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Cyclometallated platinum complexes with heterocyclic ligands

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Abstract

The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with imine ligands derived from 3-furaldehyde, 3- or 4-pyridinealdehyde and *N*,*N*-dimethylethylenediamine, and 3-furaldehyde and chlorobenzylamine are reported. The furane ligands coordinated to platinum through the nitrogen donor and could be forced to orthometallate under severe conditions. The ligands with pyridine rings gave only substitution of the ligand for the dimethylsulphide. The oxidative addition reactions of the orthometallated complexes with methyl iodide as well as the complexes' reactions with triphenylphosphine are also reported. Correlation between aromaticity of the orthometallated ring and reactivity of the complexes is observed.

Keywords: Cyclometallation; Platinum; Furane; Oxidative addition; Imine

1. Introduction

Square planar platinum (II) and specifically cyclometallated complexes are of interest for several reasons including their interesting photochemical and photophysical properties, their potential use as molecular devices, and more generally as products or intermediates in catalytic reactions [1]. Cyclometallation reactions have been widely investigated for benzene derivatives. However, heterocyclic analogues have been less explored. The latter are attractive for regioselectivity studies due to the presence of non-equivalent positions available for metallation. Following our studies on intramolecular C–H bond activation of benzene [2] and thiophene rings [3] at platinum, we decided to study the activation of such bonds in furanes and pyridines using a similar strategy. The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with imine ligands derived from 3-furaldehyde, 3- or 4-pyridinealdehyde and *N*,*N*-dimethylethylenediamine or 2-chlorobenzylamine are reported.

As shown in Chart 1, 3-substituted furanes or pyridines can be cyclometallated at two non-equivalent positions. Previous studies for 3-substituted furanes indicate that the preferred metallation site is *ortho* to the oxygen atom [4]. On the other hand, examples of activation of C–H bonds in a *meta* position to the N atom have been reported for 2,2′-bipyridine [5] and 2,4′-bipyridine [6] systems. Moreover, double metallation at the two *meta* positions of the inner pyridine has also been reported for 2,2′:6′,2″-terpyridine ligand [7]. In addition, oxidative addition reactions involving transition metals are fundamental steps in stoichiometric and catalytic processes. Therefore we also report the oxidative addition of methyl iodide to the new cyclometallated complexes.

2. Results and discussion

2.1. Furane derivatives

Ligands 3-$(Me_2NCH_2CH_2NCH)C_4H_3O$ (**2a**) and 3-$(2'\text{-}ClC_6H_4CH_2NCH)C_4H_3O$ (**2b**) were prepared as yellow oils from the condensation reaction of 3-furaldehyde and *N*,*N*-dimethylethylenediamine or 2-chlo-

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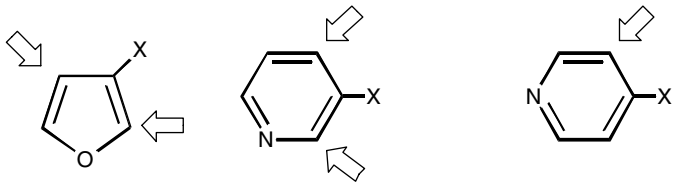
Possible metallation sites for the heterocycles under study



(a) 3 -substituted furane **(b)** 3 -substituted pyridines **(c)** 4 -substituted pyridines

Chart 1.

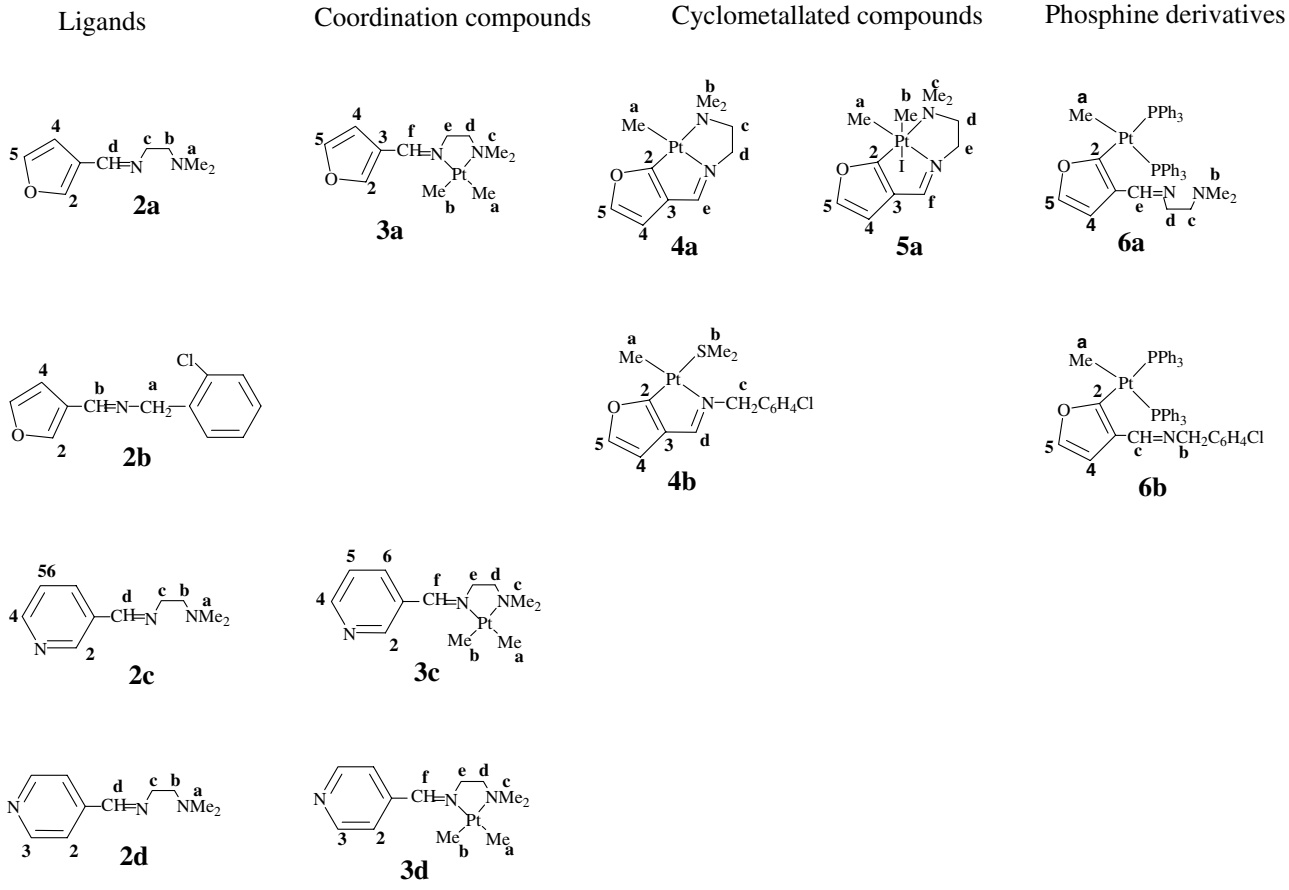
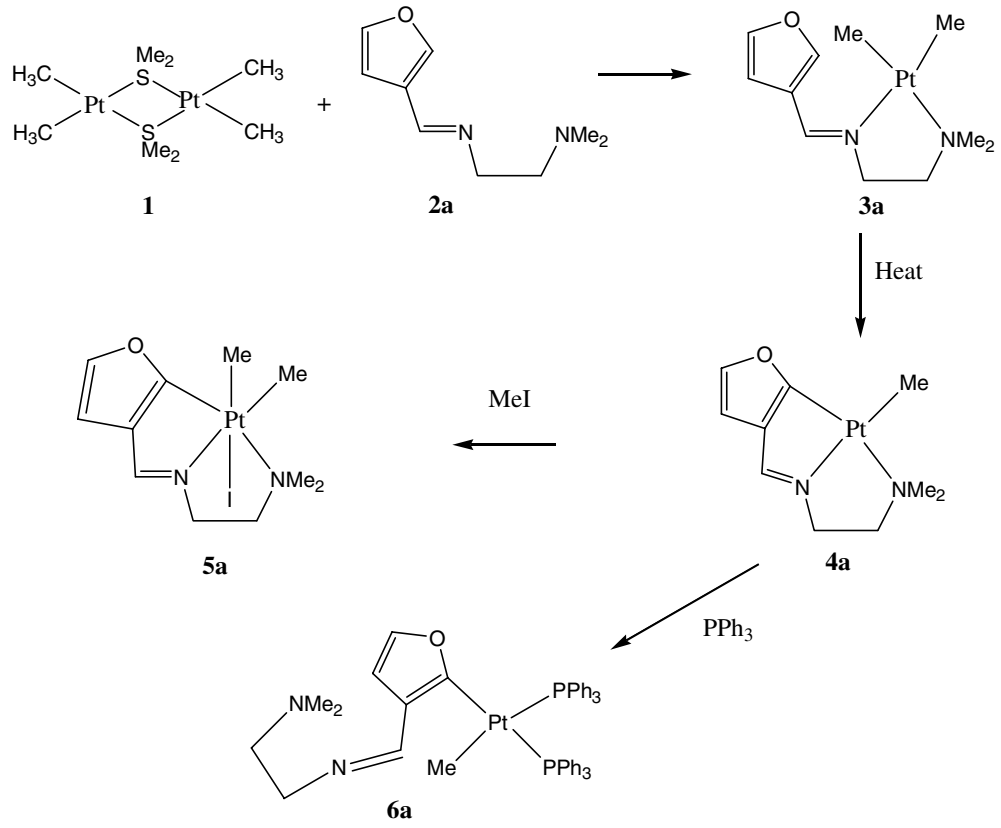


Chart 2.

robenzylamine carried out in toluene at room temperature (see Chart 2 for the structures of all new species). The resulting imines were characterized by ^{1}H and ^{13}C (**2a**) NMR spectra.

The reaction of ligand 3-($Me_2NCH_2CH_2NCH$)-C_4H_3O (**2a**) with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (**1**) carried out in acetone at room temperature produced compound [$PtMe_2${3-($Me_2NCH_2CH_2NCH$)-C_4H_3O}] (**3a**) in which the imine acts as a bidentate [N, N′] ligands (Scheme 1). Compound **3a** was characterized by ^{1}H and ^{13}C NMR spectroscopies, elemental analysis and FAB-mass spectra. In the ^{1}H NMR spectra, two distinct resonances appear in the methyl region, both coupled with ^{195}Pt. The one at higher field with a larger coupling to ^{195}Pt is assigned to the methyl *trans* to the NMe_2 [2]. The coordination of the ligand through the nitrogen atoms is confirmed by the coupling of both amine and imine protons to platinum. The chemical shifts observed for ^{195}Pt are in the expected range [8] for a platinum (II) center bound to two carbon and two nitrogen atoms. For the purpose of comparison, ^{195}Pt NMR spectra were also taken for the previously reported compounds [$PtMe_2\{Me_2NCH_2CH_2NCHC_6H_5\}$] [2] and [$PtMe_2${3-($Me_2NCH_2CH_2NCH$)$C_4H_3S$}] [3] (Table 1).



Scheme 1.

Table 1
$\delta(^{195}Pt)$ values for compounds $[PtMe_2\{3\text{-}(Me_2NCH_2CH_2NCH)Ar\}]$ (**3**) and $[PtMe\{3\text{-}(Me_2NCH_2CH_2NCH)(Ar\text{-}H)\}]$ (**4**)[a]

Aryl	Compound **3**	Compound **4**	$\Delta\delta$[b]
C_4H_3O	−3520[c]	−3732[c]	212
C_4H_3S	−3492[d]	−3669[d]	177
C_6H_5	−3466[e]	−3612[e]	146

[a] $\delta(^{195}Pt)$ in ppm referenced to H_2PtCl_6 in D_2O.
[b] $\Delta\delta = \delta(^{195}Pt$ for **3**) − $\delta(^{195}Pt$ for **4**).
[c] Prepared in this work.
[d] Synthesis reported in [3].

Compound **3a** is stable in acetone solution at room temperature for several days in contrast to the behavior of compounds $[PtMe_2\{Me_2NCH_2CH_2NCHC_6H_5\}]$ [2] and $[PtMe_2\{3\text{-}(Me_2NCH_2CH_2NCH)C_4H_3S\}]$ [3] which, under these conditions, have been reported to yield the corresponding cyclometallated compounds with elimination of methane. The lower tendency of the furane derivative towards cyclometallation is attributed to the lower degree of aromaticity of furane (16 kcal/mol) versus benzene (36 kcal/mol) or thiophene (29 kcal/mol) [9]. The aromaticity of a system containing a five-member *endo*-metallacycle fused with an aryl ring has been reported as the main driving force for the formation of platinum (II) and palladium (II) *endo*-metallacycles [10].

However, the cyclometallated compound $[PtMe\{3\text{-}(Me_2NCH_2CH_2NCH)C_4H_2O\}]$ (**4a**) containing a tridentate [C,N,N′] ligand could be obtained when a toluene solution of **3a** was refluxed for 2 h (Scheme 1) and the resulting complex was characterized by multinuclear NMR spectroscopies, elemental analysis and FAB-MS.

As previously reported for thienyl systems [3], the site of metallation was the C(2) position of the furane ring. This is consistent with the J(H–H) value of 6 Hz obtained for the two aromatic protons (H^4 and H^5). Values between 5 and 6 Hz are expected for adjacent ring hydrogens confirming the C(2) metallation site [4]. The proposed structure consisting of a three-fused ring system containing a five-membered metallacycle is shown in Chart 2. All spectral parameters for compound **4a** are in good agreement with the results obtained for analogous aryl cyclometallated compounds [2,3]. As shown in Table 1, the value obtained for $\delta(^{195}Pt)$ moves to higher fields for cyclometallated complexes when compared to the value for the corresponding non-cyclometallated precursor, an effect which is larger for the furane derivative ($\Delta\delta = 212$ PPM) than for benzene or thiophene analogues. These values are also correlated to the aromaticity of the cyclometallated rings.

Oxidative addition of methyl iodide to compound **4a** was achieved in acetone solution to give (Scheme 1) the

resulting cyclometallated platinum (IV) compound [$PtMe_2I$\{3-($Me_2NCH_2CH_2NCH$)C_4H_2O\}] (**5a**) which was characterized by NMR spectroscopy. The spectral parameters are in good agreement to those reported for analogous compounds arising from *trans* oxidative addition [11]. In particular, two examples: (1) the values of the coupling constants of the methylplatinum and the imine protons to ^{195}Pt decrease and (2) the $\delta(^{195}Pt)$ resonance is downfield shifted upon oxidation of platinum (II) to platinum (IV).

The reaction of ligand 3-(2′-$ClC_6H_4CH_2NCH$)C_4H_3O (**2b**) with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (**1**) carried out in toluene for 16 h at room temperature produced the cyclometallated platinum (II) compound [$PtMe$\{3-(2′-$ClC_6H_4CH_2NCH$)C_4H_3O\}SMe_2] (**4b**) in which the imine acts as a [C,N] ligand. Activation of the C–Cl bond that would lead to an *exo*-platinum (IV) metallacycle was not observed, which suggest that the reactivity order: C–H (*endo*) >C–Cl (*exo*) previously reported for phenyl systems [12] also holds for furane derivatives. Compound **4b** was characterized by NMR and mass spectroscopies as well as elemental analysis. Analogous to **4a**, the J(H–H) values obtained for the two hydrogen atoms of the furane ring indicate that metallation took place at the C(2) position of the furane.

The reactions of compounds **4a** and **4b** with triphenylphosphine in 1:1 and 1:2 molar ratio were studied. In the latter case, compounds [$PtMe$\{3-($Me_2NCH_2CH_2NCH$)C_4H_2O\}$(PPh_3)_2$] (**6a**) and [$PtMe$\{3-(2′-$ClC_6H_4CH_2NCH$)C_4H_3O\}$(PPh_3)_2$] (**6b**) were produced with cleavage of the metallacycles (Scheme 1), while in the former a mixture of compounds **4** and **6** is obtained. Attempts to obtain cyclometallated compounds containing only one PPh_3 were unsuccessful. For analogous phenyl derivatives, opening of the metallated ring upon reaction with triphenylphosphine had only been achieved when a chlorine [13] or a fluorine [14,15] atom was present in the position adjacent to the Pt–C(aryl) bond, while for analogous thienyl derivatives, the triphenylphosphine replaced only either the SMe_2 ligand or the NMe_2 moiety of the tridentate ligand without cleaving the corresponding metallacycles [3,16]. The lower stability of the metallacycles obtained for the furane derivatives when compared to the thiophene or the phenyl analogues, again attributed to the lower aromaticity of the furane ring, can account for the differences in reactivity towards triphenylphosphine.

Compounds **6a** and **6b** were characterized by NMR and mass spectroscopy and data are consistent with the structures depicted in Chart 2. Compounds **6** could not be isolated in a pure form due to decomposition processes during attempted crystallization in several solvents. The methylplatinum resonance is coupled to ^{195}Pt and to two non-equivalent phosphorous atoms. The imine is not coupled with platinum which is taken as evidence for the cleavage of the metallacycle. The ^{31}P NMR spectra show two sets of resonances due to non-equivalent phosphorous atoms, in mutually *cis*-positions, both coupled to platinum. In each case, the larger J(P–Pt) value (2141 (**6a**); 2147 (**6b**)) is assigned to the phosphine *trans* to the furyl group due to the smaller *trans* influence expected for this group compared to methyl. The values of the coupling constants J(P–Pt) from the ^{31}P spectra were in agreement with the values found in the ^{195}Pt NMR spectra. $\delta(^{195}Pt)$ values are well within the range expected for organoplatinum (II) compounds with phosphine ligands [14,17].

2.2. Pyridine derivatives

Ligands 3-($Me_2NCH_2CH_2NCH$)C_5H_4N (**2c**) and 4-($Me_2NCH_2CH_2NCH$)C_5H_4N (**2d**) were prepared as yellow oils from the corresponding pyridinealdehyde and *N*,*N*-dimethylethylenediamine and characterized by ^1H and ^{13}C NMR spectra. The reactions of **2c** and **2d** with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (**1**) were carried out under similar conditions described above for **2a**. The reactions gave insoluble orange solids, which could not be properly characterized. Therefore, the reactions of ligands **2c** and **2d** with **1** were monitored by ^1H NMR in acetone-d^6. In the early stages, compounds [$PtMe_2$\{3-($Me_2NCH_2CH_2NCH$)C_5H_4N\}] (**3c**) and [$PtMe_2$\{4-($Me_2NCH_2CH_2NCH$)C_5H_4N\}] (**3d**) were detected together with free ligand and quickly, within several minutes insoluble orange compounds were produced. Compound **3c** was characterized by FAB-mass spectroscopy. The FAB-mass spectrum shows intense peaks corresponding to loss of one and two methyl groups from the proposed formula of **3c**.

With the aim of obtaining cyclometallated compounds, the reactions of **2c** and **2d** with **1** in refluxing toluene were performed. Again, very insoluble orange solids were obtained and the FAB-mass spectra for the compound derived from **2c** was identical to that obtained for **3c** (see above). Since peaks corresponding to loss of methyl groups were observed for **3c**, there is no conclusive evidence whether or not cyclometallation with loss of methane took place under any of these conditions. As a whole, the poor solubility of the platinum compounds obtained from ligands derived from pyridines hindered their characterization. In spite of the results obtained for the mass spectra, the formation of polymeric species arising from coordination to platinum centers through the pyridine nitrogen can not be ruled out and this would explain the low solubility.

3. Concluding remarks

The heterocyclic furane and pyridine ligands described above react somewhat differently than the thiophene and benzene ligands previously reported. The

orthometalled furane complexes are more difficult to synthesize, as more severe reaction conditions were needed for their formation compared to the thiophene or benzene derivatives. The complexes are also less stable as witnessed by the easy cleavage of the metallocycle ring with triphenylphoshine not regularly seen for analogous complexes. These results and others, such as trends in the platinum NMR spectra are attributed to the lower aromaticity of the furane ring compared to the other rings.

The bond energy of the C–H bonds being broken may well have a role in the reactivity trends. It has been shown that the selectivity and rates of intramolecular oxidative addition for aryl halides vary inversely with the Ar–X bond energy [2]. These results compare very similar aryl systems where only the halide atom changes and the bond energies of interest span a large range of values (Ar–F = 116 kcal/mol, Ar–Br = 72 kcal/mol) [18]. However, this is much different for the furane and thiophene cases. Calculated values for the energy of C–H bonds of small heterocyclic rings exist and the difference between furane and thiophene for the bond in question is only 1.8 kcal/mol [19]. Therefore, any conclusion made with respect to the C–H bond energy being the rate-determining factor should be guarded with caution. The mechanism probably initially includes partial coordination of the heterocyclic ring followed by activation of the C–H bond through a tri-centered C–Pt–H interaction, the proximity of the bond to be broken and its approach to the metal being the most important factor in the mechanism and not the bond energy of the C–H bond. We therefore suggest that the transition state may be stabilized when a more aromatic ring is being metallated and this therefore makes thiophene faster than furane. The initial step may also include partial coordination of the sulfur in thiophene thus also increasing the rate of thiophene versus furane as sulfur is a better ligand than oxygen for platinum.

The pyridine ligands were suspected to give only coordination compounds and it was inconclusive whether any orthometallation had occurred. The complexes were difficult to characterize due to their low solubility and this is attributed to the formation of polymeric species.

4. Experimental

4.1. General

^{1}H, ^{13}C, ^{31}P and ^{195}Pt NMR spectra were recorded at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using Varian Gemini 200 (^{1}H, 200 MHz; ^{13}C, 50 MHz), Varian 500 (^{1}H, 500 MHz), and Bruker 250 (^{31}P, 101.25 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. Microanalyses and mass spectra (FAB, 3-nitrobenzyl alcohol matrix) were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona. Compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) was prepared as reported [20].

4.2. Synthesis of ligands

Compound **2a** was prepared by the reaction of 0.46 g (5.2 mmol) of *N*,*N*-dimethylethylenediamine with an equimolar amount (0.5 g) of 3-furaldehyde in toluene (20 ml). The mixture was stirred for 30 min and dried over Na_2SO_4. The solvent was removed in a rotary evaporator to yield a yellow oil. Compounds **2b**, **2c** and **2d** were similarly prepared from 0.74 g of 2-chlorobenzylamine and the equimolar amount (0.5 g) of 3-furaldehyde (**2b**) or from 0.46 g (5.2 mmol) of *N*,*N*-dimethylethylenediamine and the equimolar amount (0.56 g) of the corresponding pyridinealdehyde (**2c**, **2d**). **3-($Me_2NCH_2CH_2NCH$)C_4H_3O** (**2a**). Yield: 0.7 g (81%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.30$ [s, H^a]; 2.61 [t, $^{3}J(H^b\text{–}H^c) = 7$, H^b]; 3.64 [t, $^{3}J(H^c\text{–}H^b) = 7$, H^c]; 6.81 [d, J(H–H) = 2, H^4]; 7.41 [d, J(H–H) = 2, H^2]; 7.70 [s, H^5]; 8.25 [s, 1H, H^d]. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 45.81$ [C^a]; {59.95, 60.04, $C^{b,c}$}; 107.77 [C^4]; 125.34 [C^3]; 143.84 [C^5]; 145.00 [C^2]; 153.37 [C^d]. **3-(2′-$ClC_6H_4CH_2NCH$)C_4H_3O** (**2b**). Yield: 0.9 g (79%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 4.89$ [s, H^a]; {6.87 [d, J(H–H) = 2, 1H], 7.24–7.44 [m, 5H]; 7.75 [s, 1H], aromatics}; 8.33 [s, 1H, H^b]. **3-($Me_2NCH_2CH_2NCH$)C_5H_4N** (**2c**). Yield: 0.8 g (87%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.31$ [s, H^a]; 2.66 [t, $^{3}J(H^b\text{–}H^c) = 7$, H^b]; 3.77 [t, $^{3}J(H^c\text{–}H^b) = 7$, H^c]; 7.34 [dd, J(H–H) = 8, J(H–H) = 5, H^5]; 8.12 [dt, J(H–H) = 8, J(H–H) = 2, H^4]; 8.36 [s, H^2]; 8.65 [dd, J(H–H) = 5, J(H–H) = 2, H^6]; 8.86 [d, J(H–H) = 2, 1H, H^d]. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 45.88$ [C^a]; {59.94; 60.06, $C^{b,c}$}; {123.52, 134.39, 150.15, 151.34, aromatics}; 158.79 [C^d]. **4-($Me_2NCH_2CH_2NCH$)C_5H_4N** (**2d**). Yield: 0.8 g (87%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.31$ [s, H^a]; 2.66 [t, $^{3}J(H^b\text{–}H^c) = 7$, H^b]; 3.79 [t, $^{3}J(H^c\text{–}H^b) = 7$, H^c]; {7.59 [d, J(H–H) = 6, 2H, H^2], 8.68 [d, J(H–H) = 6, 2H, H^3], aromatics}; 8.30 [s, 1H, H^d]. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 45.85$ [C^a]; {59.75, 59.98, $C^{b,c}$}; 121.84 [C^2]; 150.26 [C^3]; 159.74 [C^d].

4.3. Synthesis of compound *3a*

Compound **3a** was obtained by adding a solution of 65 mg (3.9×10^{-4} mol) of the imine **2a** in acetone (10 ml) to a solution of 100 mg (1.74×10^{-4} mol) of compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) in acetone (10 ml). The mixture was stirred for 30 min at room temperature and compound **3** was obtained upon removal of the acetone in a rotary evaporator. The orange-yellow solid was washed with ether (3×2 ml) and dried in vacuum. **[$PtMe_2${*3*-($Me_2NCH_2CH_2NCH$)C_4H_3O}]** (**3a**). Yield: 110 mg

(81%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.45$ [s, ^2J(Pt–H) = 91, Me^a]; 0.58 [s, ^2J(Pt–H) = 84, Me^b]; 2.62 [t, J(H–H) = 5, H^d]; 2.79 [s, ^3J(Pt–H) = 21, H^c]; 4.00 [t, J(H–H) = 5, H^e]; {7.35 [d, J(H–H) = 2, 1H], 7.38 [d, J(H–H) = 2, 1H], H^{4,5}}; 8.20 [s, H^2]; 8.75 [s, ^3J(Pt–H) = 49, H^f]. ^{1}H NMR (200 MHz, acetone-d^6): $\delta = 0.30$ [s, ^2J(Pt–H) = 93, Me^a]; 0.39 [s, ^2J(Pt–H) = 85, Me^b]; 2.63 [t, J(H–H) = 5, H^d]; 2.70 [s, ^3J(H–Pt) = 22, H^c]; 3.99 [t, J(H–Pt) = 12, J(H–H) = 5, H^e]; {7.54 [d, J(H–H) = 2, 1H], 7.57 [d, J(H–H) = 2, 1H], H^{4,5}}; 8.43 [s, H^2]; 8.92 [s, ^3J(Pt–H) = 51, H^f]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3520$ [s]. FAB(+)-MS, m/z: 391 [M], 375 [M–Me], 359 [M–2Me]. Anal. Found: C, 33.4; H, 5.0; N, 6.6. Calc. for $C_{11}H_{20}N_2OPt$: C, 33.76; H, 5.15; N, 7.16%.

4.4. Detection of compounds *3c* and *3d*

15 mg of compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and 10 mg of the corresponding ligand were dissolved in 0.7 ml of acetone-d^6 in an NMR tube and ^{1}H NMR spectra were taken. After several minutes, the formed orange solids were collected by filtration, dried and analyzed by FAB-mass spectroscopy (**3c**). **[PtMe$_2${*3*-(Me$_2$NCH$_2$-CH$_2$NCH)C$_5$H$_4$N}]** (**3c**): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.01$ [s, ^2J(Pt–H) = 91, Me^a]; 0.45 [s, ^2J(Pt–H) = 85, Me^b]; 2.73 [m, H^d]; 2.77 [s, ^3J(H–Pt) = 22, H^c]; 4.10 [t, J(H–H) = 5, H^e]; 7.36 [dd, J(H–H) = 8, J(H–H) = 5, 1H, H^5]; 8.70 [dd, J(H–H) = 5, J(H–H) = 2, 1H, H^6]; 9.05 [dd, J(H–H) = 8, J(H–H) = 2, 1H, H^4]; 9.26 [s, ^3J(Pt–H) = 47, H^f]; 9.45 [s, H^2]. FAB-MS(NBA): 385 [M–Me], 370 [M–2Me]. **[PtMe$_2${*4*-(Me$_2$NCH$_2$CH$_2$-NCH)C$_5$H$_4$N}]** (**3d**): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.01$ [s, ^2J(Pt–H) = 92, Me^a]; 0.48 [s, ^2J(Pt–H) = 85, Me^b]; 2.76 [m, H^d]; 2.77 [s, ^3J(H–Pt) = 22, H^c]; 4.12 [t, J(H–H) = 5, H^e]; {8.35 [d, J(H–H) = 6], 8.62 [d, J(H–H) = 6], H^{2,3}}; 9.29 [s, ^3J(Pt–H) = 46, H^f].

4.5. Synthesis of compound *4a*

Compound **4a** was obtained by refluxing during two hours a toluene solution (20 ml) containing 100 mg of compound **3a**. The solvent was removed in a rotary evaporator and the red residue was washed with ether (3×2 ml) to yield a brown-orange solid which was washed with ether and dried in vacuum. **[PtMe{*3*-(Me$_2$NCH$_2$CH$_2$NCH)C$_4$H$_2$O}]** (**4a**). Yield: 75 mg (78%). ^{1}H NMR (200 MHz, acetone-d^6): $\delta = 1.07$ [s, ^2J(Pt–H) = 80, Me^a]; 2.81 [s, ^3J(Pt–H) = 24, Me^b]; {3.16 [t, J(H–H) = 6], 3.95 [t, J(H–H) = 6], H^{c,d}}; {6.36 [d, J(H–H) = 2], 7.37 [d, J(H–H) = 2, J(Pt–H) = 18], H^{4,5}}; 8.18 [s, ^3J(Pt–H) = 36, H^e]. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -18.27$ [J(Pt–C) = 750, Me^a]; 48.91 [C^b]; {51.40 [J(C–Pt) = 24], 68.54 [s], C^{c,d}}; 107.05 [J(C–Pt) = 25, C^4], 129.00 [C^3], 140.98 [C^2], 143.09 [J(C–Pt) = 72, C^5], 159.96 [J (Pt–C) = 45, C^e]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3732$ [s]. FAB(+)-MS, m/z: 375 [M], 359 [M–Me]. Anal. Found: C, 32.2; H, 4.5; N, 7.1. Calc. for $C_{10}H_{16}N_2OPt$: C, 32.00; H, 4.30; N, 7.46%.

4.6. Synthesis of compound *4b*

Compound **4b** was obtained by adding a solution of 77 mg (3.9×10^{-4} mol) of **2b** in toluene (10 ml) to a solution of 100 mg (1.74×10^{-4} mol) of compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) in toluene (10 ml). The mixture was stirred for 16 h at room temperature. The toluene was removed in a rotary evaporator and the residue was washed with hexane (3 × 2 ml) and dried in vacuum. **[PtMe{*3*-(2′-ClC$_6$H$_4$CH$_2$NCH)C$_4$H$_2$O}]** (**4b**). Yield: 96 mg (70%). ^{1}H NMR (200 MHz, acetone-d^6): $\delta = 1.19$ [s, ^2J(Pt–H) = 82, Me^a]; 2.02 [s, ^3J(Pt–H) = 30, Me^b]; 5.05 [s, J(Pt–H) = 13, H^c]; {6.45 [d, J(H–H) = 2, 1H], 7.23 [m, 2H], 7.37 [m, 2H], 7.48 [d, J(H–H) = 2, J(Pt–H) = 20, 1H], aromatics}; 8.19 [s, ^3J(Pt–H) = 32, H^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -4099$ [s]. FAB(+)-MS, m/z: 475 [M–Me], 428 [M–SMe$_2$], 413 [M–Me–SMe$_2$]. Anal. Found: C, 37.2; H, 3.6; N, 3.1. Calc. for $C_{15}H_{18}ClNOPtS$: C, 36.70; H, 3.70; N, 2.85%.

4.7. Synthesis of compound *5a*

An excess of methyl iodide (0.5 ml) was added to a solution of 50 mg of compound **4a**. After continuous stirring at room temperature, an insoluble red residue was filtered off and discarded. The solvent was removed and the residue was recrystallized in dichloromethane-hexane to yield an orange solid which was dried in vacuum. **[PtMe$_2$I{*3*-(Me$_2$NCH$_2$CH$_2$NCH)C$_4$H$_2$O}]** (**5a**). Yield: 35 mg (43%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.85$ [s, ^2J(Pt–H) = 69, Me^b]; 1.40 [s, ^2J(Pt–H) = 65, Me^a]; {2.58 [s, ^3J(H–Pt) = 19], 3.24 [s, ^3J(H–Pt) = 14], Me^c}; {3.04 [m, 1H], 4.01–4.24 [m, 3H], H^{d,e}}; {6.49 [d, J(H–H) = 2], 7.43 [d, J(H–H) = 2, J(Pt–H) = 12], H^{4,5}}; 8.10 [s, ^3J(Pt–H) = 32, H^f]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2657$ [s]. FAB(+)-MS, m/z: 390 [M–I], 375 [M–I–Me], 360 [M–I–2Me]. Anal. Found: C, 25.3; H, 3.8; N, 4.9. Calc. for $C_{11}H_{19}IN_2OPt$: C, 25.54 ; H, 3.70; N, 5.42%.

4.8. Reactions with triphenylphosphine

Compounds **6** were obtained by adding a solution of two equivalents of triphenylphosphine to solutions of the corresponding compound **4** in acetone (**4a**: 25 mg, 6.7×10^{-5} mol; **4b**: 25 mg, 5.1×10^{-5} mol) and stirring the resulting solutions at room temperature for 3 h. The acetone was removed in a rotary evaporator and the

residue was washed with hexane (3×2 ml) and ether (3×2 ml) and dried in vacuum.

4.9. [PtMe{3-($Me_2NCH_2CH_2NCH$)C_4H_2O}(PPh_3)$_2$] (**6a**)

Yield: 35 mg (58%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.48$ [dd, ^2J(Pt–H) = 66, J(P–H) = 9; 7, Me^a]; 2.33 [s, Me^b]; {2.53 [t, J(H–H) = 8], 3.60 [t, J(H–H) = 8], H$^{c,\,d}$}; {6.39 [d, J(H–H) = 2, 1H], 7.03–7.72 [m], aromatics}; 8.57 [s, H^e]. ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = 24.20$ [d, ^1J(Pt–P) = 1826, J(P–P) = 14]; 26.25 [d, ^1J(Pt–P) = 2141, J(P–P) = 14]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -4627$ [dd, J(P–Pt) = 2149; 1827]. FAB(+)-MS, m/z: 719 [Pt(PPh_3)$_2$], 455 [Pt(PPh_3)], 377 [M-2 PPh_3].

4.10. [PtMe{3-(2′-$ClC_6H_4CH_2NCH$)C_4H_2O}(PPh_3)$_2$] (**6b**)

Yield: 30 mg (62%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.48$ [dd, ^2J(Pt–H) = 66, J(P–H) = 9; 7, Me^a]; 4.74 [s, H^b]; {6.46 [d, J(H–H) = 2, 1H], 7.06–7.40 [m], aromatics}; 8.68 [s, H^e]. ^{31}P NMR (101.25 MHz, $CDCl_3$): $\delta = 24.11$ [d, ^1J(Pt–P) = 1824, J(P–P) = 14]; 26.21 [d, ^1J(Pt–P) = 2147, J(P–P) = 14]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -4627$ [dd, J(P–Pt) = 2164; 1828]. FAB(+)-MS, m/z: 734 [PtMe(PPh_3)$_2$], 719 [Pt(PPh_3)$_2$], 455 [Pt(PPh_3)].

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