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Five- and six-membered platinacycles derived from phenantryl and anthracenyl imines

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Abstract

The reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with ligands $Me_2NCH_2CH_2NCHAr$ (**2a**, Ar = 9-phenantryl; **2b**, Ar = 9-anthracenyl) carried out in acetone at room temperature produced the corresponding compounds $[PtMe_2\{9\text{-}(Me_2NCH_2CH_2NCH)C_{14}H_9\}]$ (**3**) in which the imines act as bidentate [N,N′] ligands. Refluxing toluene solutions of compounds **3** gave cyclometallated [C,N,N′] compounds $[PtMe\{9\text{-}(Me_2NCH_2CH_2NCH)C_{14}H_8\}]$ (**4**) as a mixture of two isomers containing either a five- or a six-membered metallacycles for **3a** and as a single isomer containing a six-membered metallacycle for **3b**. The reactions of compounds **4** with acetyl chloride and with methyl iodide produced, respectively, compounds $[PtCl\{9\text{-}(Me_2NCH_2CH_2NCH)C_{14}H_8\}]$ (**5**) and $[PtMe_2I\{9\text{-}(Me_2NCH_2CH_2NCH)C_{14}H_8\}]$ (**6**). All compounds were characterised by NMR spectroscopies and analytical data.

Keywords: Platinum; Cyclometallation; Anthracene; Phenantrene; Imine

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 platinum and palladium metallacycles with nitrogen donors in which C–H activation takes place at phenylic *ortho* positions. Metallation at heterocyclic [2–4] or fused rings [5,6] systems have been less explored.

Following our studies of imines containing aromatic groups such as benzene [7], thiophene [3], furane [4] or naphthalenes [6], we now report the reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with imines derived from phenanthrene- and anthracene-9-carboxaldehydes. As shown in Chart 1, two non-equivalent metallation sites leading to either five- or six-membered metallacycles are available for ligands derived from phenanthrene while metallation at the anthracene group can only produce six-membered metallacycles. Although several six-membered platinacycles having nitrogen donor atoms have been reported [8], they are much less common than the most prevalent five-membered analogues [9].

The cyclometallation of anthracen-9-ylmethylenephenylamine [10] and of phenantrylamines [11] with palladium (II) to yield, respectively, six- and five-membered metallacycles have been reported. However, in spite of the interesting properties of anthracene and phenanthrene derivatives [12], platinacycles derived from these groups have not been reported yet in the literature.

2. Results and discussion

2.1. Syntheses of cyclometallated compounds

Imines **2a** and **2b** derived, respectively, from 9-phenanthraldehyde and 9-anthraldehyde were easily obtained from the reaction of $Me_2N(CH_2)_2NH_2$ and the corresponding aldehyde in toluene at room temperature. They were characterised by mass, IR, and NMR spectra. According to NMR data, only one isomer was present in solution and the expected E conformation was

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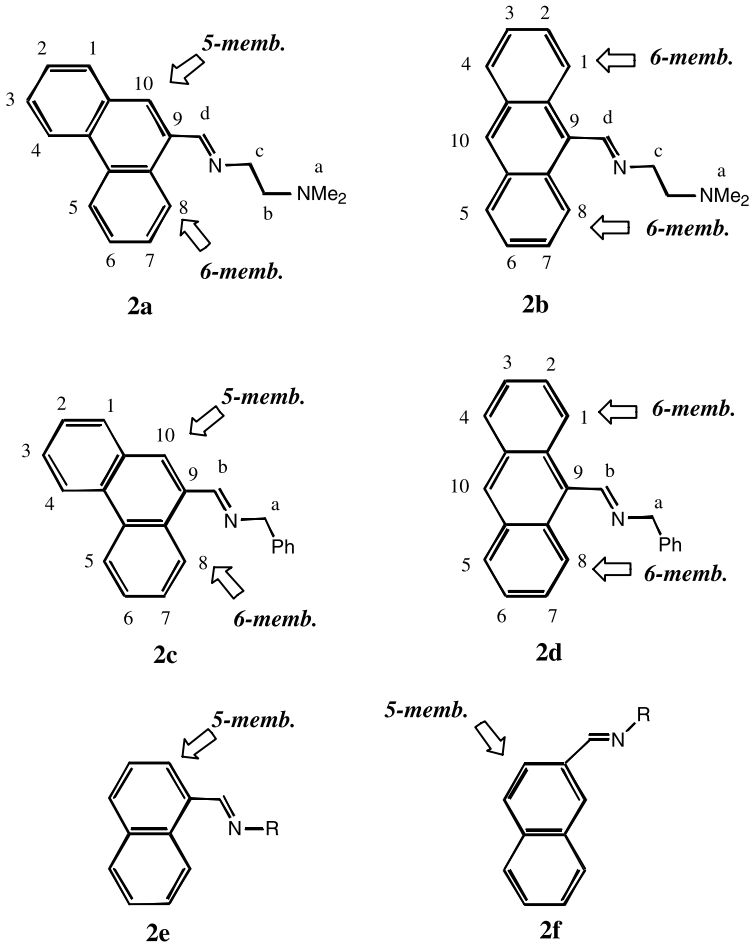
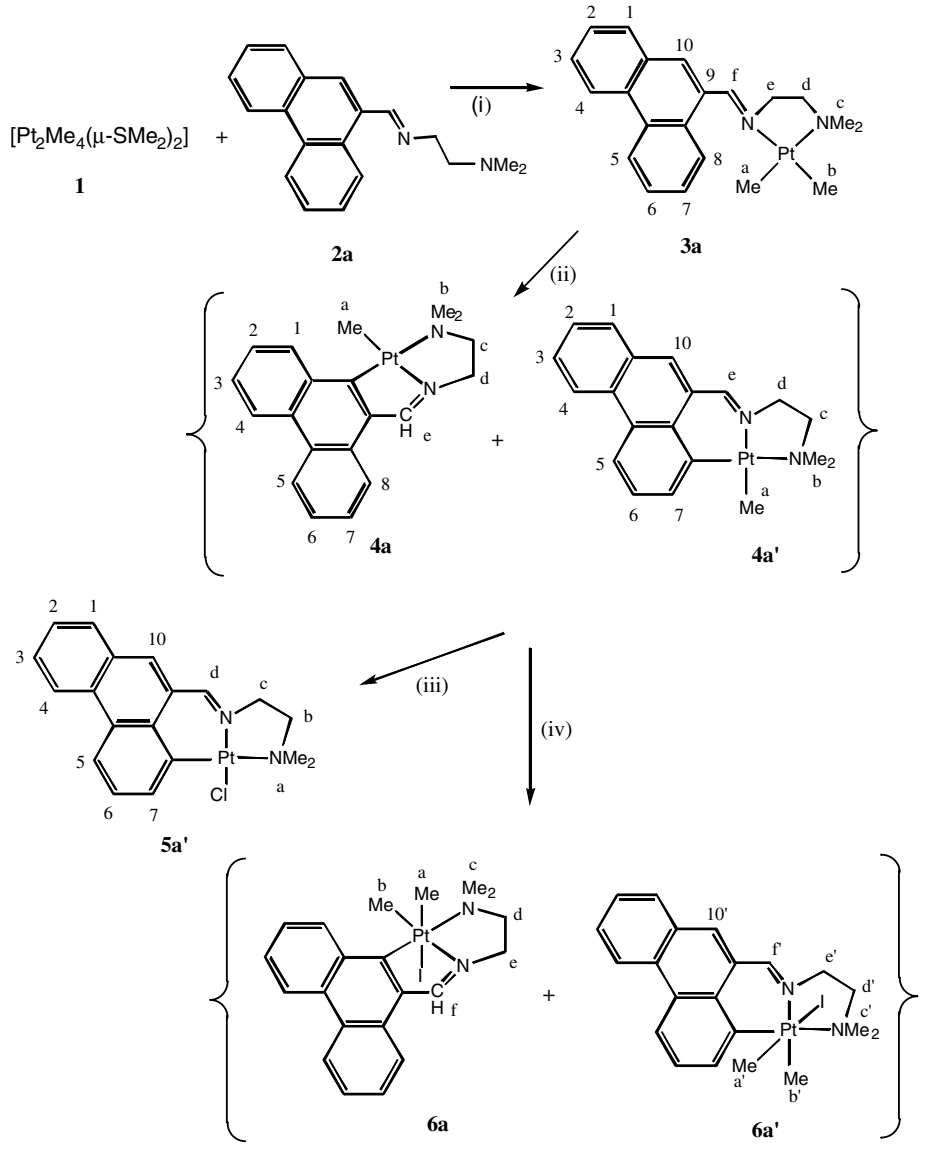


Chart 1. Possible metallation sites for ligands derived from phenanthrene (**2a** and **2c**) and anthracene-9-carboxaldehydes (**2b** and **2d**) along with the previously obtained results for ligands derived from 1- and 2-naphthaldehydes (**2e** and **2f**).

confirmed by NOESY experiments in which cross-peak signals between imine (H^d) and methylene (H^c) protons were observed.

As shown in Schemes 1 and 2, treatment of these potentially terdentate ligands with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) in acetone produced readily compounds $[PtMe_2(Me_2NCH_2CH_2NCHAr)]$ **3a** and **3b** in which the imines act as bidentate [N,N′] ligands. Compounds **3** were characterised by NMR spectroscopies, elemental analyses and FAB-mass spectra. In the ^1H 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 was assigned to the methyl *trans* to the NMe_2 moiety. The coordination of the ligand through both nitrogen atoms is confirmed by the observed coupling of both amine and imine protons to platinum. The aromatic region was assigned with the aid of ^1H–^1H correlation spectroscopy (COSY). As for the free imines, the cross-peak signals between H^e and H^f in the NOESY ^1H–^1H NMR spectra indicated an *E* conformation of the coordinated ligand. The chemical shifts observed for ^{195}Pt (−3432 ppm for **3a** and −3458 ppm for **3b**) are in the expected range for a platinum (II) centre bound to two-carbon and to two-nitrogen atoms [13].

Intramolecular activation of C–H bonds followed by methane elimination as reported for analogous systems [3,4,6,7] was achieved when toluene solutions of compounds **3** were refluxed for several hours. Work-up of the resulting solutions revealed that a mixture of two [C,N,N′] cyclometallated platinum (II) compounds (**4a** and **4a′**) were obtained from **3a**, while **3b** lead to a single isomer of [C,N,N′] cycloplatinated compound **4b**. These results indicate that formation of a five fused rings system containing a six-membered metallacycle is achieved from **3b**. The two isomers obtained from **3a** are assigned to analogous systems containing either five (**4a**) or six (**4a′**) membered metallacycles indicating that metallation is favoured at the two non-equivalent sites. As shown in Chart 1, six-membered metallacycles have not been obtained for ligands derived from 1-naphthaldehyde which have been reported to produce regioselectively a five-membered platinacycle [6] in agreement with the greater stability ascribed to five-membered rings [9]. The

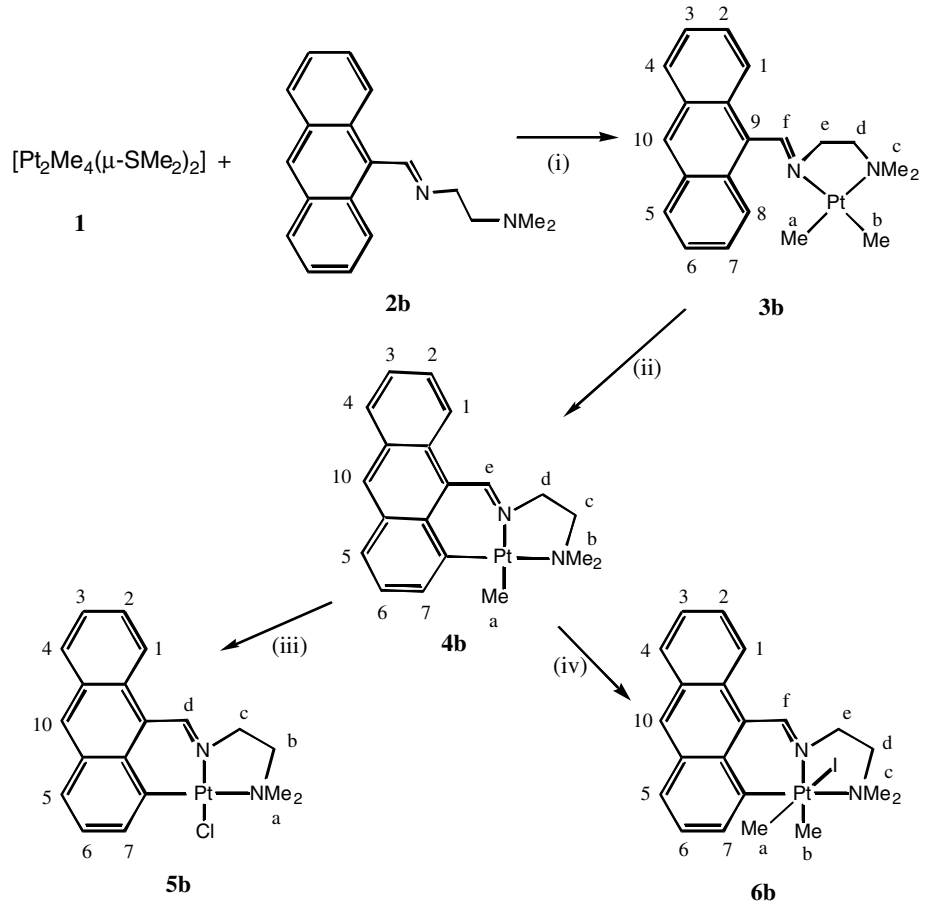


(i): acetone, r.t.; (ii): refluxing toluene;
(iii): + CH_3COCl in dichloromethane/methanol;
(iv): + CH_3I in acetone.

Scheme 1.

different result obtained for ligand **2a** can therefore be related to the steric effect of the third fused ring in the phenanthrene derivatives, which hampers formation of a five-membered metallacycle, and thus favours formation of the less stable six-membered metallacycle.

Compounds **4** were characterised by NMR spectroscopies, elemental analyses and FAB-mass spectra. Two sets of signals are observed for the mixture of compounds **4a**/**4a′** and their relatives intensities indicate a slightly higher abundance for the five-membered metallacycle (**4a**:**4a′** = 1.2:1). In the ^{1}H NMR spectra, the methyl ligand and the dimethylamino are coupled to platinum and the values of the coupling constants are in the usual range for analogous compounds [7]. In agreement with previous data, the J(H–Pt) values of the imine group increase from the coordination compound **3a** (J(H–Pt) = 49 Hz) to the cyclometallated compound **4a** (J(H–Pt) = 59 Hz) containing a five-membered metallacycle. However, lower values J(H–Pt) = 37–40 Hz were obtained for compounds **4a′** and **4b** containing a six-membered metallacycle. Moreover, while the two methylene resonances appear at lower fields than the



(i): acetone, r.t.; (ii): refluxing toluene;
(iii): + CH_3COCl in dichloromethane/methanol;
(iv): + CH_3I in acetone.

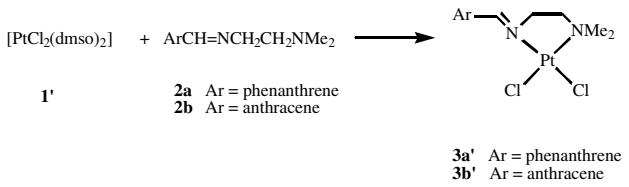
Scheme 2.

dimethylamino group for five-membered metallacycles, a different spectral pattern with the dimethylamino resonance in-between the methylene resonances is observed for the six-membered metallacycles. Assignment of the aromatic region was performed with the aid of ^1H–^1H correlation spectroscopy (COSY). The presence of 16 (**4a**/**4a′**) or eight (**4b**) crossing peaks in the aromatic region of the $\{^1H$–$^{13}C\}$-heterocorrelation spectra is consistent with metallation at two non-equivalent sites for imine **2a** and at the only available position for **2b**. In addition, the ^{195}Pt NMR spectra displays either two signals at $\delta = -3421$ and -3218 ppm assigned, respectively, to compounds **4a** and **4a′** or only one signal at $\delta = -3078$ ppm for **4b**. These values are in the expected range for a platinum (II) centre bound to two-carbon and to two-nitrogen atoms [13]. However, $\delta(^{195}Pt)$ is shifted downfield compared to the corresponding compound **3**, and this effect is larger when a six-membered metallacycle is formed as for compounds **4a′** and **4b**. This result is in contrast with the previously reported data, which indicate a highfield shift of the platinum resonance upon metallation [3,4,6].

Due to the low solubility and the lack of stability in solution of compounds **4**, these compounds could not be purified by recrystallisation and adequate crystals for X-ray analyses could not be obtained. Moreover, attempts to separate compounds **4a** and **4a′** either by fractional crystallisation or by column crystallography using $CHCl_3$/acetone mixtures as eluent were unsuccessful. After several hours in solution, hydrolysis of the coordinated imine yielding the corresponding aldehyde and a complex mixture of platinum compounds is obtained.

Attempts to produce cyclometallation of ligands **2a** and **2b** were also carried out using $[PtCl_2(dmso)_2]$ (**1′**) as metallation agent under the conditions previously reported for ligand $Me_2NCH_2CH_2N{=}CHPh$ [14]. The starting platinum compound and the corresponding ligand were refluxed in methanol during several hours to produce insoluble orange solids in high yields. Due to

the low solubility of these compounds, NMR spectra could not be taken. Based on FAB mass spectra and elemental analyses, the formula [$PtCl_2(Me_2NCH_2CH_2NCHAr)$] in which Ar is a phenantryl (**3a′**) or an anthracenyl group (**3b′**) is assigned to these compounds. The cyclometallation process leading to [$PtCl(Me_2NCH_2CH_2NCHC_{14}H_8)$] was attempted under prolonged reflux in methanol in the presence of sodium acetate. The obtained compounds show the same pattern than the coordination compounds in the FAB mass spectra and we assumed that due to their low solubility the reaction proceeds no further.



In order to attempt the syntheses of analogous [C,N] cyclometallated compounds, imines **2c** and **2d** were prepared from the reaction of $PhCH_2NH_2$with 9-phenanthraldehyde or 9-anthraldehyde in toluene at room temperature. The ligands were characterised by mass, IR, and NMR spectra. According to NMR data, only one isomer for which the expected *E* conformation was assumed was present in solution. Treatment of these potentially bidentate ligands with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (**1**) in acetone at room temperature during reaction times up to 60 h did not produce any observable reaction. When more drastic conditions such as refluxing in acetone or toluene were tested, only decomposition products such as metallic platinum and free aldehyde were obtained.

In previously reported systems [3,4,6], the results obtained for metallation processes are analogous for potentially terdentate or bidentate ligands. However, in the present case, ligands containing two nitrogen atoms proved to be superior. This result could be related to the great bulk of the antracene and phenantrene groups, which makes coordination of the ligands to the platinum centre more difficult. The presence of a second nitrogen atom in ligands **2a** and **2b** facilitates the coordination of the ligand as a [N,N′] chelate leading to compounds **3** which are precursors to the corresponding cyclometallated compounds.

2.2. Reactivity of the obtained cyclometallated compounds

As shown in Schemes 1 and 2, the reactions of cyclometallated compounds **4** with acetyl chloride and with methyl iodide were studied. According to previously reported results for analogous compounds, the reaction with acetyl chloride in methanol medium should lead to [C,N,N′] cyclometallated compounds in which the methyl ligand has been replaced for a chloro ligand [15]. As stated in the previous section, this type of compound could not be obtained from compounds **3a′** and **3b′**.

The reaction of compounds **4a/4a′** and **4b** with acetyl chloride in a mixture of dichloromethane and methanol produced, after recrystallisation in dicloromethane–hexane, a single isomer of the corresponding compound [$PtCl(Me_2NCH_2CH_2NCHC_{14}H_8)$] (**5**) in each case. The similarity of the spectral values obtained for these compounds and in particular the spectral pattern in which the dimethylamino resonance lies in-between the methylene resonances, as observed for **4a′** and **4b**, indicates that the single isomer obtained from the mixture **4a/4a′** contains a six-membered metallacycle. Unreacted compound **4a** was identified by ^1H NMR in the insoluble residue obtained in the recrystallisation of the crude product from reaction of the mixture **4a/4a′** but could not be obtained in a pure form due to the low stability of these compounds in solution. The fact that **4a** was recovered unchanged while **4a′** gave the expected reaction could be related either to a decreased reactivity or to a lower solubility of five- versus six-membered metallacycles.

The preparation of compounds **5** following this method supports the suggestion that the failure to obtain these compounds using [$PtCl_2(dmso)_2$] as metallation agent might be attributed to the low solubility of the coordination compounds [$PtCl_2(Me_2NCH_2CH_2NCHAr)$].

Compounds **5** were characterised by NMR spectroscopies, elemental analyses and FAB mass spectra. As for compounds **4**, attempts to crystallise compounds **5** in several solvents did not produce pure samples due to the low stability of the compounds in solution. The presence of the terdentate [C,N,N′] ligand is evidenced by the coupling of both NMe_2 and imine groups to ^{195}Pt, and the presence of eight crossing peaks in the aromatic region of the $\{^1H\text{–}^{13}C\}$-heterocorrelation spectra. Methyl for chloro substitution is evidenced by disappearance of the methyl-platinum resonance and by increase of the coupling constant J(H–Pt) for the imine proton, which is now *trans* to a chloro ligand. Furthermore, $\delta(^{195}Pt)$ values are shifted towards lower fields in agreement with a lower electronic density on the platinum nucleus. In the FAB mass spectra, the molecular peak as well as a peak corresponding to the loss of a chloro ligand were observed.

The reaction of compounds **4** with methyl iodide was also tested in order to obtain [C,N,N′] cyclometallated platinum (IV) compounds derived from anthracene or phenantrene. Previous studies of the oxidative addition of alkyl halides to platinum (II) compounds indicate that nitrogen donor ligands impart high nucleophilicity

to the metal centre, increasing its reactivity, which is, however, moderated by the presence of bulky ligands that might hinder or even inhibit the reaction [16]. In most cases, the oxidative addition of alkyl halides to organoplatinum (II) complexes gives *trans* stereochemistry, although subsequent isomerisation can yield products that appear to arise from *cis*-oxidative addition [17]. In spite of the presence of the bulky phenantryl or anthracenyl groups, the reaction of **4a/4a′** and **4b** with methyl iodide in acetone at room temperature gave the corresponding platinum (IV) compounds $[PtMe_2I(Me_2NCH_2CH_2NCHC_{14}H_8)]$ (**6**) arising from *trans*-oxidative addition of the alkyl halide.

Compounds **6** were characterised by NMR spectroscopies, elemental analyses and FAB mass spectra. As for compounds **4a** and **4a′**, two sets of signals are observed for the mixture of compounds **6a/6a′** and their relatives intensities (**6a**:**6a′** = 1.2:1) indicate that the relative amounts of five- and six-membered metallacycles is maintained. In the ^1H NMR spectra, the methyl ligands are coupled to platinum and the values of the coupling constants, in particular for the methyl *trans* to the imine nitrogen, are reduced when compared to the corresponding platinum (II) compounds. As observed for analogous octahedral systems [7], the dimethylamino and the methylene protons are non-equivalent. In agreement with the higher oxidation state of platinum, the J(H–Pt) values of the imine group decreases for **6a** and **6b** when compared to the corresponding values for **4a** and **4b**, while the platinum satellites for the imine resonance of **6a′** are overlapped by the aromatic resonances. The presence of 16 (**6a/6a′**) or eight (**6b**) crossing peaks in the aromatic region of the $\{^1H–^{13}C\}$-heterocorrelation spectra is consistent with the proposed structures. The ^{195}Pt NMR spectra displays two signals at $\delta = -2429$ and -2524 ppm assigned, respectively, to compounds **6a** and **6a′** or one signal at $\delta = -2433$ ppm for **6b**. These values show the expected downfield shift on increasing the oxidation state of the platinum.

In conclusion, [C,N,N′] cyclometallated platinum (II) compounds containing five- or six-membered metallacycles were easily prepared from intramolecular C–H bond activation at phenantrene or anthracene. Studies of reactivity of the obtained compounds $[PtMe\{9\text{-}(Me_2NCH_2CH_2N{=}CH)C_{14}H_8\}]$ revealed that they are adequate precursors for the syntheses of two other types of [C,N,N′] cyclometallated platinum compounds: (i) analogous platinum (II) compounds containing a chloro ligand $[PtCl\{9\text{-}(Me_2NCH_2CH_2N{=}CH)C_{14}H_8\}]$ and (ii) cyclometallated platinum (IV) compounds $[PtMe_2I\{9\text{-}(Me_2NCH_2CH_2N{=}CH)C_{14}H_8\}]$. Therefore, the syntheses of several classes of platinacycles derived from anthracene and phenantrene groups, including new examples of six-memebered metallacycles, have been achieved.

3. Experimental

3.1. General

NMR spectra were recorded at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using Varian Gemini 200 (^1H, 200 MHz; ^{13}C, 50 MHz), Bruker 250 (^{13}C, 62.5 MHz; ^{195}Pt, 54 MHz) Varian XL300FT (^{13}C, 75.4 MHz), Mercury 400 ($^1H–^{13}C$ ghsqc) and Varian 500 (^1H, $^1H–^1H$ COSY, $^1H–^1H$ NOESY, 500 MHz) spectrometers, and referenced to $SiMe_4$ (^1H, ^{13}C) and H_2PtCl_6 in D_2O (^{195}Pt). δ values are given in ppm and J values in Hz. Microanalyses were performed at the Serveis Científico-Tècnics de la Universitat de Barcelona and at the Servei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili. Mass spectra were performed at the Servei d'Espectrometria de Masses de la Universitat de Barcelona using HP 5988A (CI, NH_3), VG-Quattro (FAB, NBA) and Voyager DE-RP (Maldi-TOF) spectrometers. IR spectra were taken on a Nicolet Impact 400 using KBr pellets.

3.2. Preparation of the compounds

Compounds $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) [18] and $[PtCl_2(dmso)_2]$ (**1′**) [19] were prepared as reported.

3.2.1. Synthetic procedure for the ligands

9-$(Me_2NCH_2CH_2N{=}CH)C_{14}H_9$ (**2a**) was obtained as a yellow oil from the reaction of phenanthrene-9-aldehyde (1 g, 4.8 mmol) and the equimolar amount (427 mg) of *N*,*N*-dimethylethylenediamine in toluene (20 ml). The mixture was stirred for 1 h and dried over Na_2SO_4. The solvent was removed in a rotary evaporator to yield a yellow oil. Yield: 1.25 g (93%). IR: ν(CH=N) = 1642 cm^{-1}. ^1H NMR (500 MHz, acetone-d_6): $\delta = 2.29$ [s, H^a], 2.68 [t, ^3J(H–H) = 6.0, H^b], 3.85 [t, ^3J(H–H) = 6.0, H^c], 7.67 [td, ^3J(H–H) = 8.0, ^4J(H–H) = 1.2, H^2], 7.69 [td, ^3J(H–H) = 8.0, ^4J(H–H) = 1.2, H^7], 7.73 [td, ^3J(H–H) = 8.0, ^4J(H–H) = 1.2, H^6], 7.75 [td, ^3J(H–H) = 8.0, ^4J(H–H) = 1.2, H^3], 8.05 [dd, ^3J(H–H) = 7.0, ^4J(H–H) = 1.2, H^1], 8.51 [s, H^{10}], 8.82 [d, ^3J(H–H) = 8.0, H^4], 8.87 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.2, H^5], 9.41 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.2, H^8], 8.97 [s, H^d]. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 45.9$ [C^a], {60.2, 60.9, C^b, C^c}, {122.5, 122.9, 125.2, 126.7, 126.8, 127.0, 127.8, 129.4, 130.6, CH^{Ar}}, {128.2, 129.0, 129.8, 130.3, 131.0, C^{Ar}}, 167.7 [C^d]. MS-CI (NH_3, m/z): 277 $[M + H]^+$.

9-$(Me_2NCH_2CH_2N{=}CH)C_{14}H_9$ (**2b**) was obtained as a red oil using the same procedure than for **2a** from anthracene-9-aldehyde. Yield: 1.14 g (85%). IR: ν(CH=N) = 1643 cm^{-1}. ^1H NMR (500 MHz, acetone-d_6): $\delta = 2.39$ [s, H^a], 2.87 [t, ^3J(H–H) = 6.0, H^b], 4.08 [t, ^3J(H–H) = 6.0, H^c], 7.50 [td, ^3J(H–H) = 7.5, ^4J(H–H) = 1.5, H^2], 7.52 [td, ^3J(H–H) = 7.5, ^4J(H–H) = 1.5, H^3], 7.54 [td, ^3J(H–H) = 9.0, ^4J(H–H) = 1.5, H^7], 7.55

[td, ^3J(H–H) = 6.5, ^4J(H–H) = 1.5, H^6], 8.03 [dd, ^3J(H–H) = 6.5, ^4J(H–H) = 1.5, H^5], 8.04 [dd, ^3J(H–H) = 7.5, ^4J(H–H) = 1.5, H^4], 8.50 [s, H^{10}], 8.53 [dd, ^3J(H–H) = 7.5, ^4J(H–H) = 1.5, H^1], 8.55 [dd, ^3J(H–H) = 9.0, ^4J(H–H) = 1.5, H^8], 9.46 [s, H^d]. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 45.8 [C^a], {60.0, 61.1, C^b, C^c}, {124.9 [2C], 125.1 [2C], 126.5 [2C], 128.7 [2C], 129.0 [C^{10}], CH^{Ar}}, {123.5 [C^9], 129.8 [2C], 131.2 [2C], C^{Ar}}, 161.0 [C^d]. MS-CI (NH_3, m/z): 277 $[M+H]^+$.

9-($C_6H_5CH_2N$=CH)$C_{14}H_9$ (**2c**) was obtained as a white solid from of phenanthrene-9-aldehyde (500 mg, 2.42 mmol) and the equimolar amount (260 mg) of benzylamine using an analogous procedure than for **2a** and **2b**. Yield: 530 mg (74%). IR: ν(CH=N) = 1641 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.96 [s, H^a], {7.20–7.50 [m, 5H], 7.59–7.77 [m, 4H], 7.92 [dd, ^3J(H–H) = 7.0, 1H], 8.15 [s, H^{10}], 8.62–8.74 [m, 2H], 9.09 [m, 1H], aromatics}, 9.02 [s, H^b]. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 66.1 [C^a], {122.5, 122.9, 125.3, 126.7, 126.8, 126.9, 126.8, 127.1, 127.9, 128.5, 129.4, 131.2, CH^{Ar}}, 162.1 [C^b]. MS-CI (NH_3, m/z): 296 $[M+H]^+$.

9-($C_6H_5CH_2N$=CH)$C_{14}H_9$ (**2d**) was obtained as a yellow solid using the same procedure than for **2c** from anthracene-9-aldehyde. Yield: 600 mg (84%). IR: ν(CH=N) = 1635 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.20 [s, H^a], {7.29–7.43 [m, 3H], 7.45–7.56 [m, 6H], 8.08–8.14 [m, 2H], 8.65 [s, 1H], 8.73–8.75 [m, 2H], aromatics}, 9.72 [s, H^b]. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 67.2 [C^a], {126.0 [2C], 126.2 [2C], 127.6 [2C], 127.8, 129.1 [2C], 129.4 [2C], 129.8 [2C], 130.4, CH^{Ar}}, {131.1 [2C], 132.4 [2C], 141.0, C^{Ar}}, 161.8 [C^b]. MS-CI (NH_3, m/z): 296 $[M+H]^+$.

3.2.2. Synthetic procedure for the platinum compounds

Compounds **3** were obtained by adding a solution of the corresponding imine (96 mg, 0.348 mmol) in acetone (10 ml) to a solution of compound [$Pt_2Me_4(\mu$-$SMe_2)_2$] (**1**) (100 mg, 0.174 mmol) in acetone (10 ml). The mixture was stirred for 30 min at room temperature, and the solvent was removed in a rotary evaporator. The yellow (**3a**) or orange (**3b**) solids were washed with ether (3×2 ml) and dried in vacuum. [$PtMe_2${9-($Me_2NCH_2CH_2$NCH)$C_{14}H_9$}] (**3a**). Yield: 157 mg (90%). ^{1}H NMR (500 MHz, acetone-d_6): δ = −0.06 [s, ^2J(Pt–H) = 94, Me^a], 0.52 [s, ^2J(Pt–H) = 88, Me^b], 2.95 [s, ^3J(Pt–H) = 25, H^c], 2.98 [t, ^3J(H–H) = 6.0, H^d], 4.34 [t, ^3J(H–H) = 6.0, H^e], 7.67 [td, ^3J(H–H) = 8.0, ^4J(H–H) = 1.0, H^2], 7.71 [td, ^3J(H–H) = 8.0, ^4J(H–H) = 1.0, H^7], 7.73 [td, ^3J(H–H) = 8.0, ^4J(H–H) = 1.0, H^6], 7.78 [td, ^3J(H–H) = 8.0, ^4J(H–H) = 1.0, H^3], 8.17 [d, ^3J(H–H) = 8.0, H^1], 8.31 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.0, H^8], 8.94 [d, ^3J(H–H) = 8.0, H^4], 9.01 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.0, H^5], 9.53 [s, H^{10}], 10.04 [s, ^3J(Pt–H) = 49, H^f]. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = −24.8 [C^a, ^1J(Pt–C) = 1158], −18.4 [C^b, ^1J(Pt–C) = 912], 49.5 [C^c], {65.3, 65.2, C^d, C^e}, {122.6, 123.4, 123.5, 126.8, 126.9, 127.0, 127.2, 127.9, 130.11, CH^{Ar}}, {128.44, 129.0, 130.4, 130.7, 131.1, C^{Ar}}, 161.0 [^2J(Pt–C) = 92, C^f]. ^{195}Pt NMR (54 MHz, $CDCl_3$): δ = −3432 [s]. MS-FAB (+) (NBA, m/z): 486 $[M-Me]^+$, 471 $[M-2Me]^+$. Anal. Found: C, 49.9; H, 5.2; N, 5.5. Calc. for $C_{21}H_{26}N_2Pt$: C, 50.29; H, 5.23; N, 5.59%.

[$PtMe_2${9-($Me_2NCH_2CH_2$NCH)$C_{14}H_9$}] (**3b**). Yield: 137 mg (78%). ^{1}H NMR (500 MHz, acetone-d_6): δ = −0.93 [s, ^2J(Pt–H) = 93, Me^a], 0.19 [s, ^2J(Pt–H) = 86, Me^b], 2.80 [s, ^3J(Pt–H) = 20, H^c], 3.00 [t, ^3J(H–H) = 6.0, H^d], 4.41 [td, ^3J(H–H) = 6.0, H^e], 7.49 [t, ^3J(H–H) = 7.0, ^4J(H–H) = 1.0, H^2], 7.50 [td, ^3J(H–H) = 7.0, ^4J(H–H) = 1.0, H^3], 7.54 [td, ^3J(H–H) = 9.0, ^4J(H–H) = 1.0, H^7], 7.55 [td, ^3J(H–H) = 6.0, ^4J(H–H) = 1.0, H^6], 8.08 [dd, ^3J(H–H) = 6.0, ^4J(H–H) = 1.0, H^5], 8.10 [dd, ^3J(H–H) = 7.0, ^4J(H–H) = 1.0, H^4], 8.30 [dd, ^3J(H–H) = 7.0, ^4J(H–H) = 1.0, H^1], 8.32 [dd, ^3J(H–H) = 9.0, ^4J(H–H) = 1.0, H^8], 8.64 [s, H^{10}], 10.12 [s, ^3J(Pt–H) = 54, H^f]. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = −26.6 [Me^a], −17.6 [Me^b], 48.8 [C^c], 65.9 [C^d], 66.0 [C^e], {125.7 [2C], 125.8 [2C], 126.0 [2C], 128.6 [C^{10}], 128.8 [2C], CH^{Ar}}, {126.7 [C^9], 128.4 [2C], 131.7 [2C], C^{Ar}}, 161.5 [C^f]. ^{195}Pt NMR (54 MHz, $CDCl_3$): δ = −3458 [s]. MS-FAB (+) (NBA, m/z): 486 $[M-Me]^+$, 471 $[M-2Me]^+$. Anal. Found: C, 48.6; H, 5.4; N, 5.4. Calc. for $C_{21}H_{26}N_2Pt\cdot H_2O$: C, 48.55; H, 5.43; N, 5.39%.

Compounds **4a**/**4a′** and **4b** were obtained by refluxing during 2 h (**4a**/**4a′**) or 3 h (**4b**) a toluene solution (20 ml) containing, respectively, **3a** (118 mg, 0.24 mmol) or **3b** (95 mg, 0.2 mmol). The solvent was removed in a rotary evaporator and the red residue was washed with ether (3×2 ml) to yield light brown (**4a**/**4a′**) or dark red (**4b**) solids which were dried in vacuum.

[PtMe{9-($Me_2NCH_2CH_2$NCH)$C_{14}H_8$}] (**4a**/**4a′**). Yield: 90 mg (79%). ^{1}H NMR (500 MHz): **4a** = 1.34 [s, ^2J(Pt–H) = 72, Me^a], 2.74 [s, ^3J(Pt–H) = 14, H^b], 3.15 [t, ^3J(H–H) = 6.5, H^c], 4.02 [t, ^3J(H–H) = 5.5, H^d], 7.42 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.0, H^7], 7.43–7.47 [m, H^2], 7.55 [td, ^3J(H–H) = 7.5, ^4J(H–H) = 1.0, H^3], 7.61 [td, ^3J(H–H) = 7.0, ^4J(H–H) = 1.0, H^6], 8.47 [d, ^3J(H–H) = 8.0, H^4], 8.59 [d, ^3J(H–H) = 8.0, H^5], 8.63 [d, ^3J(H–H) = 8.0, H^8], 8.91 [td, ^3J(H–H) = 7.0, H^1], 9.43 [s, ^3J(Pt–H) = 59, H^e]. **4a′** δ = 0.91 [s, ^2J(Pt–H) = 77, Me^a], 2.72 [t, ^3J(H–H) = 6.0, H^c], 2.80 [s, ^3J(Pt–H) = 18, H^b], 3.96 [t, ^3J(H–H) = 6.5, H^d], 7.35–7.45 [m, H^3, H^6], 7.78 [s, H^{10}], 7.81 [d, ^3J(H–H) = 7.5, H^2], 7.92 [dd, ^3J(H–H) = 8.5, ^4J(H–H) = 1.0, H^1], 8.09 [dd, ^3J(H–H) = 7.5, ^4J(H–H) = 1.0, H^4], 8.35 [d, ^3J(H–H) = 8.0, H^5], 8.53 [dd, ^3J(H–H) = 8.8, ^4J(H–H) = 1.0, H^7], 8.72 [s, ^3J(Pt–H) = 37, H^e]. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.21 [C^a], 1.24 [C$^{a'}$], 48.6 [C^b], 49.4 [C$^{b'}$], 52.7 [C^c], 60.1 [C$^{c'}$], 65.2 [C$^{d'}$], 68.6 [C^d], {119.2 [C$^{5'}$], 122.1 [m, C$^{1'}$, C^4], 122.8 [C$^{10'}$], 123.5–123.7 [4s, C^8, C^5, C$^{7'}$, C^1], 124.0, 125.6, 126.1, 126.7, 127.0, 128.1 [C^3], 128.7 [C^6], 129.2 [C$^{2'}$], CH^{Ar}}, 157.7 [s, C$^{e'}$], 165.2 [s, C^e]. ^{195}Pt NMR (54 MHz, $CDCl_3$): δ = −3218 [s, **4a′**], −3421 [s, **4a**].

MS-FAB (+) (NBA, m/z): 485 $[M]^+$, 470 $[M–Me]^+$ Anal. Found: C, 48.9; H, 5.0; N, 5.3. Calc. for $C_{20}H_{22}N_2Pt$: C, 49.48; H, 4.57; N, 5.77%.

[PtMe{9-($Me_2NCH_2CH_2NCH$)$C_{14}H_8$}] (**4b**). Yield: 74 mg (80%). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.07$ [s, ^2J(Pt–H) = 76, Me^a], 2.91 [t, ^3J(H–H) = 6.0, H^c], 2.92 [s, ^3J(Pt–H) = 17, H^b], 4.31 [t, ^3J(H–H) = 6.0, H^d], 7.32 [dd, ^3J(H–H) = 7.5, ^4J(H–H) = 1.0, H^6], 7.43 [dd, ^3J(H–H) = 6.5, ^4J(H–H) = 1.0, H^3], 7.59 [ddd, ^3J(H–H) = 9.0, ^3J(H–H) = 6.5, ^4J(H–H) = 1.5, H^2], 7.74 [d, ^3J(H–H) = 8.0, H^5], 8.04 [d, ^3J(H–H) = 8.0, H^4], 8.26 [dd, ^3J(H–H) = 7.0, ^4J(H–H) = 1.0, H^7], 8.41 [d, ^3J(H–H) = 9.0, H^1], 8.67 [s, H^{10}], 10.04 [s, ^3J(Pt–H) = 40, H^e]. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -3.8$ [^1J(Pt–C) = 854, C^a], 49.3 [C^b], 61.4 [C^c], 65.1 [C^d], 121.8 [C^1], 124.0 [C^3], 125.4 [C^6], 126.4 [C^5], 127.4 [C^2], 129.7 [C^4], 137.1 [C^{10}], 140.8 [C^7], {124.8, 125.9, 129.2, 130.0, 132.48, 133.50, C^{Ar}}, 150.1 [C^e]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -3078$ [s]. MS-FAB (+) (NBA, m/z): 485 $[M]^+$, 470 $[M–Me]^+$. Anal. Found: C, 46.5; H, 5.3; N, 5.2. Calc. for $C_{20}H_{22}N_2Pt \cdot 2H_2O$: C, 46.06; H, 5.03; N, 5.37%.

Compounds **3a′** and **3b′** were obtained from reaction of *cis*-[$PtCl_2$(dmso)$_2$] (**1′**) (150 mg, 0.36 mol) with the equimolecular amount (98 mg) of the corresponding imine in dry methanol. The mixture was refluxed during 4 h, and the insoluble orange solids were filtered and dried in vacuo.

[$PtCl_2${9-($Me_2NCH_2CH_2NCH$)$C_{14}H_9$}] (**3a′**). Yield: 200 mg (97%). IR ν(CH=N) = 1650 cm^{-1}. MS-MALDI (m/z): 505.0 $[M–Cl]^+$, 468.0 $[M–2Cl]^+$. Anal. Found: C, 42.1; H, 4.1; N, 5.0. Calc. for $C_{19}H_{20}Cl_2N_2Pt$: C, 42.08; H, 3.72; N, 5.16%.

[$PtCl_2${9-($Me_2NCH_2CH_2NCH$)$C_{14}H_9$}] (**3b′**). Yield: 185 mg (90%). IR ν(CH=N) = 1623 cm^{-1}. MS-MALDI (m/z): 505.0 $[M–Cl]^+$, 468.0 $[M–2Cl]^+$. Anal. Found: C, 42.2; H, 4.0; N, 5.0. Calc. for $C_{19}H_{20}Cl_2N_2Pt$: C, 42.08; H, 3.72; N, 5.16%.

Compounds **5** were obtained when acetylchloride (0.5 ml) was slowly added to a stirred solution of **4a/4a′** or **4b** (100 mg) in a 1:1 mixture of dichloromethane and methanol (20 ml). Continuous stirring was maintained during 15 min and the solvents were removed. Crystallisation of the obtained residues in dichloromethane/hexane afforded yellow compounds, which were dried in vacuum.

[PtCl{9-($Me_2NCH_2CH_2NCH$)$C_{14}H_8$}] (**5a′**). Yield: 40 mg (38%). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.63$ [s, ^3J(H–H) = 6.0, H^b], 2.94 [s, ^3J(Pt–H) = 14, H^a], 3.91 [t, ^3J(H–H) = 6.0, H^c], 7.44 [s, H^{10}], 7.47 [m, H^3, H^6], 7.58 [dd, ^3J(H–H) = 7.0, ^4J(H–H) = 1, H^2], 7.71 [dd, ^3J(H–H) = 7.0, ^4J(H–H) = 1.0, H^1], 8.43 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.0, H^4], 8.65 [d, ^3J(H–H) = 8.0, H^5], 8.83 [dd, ^3J(H–H) = 7.0, ^4J(H–H) = 1.0, H^7], 8.09 [s, ^3J(Pt–H) = 117, H^d]. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 49.7$ [C^a], 63.2 [C^b] 63.3 [C^c], 120.3 [C^4], 123.5 [C^5], 126.0 [C^3 or C^6], 126.4 [C^3 or C^6], 129.1 [C^2], 129.5 [C^1], 139.2 [C^{10}], 141.4 [C^7], {125.9, 129.1, 133.0, 136.0, C^{Ar}}, 157.4 [C^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2944$ [s]. MS-FAB(+) (NBA, m/z): 505 $[M]^+$, 470 $[M–Cl]^+$. Anal. Found: C, 44.6; H, 4.0; N, 4.9. Calc. for $C_{19}H_{19}ClN_2Pt$: C, 45.11; H, 3.79; N, 5.54%.

[PtCl{9-($Me_2NCH_2CH_2NCH$)$C_{14}H_8$}] (**5b**). Yield: 60 mg (58%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.76$ [t, ^3J(H–H) = 6.0, H^b], 2.98 [s, ^3J(Pt–H) = 12, H^a], 4.27 [t, ^3J(H–H) = 6.0, H^c], 7.42 [t, ^3J(H–H) = 8.0, H^6], 7.46 [td, ^3J(H–H) = 8.0, ^4J(H–H) = 1.0, H^3], 7.62 [t, ^3J(H–H) = 8.0, H^2], 7.77 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.0, H^5], 8.02 [d, ^3J(H–H) = 8.0, H^4], 8.27 [d, ^3J(H–H) = 8.0, H^1], 8.67 [s, H^{10}], 8.86 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.0, ^3J(Pt–H) = 57, H^7], 9.64 [s, ^3J(Pt–H) = 119, H^d]. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 49.7$ [C^a], 63.4 [C^c] 64.6 [C^b], 123.8 [C^1], 125.4 [C^6], 125.9 [C^3], 128.0 [C^5], 129.4 [C^2], 129.5 [C^4], 138.8 [C^{10}] 144.2 [C^7], 150.3 [C^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2891$ [s]. MS-FAB(+) (NBA, m/z): 505 $[M]^+$, 470 $[M–Cl]^+$. Anal. Found: C, 39.5; H, 4.5; N, 5.2. Calc. for $C_{19}H_{19}ClN_2Pt \cdot 4H_2O$: C, 39.48; H, 4.71; N, 4.85%.

Compounds **6** were obtained when methyl iodide (0.5 ml) was added to a stirred solution of **4a/4a′** or **4b** (52 mg, 0.11 mmol) in acetone (20 ml). Continuous stirring was maintained during 30 min. The solvent was removed in the rotary evaporator and the residue was washed with hexane and the yellow (**4a/4a′**) or orange (**4b**) solid was dried in vacuum.

[$PtMe_2I${9-($Me_2NCH_2CH_2NCH$)$C_{14}H_8$}] (**6a/6a′**). Yield: 55 mg (82%). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.77$ [s, ^2J(Pt–H) = 71, Me^a], 0.98 [s, ^2J(Pt–H) = 71, $Me^{a'}$], 1.44 [s, ^2J(Pt–H) = 65, Me^b], 1.64 [s, ^2J(Pt–H) = 59, $Me^{b'}$], {2.49 [s, ^3J(Pt–H) = 16, 3H], 2.52 [s, ^3J(Pt–H) = 15, 3H], 3.13 [s, ^3J(Pt–H) = 12, 3H], 3.24 [s, ^3J(Pt–H) = 11, 3H], H^c, $H^{c'}$}, {2.67 [m, 1H], 3.72 [td, ^2J(H–H) = 15, ^3J(H–H) = 4.0, 1H], H^d}, {2.99 [m, 1H], 4.27 [td, ^2J(H–H) = 10, ^3J(H–H) = 5.0, 1H], $H^{d'}$}, {4.01 [m, 1H], 4.15 [m, 1H], H^e}, {4.08 [m, 1H], 4.11 [m, 1H], $H^{e'}$}, {7.39 [t, ^3J(H–H) = 8.0, 1H], 7.49–7.57 [m, 3H], 7.61–7.69 [m, 3H], 7.82 [d, ^3J(H–H) = 7.0, 1H], 7.83 [dd, ^3J(H–H) = 7.0, ^4J(H–H) = 1.0, 1H], 7.88 [s, $H^{10'}$], 8.07 [m, 1H], 8.33 [d, ^3J(H–H) = 8.0, 1H], 8.53 [d, ^3J(H–H) = 8.0, 1H], 8.60 [m, 2H], 8.71 [m, 1H], aromatics}, 8.57 [s, $H^{f'}$], 9.42 [s, ^3J(Pt–H) = 48, H^f]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -3.5$ [Me^a], 2.1 [$Me^{a'}$], 10.6 [Me^b], 12.1 [$Me^{b'}$], {46.4, 47.2, 52.7, 54.5, $C^{cc'}$}, {52.1, 59.2, 64.1, 68.3 $C^{dd'ee'}$}, {120.1, 122.2, 123.0, 123.5, 123.6, 125.5, 126.5, 126.9, 127.2, 127.3, 129.1, 129.7, 129.8, 134.8, 136.1, 141.0, CH^{Ar}}, 162.8 [$C^{f'}$], 167.1 [C^f]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2429$ [s]; −2524 [s]. MS-FAB(+) (NBA, m/z): 500 $[M–I]^+$, 485 $[M–I–Me]^+$. Anal. Found: C, 40.8; H, 4.4; N, 4.3. Calc. for $C_{21}H_{25}IN_2Pt$: C, 40.20; H, 4.02; N, 4.46%.

[$PtMe_2I${9-($Me_2NCH_2CH_2NCH$)$C_{14}H_8$}] (**6b**). Yield: 60 mg (90%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.20$ [s, ^2J(Pt–H) = 72, Me^a], 1.47 [s, ^2J(Pt–H) = 65, Me^b], {2.59

[s, ^3J(Pt–H) = 13, 3H], 3.31 [s, ^3J(Pt–H) = 10, 3H], H^c}, {2.76 [m, 1H], 3.73 [m, 1H], H^d}, {4.22 [m, 1H], 4.39 [m, 1H], H^e}, {7.31 [t, ^3J(H–H) = 7.8, 1H], 7.47 [t, ^3J(H–H) = 7.4, 1H], 7.58 [t, ^3J(H–H) = 8.0, 1H], H^2, H^3, H^6}, {7.62 [d, ^3J(H–H) = 8.0, 1H], 7.87 [d, ^3J(H–H) = 8.0, ^2J(Pt–H) = 63, 1H], 7.99 [d, ^3J(H–H) = 8.0, 1H], 8.39 [d, ^3J(H–H) = 8.0, 1H], H^1, H^4, H^5, H^7}, 8.61 [s, H^{10}], aromatics}, 9.70 [s, ^3J(Pt–H) = 32, H^f]. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 1.9$ [^1J(Pt–C) = 670, Me^a], 12.13 [^1J(Pt–C) = 678, Me^b], {47.3, 54.7, C^c}, {60.9,C^e}, {64.3, C^d}, {121.9, 127.4, 130.1, 137.6, C^1, C^4, C^5, C^7}, {124.8, 126.0 [^2J(Pt–C) = 66], 128.4, C^2, C^3, C^6}, 138.6 [C^{10}], {123.7, 128.5, 130.2, 132.3, 134.3, 134.9, C^{Ar}}, 156.0 [C^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): $\delta = -2433$ [s]. MS-FAB(+) (NBA, m/z): 500 $[M–I]^+$, 485 $[M–I–Me]^+$, 470 $[M–I–2Me]^+$. Anal. Found: C, 39.1; H, 4.2; N, 4.3. Calc. for $C_{21}H_{25}IN_2Pt \cdot H_2O$: C, 39.08; H, 4.22; N, 4.34%.

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