_3 which were allowed to react in acetone (20 ml) at room temperature for 2 h. The solvent was removed in a rotary evaporator and the residue was washed with hexane and dried in vacuo. Yield 60 mg (76%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.27 (s, H^{a}), 3.15 (m, H^{b}), 4.43 (m, H^{c}), 6.26 (d, J(H–H) = 7 Hz, J(H–Pt) = 50 Hz, H^{5}), 6.53 (t, J(H–H) = 7 Hz), 6.90 (t, J(H–H) = 7 Hz) H^{3}, H^{4}, 7.34–7.45 (m), 7.72–7.77 (m) PPh_3 and H^{2}, 8.77 (d, J(H–P) = 6 Hz, J(H–Pt) = 94 Hz, H^{d}) ppm. ^{31}P-NMR (101 MHz, $CDCl_3$): δ 24.35 (s, J(P–Pt) = 4042 Hz) ppm. ^{195}Pt-NMR (54 MHz, $CDCl_3$): δ −4227 (d, br, J(P–Pt) ca. 4000 Hz) ppm. FAB-MS, m/z: 632 [M–Br], 457 [$PtPPh_3$]. Anal. Found: C, 49.0; H, 4.5; N, 3.9. Calc. for $C_{29}H_{30}BrN_2PPt$: C, 48.88; H, 4.24; N, 3.93%.

Compound [PtCl(2,3-$C_6H_2Cl_2CHNCH_2CH_2NMe_2$)-$PPh_3$] (**2c**) was obtained as a yellow solid by an analogous procedure using 50 mg (1.1×10^{-4} mol) of compound **1e** and 28 mg (1.1×10^{-4} mol) of PPh_3. Yield 60 mg (75%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.32 (s, H^{a}), 2.89 (m, H^{b}), 4.25 (m, H^{c}), 6.36 (d, J(HH) = 8 Hz, J(H–Pt) = 55 Hz, 1H, H^{5}), 6.58 (d, J(HH) = 8 Hz, 1H, H^{4}), 7.43 (m), 7.65 (m) PPh_3, 8.82 (d, J(H–P) = 9 Hz, J(H–Pt) = 95 Hz, H^{d}) ppm. ^{31}P-NMR (101 MHz, $CDCl_3$): δ 22.0 (s, J(P–Pt) = 4080 Hz) ppm. ^{195}Pt-NMR (54 MHz, $CDCl_3$): δ −4155 (d, J(P–Pt) = 4080 Hz) ppm. Anal. Found: C, 47.2; H, 3.8; N, 3.9. Calc. for $C_{29}H_{28}Cl_3N_2PPt$: C, 47.26; H, 3.83; N, 3.80%.

Compound [PtCl(2-$C_6H_3ClCHNCH_2CH_2NMe_2$)-PPh_3] (**2d**) was obtained as a yellow solid by an analogous procedure using 60 mg (1.4×10^{-4} mol) of compound **1e** and 35 mg (1.4×10^{-4} mol) of PPh_3. Yield 76 mg (80%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.32 (s, H^{a}), 2.89 (t, J(H–H) = 6 Hz, H^{b}), 4.25 (m, H^{c}), 6.36 (m, J(H–Pt) = 55 Hz, 1H, H^{5}), 6.45 (t, J(HH) = 8 Hz, 1H, H^{4}), 6.82 (d, J(HH) = 8 Hz, 1H, H^{3}), 7.43 (m), 7.65 (m) PPh_3, 8.82 (d, J(H–P) = 9 Hz, J(H–Pt) = 95 Hz, H^{d}) ppm. ^{31}P-NMR (101 MHz, $CDCl_3$): δ 21.50 (s, J(P–Pt) = 4140 Hz) ppm. ^{195}Pt-NMR (54 MHz, $CDCl_3$): δ −4166 (d, J(P–Pt) = 4120 Hz) ppm. FAB-MS, m/z: 666 [M–Cl]. Anal. Found. C, 49.1; H, 4.0; N, 4.0. Calc. for $C_{29}H_{29}Cl_2N_2PPt$: C, 49.58; H, 4.16; N, 3.99%.

Compound [PtCl($C_6H_4CHNCH_2CH_2NMe_2$)PPh_3] (**2e**) was obtained as a yellow solid by an analogous procedure using 50 mg (1.2×10^{-4} mol) of compound **1e** and 32 mg (1.2×10^{-4} mol) of PPh_3. Yield 60 mg (73%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.43 (s, H^{a}), 2.89 (t, J(H–H) = 6 Hz, H^{b}), 4.25 (t, J(H–H) = 6 Hz, J(H–Pt) = 27 Hz, H^{c}), 6.51 (m, 2H), 6.89 (m, 2H) H$^{2-5}$, 7.43 (m), 7.64 (m) PPh_3; 8.66 (d, J(H–P) = 10 Hz, J(H–Pt) = 91 Hz, H^{d}) ppm. ^{31}P-NMR (101 MHz, $CDCl_3$): δ 24.21 (s, J(P–Pt) = 4159 Hz) ppm. ^{195}Pt-NMR (54 MHz, $CDCl_3$): δ −4221 (d, br, J(P–Pt) ca. 4200 Hz) ppm. Λ (10^{-3} M in acetone): 26.2 Ω^{-1} cm^{2} mol^{-1}. FAB-MS, m/z: 632 [M–Cl]. Anal. Found: C, 49.0; H, 4.4; N, 4.0. Calc. for $C_{29}H_{30}ClN_2PPt \cdot 2H_2O$: C, 49.47; H, 4.87; N, 3.98%.

Compound [Pt($C_6H_4CHNCH_2CH_2NMe_2$)dppe]Cl (**3e**) was obtained as a light yellow solid by an analogous procedure using 25 mg (6.2×10^{-5} mol) of compound **1e** and 25 mg (6.3×10^{-5} mol) of dppe. Yield 40 mg (81%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.04 (s, H^{a}), 1.93 (m, 2H), 2.45–2.53 (m, 4H), 3.59 (m, 2H) H^{b,c,e,f}, 6.84 (m, 1H), 7.09 (m, 1H), 7.60 (m), 7.90 (m) aromatics, 8.63 (d, J(H–P) = 8 Hz, J(H–Pt) = 87 Hz, H^{d}) ppm. ^{31}P-NMR (101 MHz, $CDCl_3$): δ 42.72 (s, J(P–Pt) = 3635 Hz, P^{b}), 50.24 (s, J(P–Pt) = 1876 Hz, P^{a}) ppm. ^{195}Pt-NMR (54 MHz, $CDCl_3$): δ −4673 (dd, J(P^{b}–Pt) =

3628 Hz, $J(P^a–Pt) = 1876$ Hz) ppm. Λ (10^{-3} M in acetone): 98 Ω^{-1} cm^2 mol^{-1}. FAB-MS, m/z: 768 [M–Cl].

Compound [PtCl($C_6Cl_4CHNCH_2CH_2NMe_2$)(PPh_3)$_2$] (**4b**) was obtained as a white solid by an analogous procedure using 50 mg (9.2×10^{-5} mol) of compound **1b** and 48 mg (1.8×10^{-4} mol) of PPh_3. Yield 70 mg (71%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.10 (s, H^a), 1.97 (t, $J(H–H) = 7$ Hz, H^b), 3.57 (t, $J(H–H) = 7$ Hz, H^c), 7.39 (m), 7.77 (m) PPh_3, 8.27 (s, H^d) ppm. ^{31}P-NMR (101 MHz, $CDCl_3$): δ 19.33 (s, $J(P–Pt) = 3052$ Hz) ppm. ^{195}Pt-NMR (54 MHz, $CDCl_3$): δ −4214 (t, $J(P–Pt) = 3054$ Hz) ppm. FAB-MS, m/z: 1065 [M], 998 [M–2Cl], 961 [M–3Cl], 803 [M–PPh_3], 769 [M–PPh_3–Cl], 718 [Pt(PPh_3)$_2$]. Anal. Found: C, 49.2; H, 4.1; N, 2.5. Calc. for $C_{47}H_{41}Cl_5N_2P_2Pt \cdot 4H_2O$: C, 49.51; H, 4.33; N, 2.46%.

Compound [PtCl(3,5-$C_6H_2Cl_2CHNCH_2CH_2NMe_2$)-($PPh_3$)$_2$] (**4f**) was obtained as a white solid by an analogous procedure using 50 mg (1.0×10^{-4} mol) of compound **1f** and 54 mg (2.1×10^{-4} mol) of PPh_3. Yield 74 mg (71%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.32 (s, H^a), 2.37 (m, H^b), 3.39 (t, $J(H–H) = 7$ Hz, H^c), 6.18 (d, $J(H–H) = 2$ Hz, 1H), 7.06 (d, $J(H–H) = 2$ Hz, 1H) H^2, H^4, 7.26–7.38 (m), 7.54–7.60 (m) PPh_3, 9.33 (s, H^d) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ 45.42 (s, C^a), 58.77 (s), 59.59 (s) C^c, C^b, 123.88 (s, $J(C–Pt) = 53$ Hz), 141.36 (s) C^2, C^4, 127.93 (s), 130.49 (s), 134.57 (s) PPh_3, 165.64 (s, $J(Pt–C) = 90$ Hz, C^d) ppm. ^{31}P-NMR (101 MHz, $CDCl_3$): δ 22.05 (s, $J(P–Pt) = 2921$ Hz) ppm. ^{195}Pt-NMR (54 MHz, $CDCl_3$): δ −4295 (t, $J(P–Pt) = 2930$ Hz) ppm. FAB-MS, m/z: 997 [M], 735 [M–PPh_3], 718 [Pt(PPh_3)$_2$], 700 [M–PPh_3–Cl]. Anal. Found: C, 56.5; H, 4.5; N, 2.1. Calc. for $C_{47}H_{43}Cl_3N_2P_2Pt$: C, 56.49; H, 4.34; N, 2.80%.

3.3. X-ray structure analysis

3.3.1. Data collection

A prismatic crystal was selected and mounted on a MAR345 diffractometer with an image plate detector. Unit cell parameters were determined from automatic centering of 11 247 reflections ($3° < \theta < 31°$) and refined by least-squares method. Intensities were collected with graphite monochromatised Mo–K_α radiation. 11 307 reflections were measured in the range $2.68° < \theta < 28.93°$, 7339 of which were non-equivalent by symmetry (R_{int} (on I) = 0.023) and 6425 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz polarisation and absorption corrections were made. Further details are given in Table 2.

3.3.2. Structure solution and refinement

The structure was solved by Patterson synthesis using SHELXS computer program [19] and refined by the full-matrix least-squares method, with the SHELXL97 computer program [19] using 7339 reflections (very negative intensities were not assumed). The function minimised was $\Sigma w||F_o|^2-|F_c|^2|^2$, where $w = [\sigma^2(I)+(0.0584P)^2+1.3536P]^{-1}$ and $P = (|F_o|^2+2|F_c|^2)/3$. f, f' and f'' were taken from International Tables of X-ray Crystallography [20]. All hydrogen atoms were computed and refined using a riding model with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom to which they are linked. Further details are given in Table 2.

Table 2
Crystallographic and refinement data for compound **4f**

Empirical formula	$C_{47}H_{43}Cl_3N_2P_2Pt \cdot 0.5C_3H_6O$
Formula weight	1028.25
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	12.1960(10)
b (Å)	13.4760(10)
c (Å)	16.6550(10)
α (°)	92.03
β (°)	106.63
γ (°)	114.79
V (Å^3); Z	2342.8(3); 2
d_{calcd} (Mg m^{-3})	1.458
Abs coefficient (mm^{-1})	3.269
F(0 0 0)	1028
Reflections coll./unique	11 307/7339 [$R_{int} = 0.0235$]
Data/restraint/parameters	7339/0/509
GOF on F^2	1.060
R_1 ($I > 2\sigma(I)$)	0.0313
wR_2 (all data)	0.0902
Peak and hole (e Å^{-3})	0.977 and −0.736

4. Supplementary material

The crystallographic data of compound **4f** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 206995. 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).

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[11] NMR data obtained at 228 K in $CDCl_3$ solution: ^{31}P-NMR: δ 23.1 ($J = 4223$ Hz) ppm, **2e**; 23.3 ($J = 3946$ Hz) ppm, **2e′**. ^{1}H-NMR δ 2.26 (6H), 3.31 (2H), 4.48 (2H), 8.97 (1H, $J = 90$ Hz) ppm, **2e**; 2,86 (6H), 3.58 (2H), 4.64 (2H), 8.62 (1H, $J = 75$ Hz) ppm, **2e′**.

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[17] Compound **1g** is the minor isomer obtained when $[Pt(dba)_2]$ reacted with 2,3,6-$Cl_3C_6H_2CHNCH_2CH_2NMe_2$ (see Ref. [9]). In this case, the reaction with triphenylphosphine has been carried out with the mixture of isomers **1c** and **1g** to afford **2c** and **4g**, respectively. NMR data for **4g**: ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.23 (s, H^a), 2.89 (m, $J(H–H) = 6$ Hz, H^b), 4.27 (m, H^c), 6.10 (d, $J(H–H) = 8$ Hz, 1H), 6.35 (d, $J(H–H) = 8$ Hz, 1H) H^3, H^4, 7.26–7.38 (m), 7.54–7.60 (m) PPh_3, 8.50 (s, H^d) ppm. ^{31}P-NMR (101 MHz, $CDCl_3$): δ 18.20 (s, $J(P–Pt) = 3054$ Hz) ppm.

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