

Oxidative addition to dimethylplatinum (II) compounds containing bulky nitrogen ligands: crystal structures of compounds $[\text{PtMe}_2\text{I}\{(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NCH})\text{Ar}\}]$ (Ar = phenanthryl or anthryl)

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Abstract

Oxidative addition of methyl iodide to platinum (II) compounds $[\text{PtMe}_2\{(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NCH})\text{Ar}\}]$ (Ar = phenanthryl or anthryl) produced the corresponding platinum (IV) compounds. Processes aimed at reducing the steric crowding at the coordination sphere of the platinum (IV) centre such as C–C restricted rotation of the pendant part of the ligand leading to rotamers and isomerisation of the C=N moiety have been detected in solution. The obtained platinum (IV) compounds were characterised by elemental analyses, mass spectrometry and NMR spectroscopy. According to the crystallographic characterisation, the anthracene derivative gave an *E* conformer while a *Z* conformation was obtained for the phenanthrene derivative. In order to rationalize the experimental results, DFT calculations have been performed.

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1. Introduction

Oxidative addition reactions involving transition metals are fundamental steps in stoichiometric and catalytic processes. The great majority of such processes reported to date involve the reaction of alkyl halides with organoplatinum(II) complexes containing nitrogen donor ligands [1]. In particular, rigid bidentate diimines such as 2,2'-bipyridine or 1,10-phenanthroline have been extensively used [2–5]. The oxidative addition process is inhibited by the presence of highly electron-withdrawing groups or by steric hindrance [6]. Recent advances in

organometallic chemistry and homogeneous catalysis have emphasized the important role of ligand steric effects. In particular, bulky substituents on diimine ligands influence processes involving square-planar compounds such as catalysed olefin polymerization [7], C–H activation [8] and oxidative addition reactions [9].

Interest in the less explored amine–imine ligands such as $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NCHAr}$ arise from their increased flexibility compared to rigid diimine ligands as well as from the fact that a range of aryl groups Ar with different steric requirements can be easily introduced. The increased bulk of octahedral platinum (IV) versus square-planar platinum (II) centres led to processes aimed at reducing the steric crowding at the coordination sphere of the metal centre such as C–C restricted

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rotation of the pendant part of the ligand or, at higher temperatures, to an *E–Z* isomerisation of the imine for a naphthyl derivative [10]. For diplatinum compounds, the oxidation to platinum (IV) is also accompanied by conformational changes [11] related to the steric requirements of the compounds. In most cases, the oxidative addition of alkyl halides to organoplatinum (II) complexes gives *trans* stereochemistry, although subsequent isomerization can yield products that appear to arise from *cis*-oxidative addition [12]. Here we attempt to assess the influence of bulky groups such as phenanthrene or anthracene on: (i) the reactivity of the corresponding compounds [PtMe₂(Me₂NCH₂CH₂NCHAr)] towards methyl iodide, and ii) the conformations adopted by the corresponding compounds [PtMe₃I(Me₂NCH₂CH₂NCHAr)].

2. Results and discussion

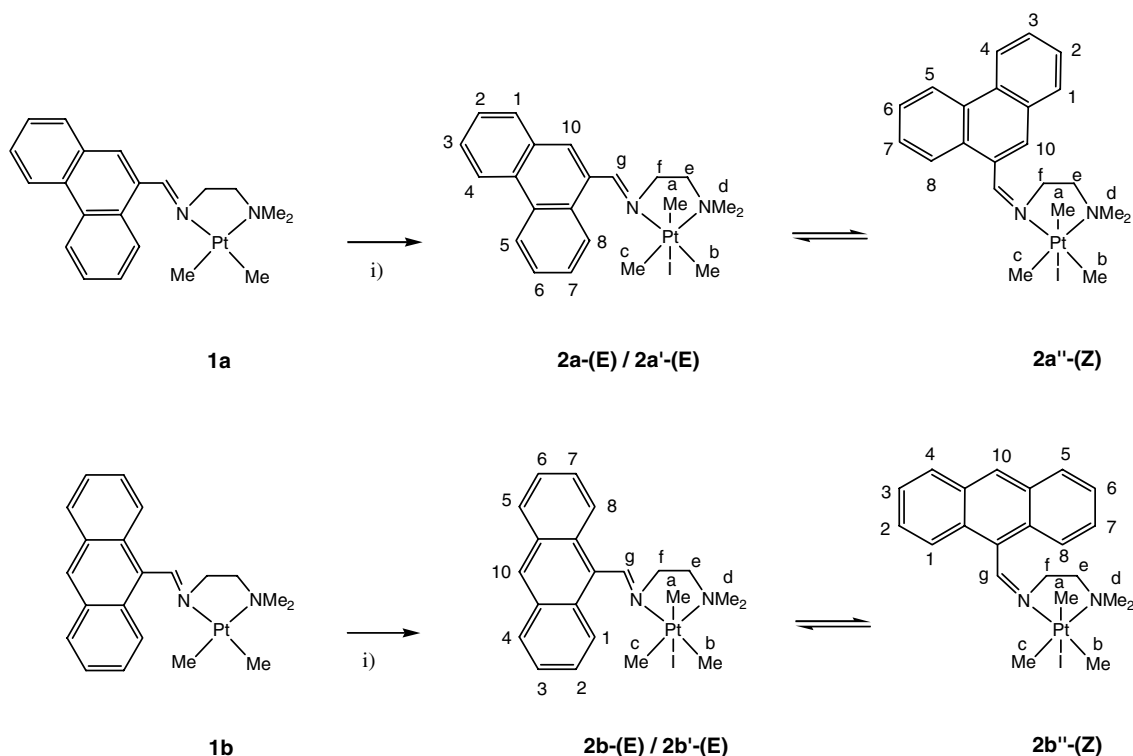
2.1. Oxidative addition of methyl iodide to compounds **1a** and **1b**

Compounds [PtMe₂{(Me₂NCH₂CH₂NCH)C₁₄H₉}] containing a phenanthryl or an anthryl group have been previously synthesised from [Pt₂Me₄(μ-SMe₂)₂] and the corresponding ligand Me₂NCH₂CH₂NCHAr as precursors for cyclometallated compounds containing a terd-

entate [C,*N,N'*] ligand [13]. 2D-NOESY NMR taken for **1a** and **1b** indicated that in both cases, the ligand adopts the *E* form.

Compounds **1a** (R = phenanthryl) and **1b** (R = anthryl) are also appropriate substrates to study whether oxidative addition of methyl iodide is plausible when bulky groups are present. Upon addition of methyl iodide to a solution of compound **1a** or **1b** in acetone the colour of the solution changed from orange to light yellow and work-up of the final solution allowed isolation of the corresponding platinum (IV) compound [PtMe₃I{(Me₂NCH₂CH₂NCH)C₁₄H₉}] (**2a** or **2b**) in high yield. The new compounds shown in Scheme 1 were characterised by elemental analysis, FAB-MS, ¹H, and ¹⁹⁵Pt NMR spectra.

Compounds **2a** and **2b** consist of a single isomer for which three distinct methyl-platinum resonances coupled to platinum are observed. The values of the ²J(Pt–H) coupling constants are smaller than those for the corresponding platinum (II) compound, which is consistent with the higher oxidation state of platinum, and the values obtained (71–73 Hz) indicated the expected *fac*-PtMe₃ geometry [5]. For **2b**, a 2D-NOESY NMR spectrum allows the assignment of the methyl-platinum resonances since cross-peaks between Me^b and the two dimethylamino resonances and between Me^a and one dimethylamino resonance are expected.



Scheme 1.

On these grounds, the resonances at 0.56 and 0.98 ppm are assigned respectively to the methyl *trans* to the iodo (Me^a) and *trans* to the imine (Me^b). The resonance at higher field ($\delta = -0.06$ ppm) is assigned to the methyl *trans* to the amine (Me^c) and its low chemical shift as well as that reported for the methyl *trans* to the amine in **1b** ($\delta = -0.95$ ppm) [13] might be related to the proximity of these methyl ligands to the anthracene group which is nearly perpendicular to the $[\text{PtC}_2\text{N}_2]$ plane. In agreement with co-ordination through both nitrogen atoms, the diastereotopic methyl groups of the NMe_2 unit and the imine proton are also coupled to platinum. In both cases, the $J(\text{H-Pt})$ values for the imine proton indicate an *E* conformation of the imine in the platinum(IV) compounds initially formed [14].

For **2a**, the ^{195}Pt NMR spectrum confirms the presence of a single isomer of the obtained platinum (IV) compound. After **2a** has been allowed to stand in solution, a second isomer (**2a'**) is formed and after several hours both isomers are present in a ratio **2a**:**2a'** = 2:1. For both isomers, the value of the coupling constant of the imine proton with ^{195}Pt ($J(\text{H-Pt}) = 32\text{--}34$ Hz) is in the range expected for an *E*-conformation across the C=N bond [14]. Therefore, the two species might be assigned to two different rotamers, both with the imine in an *E* form, in which the phenanthryl group points either towards the iodide or the axial methyl ligands. Molecular models suggest that rotation about the C–C bond of the pendant part of the ligand is likely to be restricted due to steric hindrance between the bulky aryl group and the equatorial methyl *cis* to the imine. Assignment of the ^1H NMR spectrum of the mixture of isomers was based on a COSY $^1\text{H}\text{--}^1\text{H}$ experiment. After 24 h, at room temperature, in addition to the signals observed for both rotamers, formation of a third isomer (**2a''**) was observed and its amount increased up to 14% of the final mixture. A reduced $J(\text{H-Pt})$ value for the imine indicated a *Z* conformation for **2a''**.

For **2b**, isomerization of the imine from *E* to *Z* (**2b'**) takes place readily. Within several hours, both ^1H and ^{195}Pt NMR indicated a (*Z*):(*E*) ratio of 2:1. Very minor resonances (<5% of the final mixture) corresponding to a third isomer (**2b''**) were also observed. In an independent experiment using shorter times in solution (≈ 1 h) only **2b** and **2b'** were identified and the value of the coupling of the imine proton to platinum is consistent with an *E*-conformation for **2b'**. Assignment of the ^1H NMR spectrum of the final mixture was based on a COSY $^1\text{H}\text{--}^1\text{H}$ experiment.

2.2. Oxidative addition of CD_3I to compound **1b**

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 [5,12,15]. In order to analyse the stereochemistry of the platinum (IV) compound initially formed the oxidative addition of CD_3I to compound **1b** was monitored by ^1H NMR at low temperature. Upon addition of CD_3I to an acetone- d_6 solution of **1b** at -40 °C, the two methyl–platinum resonances corresponding to **1b** are replaced by those corresponding to Me^b and Me^c of the platinum (IV) compound as shown in Fig. 1. The absence of the resonance assigned to the axial methyl group indicates that *trans* addition of CD_3I occurred. On warming to 10 °C, the methyl platinum (IV) resonance assigned to the axial methyl (Me^a) appears, and further warming resulted in an increase of the intensity of this new signal while those corresponding to Me^b and Me^c decreased. These results are consistent with an initial *trans* oxidative addition of CD_3I followed by scrambling of the CH_3 and CD_3 ligands [5].

2.3. Crystal structures

Suitable crystals of **2a** and **2b** were grown from acetone solution. The crystal structures are composed of discrete molecules separated by van der Waals interactions. For **2a**, two independent molecules with bond parameters equal within experimental error [3σ] are present in the asymmetric unit. An interplanar separation of 3.67 Å (**2a**) or 3.76 Å (**2b**) between the phenanthrene or the anthracene planes suggests a weak $\pi\text{--}\pi$ stacking, as reported in the literature for analogous compounds [16]. Selected bond lengths and angles are given in Table 1 and the molecular structures are shown in Figs. 2 and 3. The study confirms the octahedral co-ordination for the platinum atom with the facial arrangement of the three methyl groups. For both compounds, the Pt–N distances are unequal with the bond to the amine nitrogen being slightly longer than that to the imine nitrogen, that is consistent with the relatively weak ligating ability of tertiary amines for platinum. The Pt–C and Pt–I distances are within the range of expected values for reported *fac*-PtMe $_3$ I complexes [14,17,18]. As expected, the octahedron around platinum is somewhat distorted, the main distortion being due to the small “bite angle” for the chelate ring of $81.16(19)^\circ$ for **2a** and $80.6(3)^\circ$ for **2b**. The most striking feature of these structures is the different arrangement around the imine bond. For **2a**, the imine adopts the *Z* conformation, the torsion angle C(17)–N(12)–C(18)–C(19) being $0.0(12)$ Å for molecule 1. The dangling phenanthryl group forms a dihedral angle of $125.29(5)^\circ$ with the co-ordination plane Pt–C(11)–C(13)–N(11)–N(12). The chelate ring Pt–N(12)–C(17)–C(16)–N(11) is nearly coplanar with the aforementioned co-ordination plane, the dihedral angle being $6.64(5)^\circ$. For **2b**, the imine adopts the *E* conformation, the torsion angle C(7)–N(2)–C(8)–C(9) being $175.5(8)$ Å. The

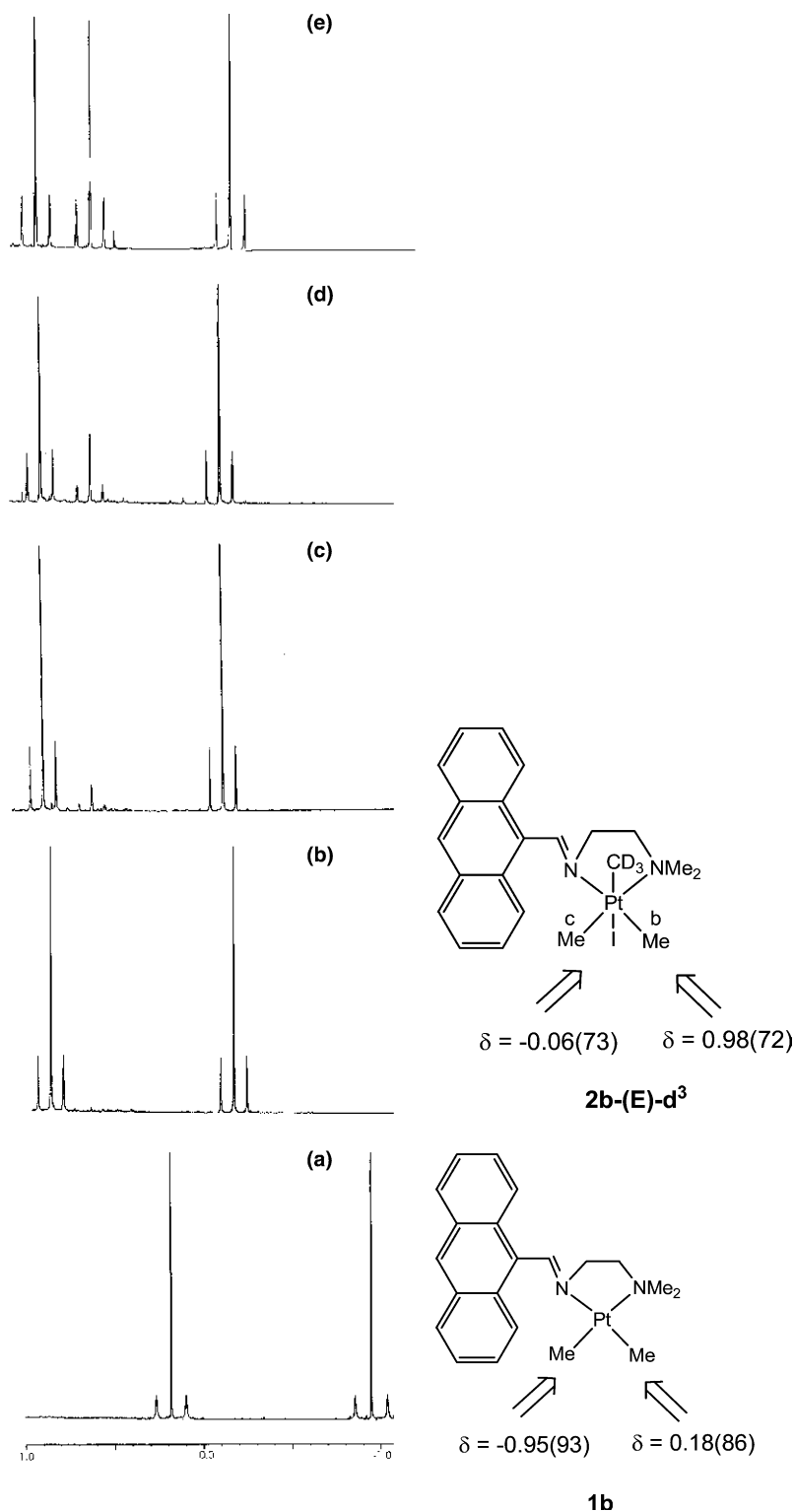


Fig. 1. ^1H NMR spectra (500 MHz) in the methyl region during the reaction of **1b** with CD_3I in acetone-d_6 : (a) before addition of CD_3I ; (b) at -40°C ; (c) at 10°C ; (d) at 20°C ; (e) at 20°C after 1 h.

dangling anthryl group forms a dihedral angle of $81.90(5)^\circ$ with the co-ordination plane $\text{Pt}-\text{C}(1)-\text{C}(2)-\text{N}(1)-\text{N}(2)$. The chelate ring $\text{Pt}-\text{N}(2)-\text{C}(7)-\text{C}(6)-\text{N}(1)$ is nearly coplanar with the aforementioned co-ordination plane, the dihedral angle being $5.40(5)^\circ$.

2.4. Theoretical studies

In order to compare the stability of the different platinum derivatives, we have performed DFT calculations on **1a**, **1b**, **2a**, **2a''**, **2b** and **2b''**, using the GAUSSIAN-03

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

Compound 2a''		Compound 2b	
Pt–C(12)	2.067(8)	Pt–C(3)	2.072(10)
Pt–C(13)	2.084(8)	Pt–C(2)	2.089(10)
Pt–C(11)	2.102(8)	Pt–C(1)	2.108(8)
Pt–N(11)	2.267(6)	Pt–N(1)	2.263(7)
Pt–N(12)	2.151(5)	Pt–N(2)	2.183(7)
Pt–I(1)	2.7709(6)	Pt–I(1)	2.8058(8)
C(12)–Pt–C(13)	89.1(4)	C(3)–Pt–C(2)	87.0(4)
C(12)–Pt–C(11)	85.7(4)	C(3)–Pt–C(1)	88.3(5)
C(13)–Pt–C(11)	88.3(3)	C(2)–Pt–C(1)	87.4(4)
C(12)–Pt–N(12)	91.2(3)	C(3)–Pt–N(2)	90.2(4)
C(11)–Pt–N(12)	95.7(3)	C(1)–Pt–N(2)	97.3(4)
C(12)–Pt–N(11)	95.2(3)	C(3)–Pt–N(1)	91.0(4)
C(13)–Pt–N(11)	94.9(3)	C(2)–Pt–N(1)	94.7(3)
N(12)–Pt–N(11)	81.16(19)	N(2)–Pt–N(1)	80.6(3)
C(13)–Pt–I(1)	93.6(3)	C(2)–Pt–I(1)	92.5(3)
C(11)–Pt–I(1)	87.4(3)	C(1)–Pt–I(1)	88.0(4)
N(12)–Pt–I(1)	86.58(13)	N(2)–Pt–I(1)	90.63(18)
N(11)–Pt–I(1)	91.52(15)	N(1)–Pt–I(1)	92.7(2)

[19] suite of programs. On every molecule a geometry optimization has been performed without any constraint. No solvent effects have been taken into account. The relative energies are shown in Table 3.

In a first stage, we have studied the oxidative addition of methyl iodide to the platinum(II) compounds. This reaction is in both cases energetically favourable, by

16.7 kcal/mol (**1a**) and 14.8 kcal/mol (**1b**); in all cases the *E* conformation has been chosen. The complexes with a phenanthryl group that have been calculated are always more stable than the compounds with an anthryl moiety; the difference in energy is 6.5 kcal/mol for the platinum(II) derivatives and 8.3 kcal/mol for the platinum(IV) ones. This fact can be attributed to the greater stability of the phenanthrene compared to the anthracene, with the former being 5.3 kcal/mol more stable than the latter, at the same level of theory.

We have also studied the difference in energy between the *E* and *Z* isomers for the Pt(II) and Pt(IV) derivatives. In all the cases the *Z* isomers are more stable, although this effect is slightly more pronounced in the platinum(IV) complexes (about 4.5 kcal/mol) than in the platinum(II) compounds (3.1 kcal/mol for **1a**, 3.8 kcal/mol for **1b**). Thus, the fact that the *E* complexes are isolated could be due to the adoption of this conformation by the free imine in solution.

In relation to the existence of two isomers of **2a** and **2b** in solution, we have tried to discard the possibility of the existence of two different conformations of the chelate ring. In order to achieve this, geometry optimizations have been performed on the δ and λ conformations of **2a''** and **2b**. In both cases, the most stable conformation is the same that is adopted experimentally (δ for **2a''**, λ for **2b**), according to the crystal structures; the difference in energy between conforma-

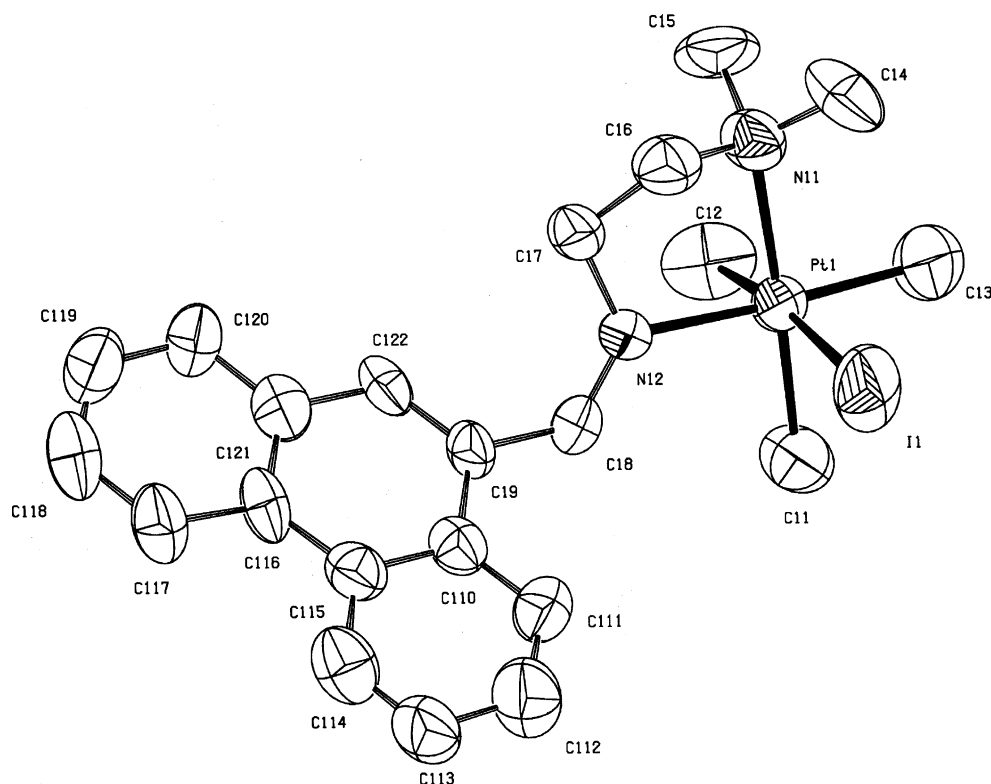
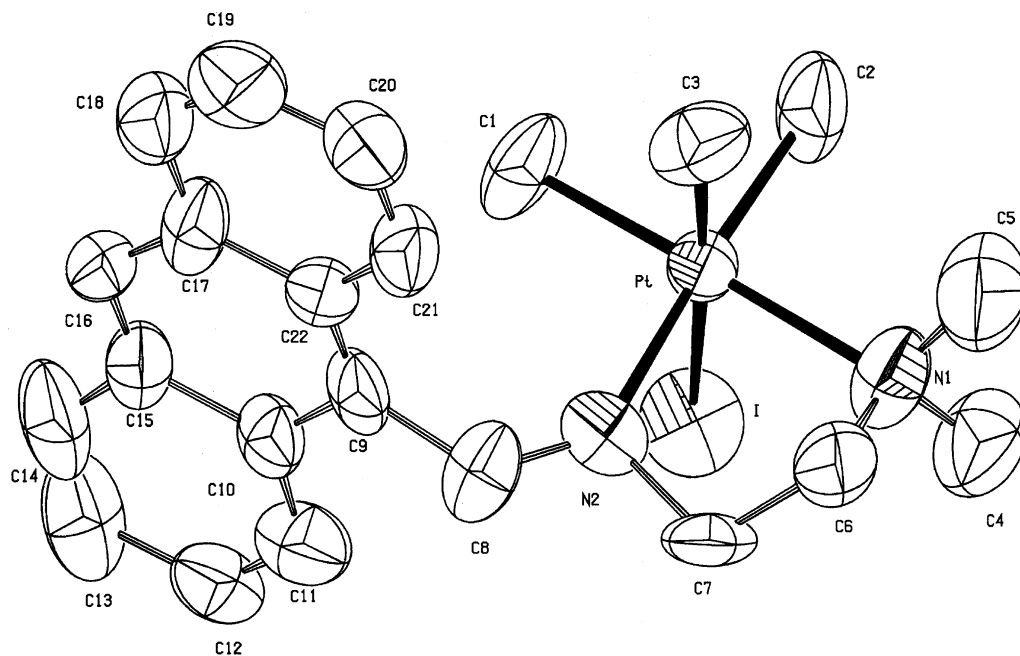


Fig. 2. Molecular structure of compound **2a''**.

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

tions is larger in **2a''** (1.7 kcal/mol) than in **2b** (0.4 kcal/mol). In order to have an estimation of the energy barrier for the interconversion process, we have optimized the geometries of **2a''** and **2b** forcing the rings to be planar. The obtained values (12.7 and 13.3 kcal/mol respectively) are sufficiently small to allow a fast interconversion between both conformations.

Finally, we have studied the energy profile corresponding to the rotation of the organic group (phenanthryl- or anthryl-), in order to ascertain if there are different rotamers in solution. With this aim, we have calculated the energy profile corresponding to the rotation of the dangling group around the C_{ipso}–C_{iminic} bond. As the molecules are rather complex we have performed this calculation at the semiempirical PM3(tm) level, using the Spartan program [20]. The calculations have been performed every 12°, and the remaining geometrical parameters have been optimised. The computed energy barriers are rather high [31.0 kcal/mol (**2a**), 29.5 kcal/mol (**2b**), 29.3 kcal/mol (**2a''**), 26.0 kcal/mol (**2b''**)], so the rotation of these bulky organic groups should be hindered, and the existence of two rotamers should be expected.

Summarising, for the platinum (II) compounds under study, oxidative addition of methyl iodide is not inhibited by the presence of bulky groups such as phenanthryl (**1a**) or anthryl (**1b**). The reaction of **1b** with CD₃I confirmed that *trans*-oxidative addition took place. Processes aimed at reducing the steric crowding at the coordination sphere of the platinum(IV) centre such as C–C restricted rotation of the pendant part of the ligand leading to rotamers and isomerization of the C=N moi-

ety leading to *Z* conformers have been detected in solution at room temperature. Crystallisation of the resulting platinum (IV) compounds gave the initially formed *E* conformer for the anthracene derivative and the *Z* conformer for the phenanthrene.

3. Experimental

3.1. General

NMR spectra were recorded at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using Gemini 200 (¹H, 200 MHz), Bruker 250 (¹⁹⁵Pt, 54 MHz) and Varian 500 (¹H-variable temperature, ¹H–¹H COSY, ¹H–¹H NOESY, 500 MHz) spectrometers, and referenced to SiMe₄ (¹H) and H₂PtCl₆ in D₂O (¹⁹⁵Pt). δ Values are given in ppm and *J* values in Hz. Microanalyses were performed at the Serveis Científico-Tècnics de la Universitat de Barcelona. Mass spectra were performed at the Servei d'Espectrometria de Masses de la Universitat de Barcelona using a VG-Quattro (FAB, NBA) spectrometer.

3.2. Preparation of the compounds

Compounds (**1a**) and (**1b**) were prepared as reported [13].

[PtMe₃I{9-(Me₂NCH₂CH₂N=CH)C₁₄H₉}] (**2a**) was obtained when 0.5 mL of methyl iodide were added to a stirred solution of 50 mg (0.099 mmol) of **1a** in dichloromethane (20 mL). Continuous stirring was maintained

during 10 min. The solvent was removed in the rotary evaporator, the residue was washed with ether (3 × 2 ml) and the pale yellow solid was dried in vacuum. Yield: 45 mg (68%).

¹H NMR (CDCl₃, 500 MHz): **2a-(E)**: δ = {0.70 [s, ²J(Pt–H) = 73], 0.78 [s, ²J(Pt–H) = 71], 1.12 [s, ²J(Pt–H) = 71], Me^{a,b,c}}, {2.50 [s, ³J(H–H) = 14, 3H], 3.25 [s, ³J(Pt–H) = 11, 3H], H^d}, {2.78–2.82 [m, 1H], 3.55–3.60 [m, 1H], H^e}, {4.04–4.08 [m, 1H], 4.24–4.27 [m, 1H], H^f}, {7.77–7.79 [m, 2H], 8.10 [d, ³J(H–H) = 7, 1H, H¹], 8.69 [s, 1H, H¹⁰], 8.72 [d, ³J(H–H) = 8, 1H, H⁸], 9.36 [s, ³J(Pt–H) = 34, H^g]. **2a'-(E)**: δ = {0.50 [s, ²J(Pt–H) = 72], 0.58 [s, ²J(Pt–H) = 74], 0.93 [s, ²J(Pt–H) = 71] Me^{a,b,c}}, {2.50 [s, ³J(Pt–H) = 14, 3H], 2.99 [s, ³J(Pt–H) = 10, 3H], H^d}, {2.69–2.73 [m, 1H], 3.40–3.47 [m, 1H], 4.10–4.13 [m, 2H], H^{e,f}}, {7.60–7.64 [m, 4H], 8.11 [d, ³J(H–H) = 7.5, 1H, H¹], 8.65 [d, ³J(H–H) = 7, 1H, H⁸], 8.85 [s, 1H, H¹⁰], 9.39 [s, ³J(Pt–H) = 32, H^g]. 7.68–7.71 (m, 4H of **2a-(E)** and 2H of **2a'-(E)**). **2a''-(Z)**: δ = {0.90 [s, ²J(Pt–H) = 71], 1.02 [s, ²J(Pt–H) = 72], 1.05 [s, ²J(Pt–H) = 71], Me^{a,b,c}}, {3.12 [s, ³J(Pt–H) = 10, 3H], 3.25 [s, ³J(Pt–H) = 10, 3H], H^d}, 9.29 [s, ³J(Pt–H) = 22, H^g]. ¹⁹⁵Pt-NMR (CDCl₃, 54 MHz): δ = –2545.6 [s, **2a-(E)**]. FAB(+)-MS (NBA, m/z): 516 [M–I]⁺, 471 [M–I–3Me]⁺. Anal. Found: C, 41.2; H, 4.6; N, 4.3. Calc. for C₂₂H₂₉N₂IPt: C, 41.06; H, 4.54; N, 4.35%.

[PtMe₃I{9-(Me₂NCH₂CH₂N=CH)C₁₄H₉}] (**2b**) was obtained as a pale yellow solid using an analogous procedure from **1b**. Yield: 52 mg (72%). ¹H NMR (CDCl₃, 500 MHz): **2b-(E)**: δ = –0.06 [s, ²J(Pt–H) = 73, Me^c], 0.56 [s, ²J(Pt–H) = 71, Me^a], 0.98 [s, ²J(Pt–H) = 72, Me^b], {2.50 [s, ³J(H–H) = 15, 3H], 3.26 [s, ³J(Pt–H) = 10, 3H], H^d}, {2.89–2.92 [m, 1H], 3.34–3.37 [m, 1H], H^e}, {4.19–4.24 [m, 1H], 4.86–4.91 [m, 1H], H^f}, {7.67–7.71 [m, 1H], 7.97 [m, 2H, H^{4,5}], 8.24 [dd, ³J(H–H) = 8, ⁴J(H–H) = 1, 2H, H^{1,8}], 8.48 [s, 1H, H¹⁰], 9.67 [s, ³J(Pt–H) = 34, H^g]. **2b'-(Z)**: δ = 1.05 [s, ²J(Pt–H) = 72, Me^a], {1.21 [s, ²J(Pt–H) = 69], 1.62 [s, ²J(Pt–H) = 70], Me^{b,c}}, {2.49 [s, ³J(Pt–H) = 14, 3H], 3.21 [s, ³J(Pt–H) = 11, 3H], H^d}, {2.41–2.45 [m, 1H], 3.38–3.41 [m, 2H], 3.60–3.54 [m, 1H], H^{e,f}}, {7.60–7.65 [m, 2H], 8.02 [m, 1H], 8.44 [dd, ³J(H–H) = 8, ⁴J(H–H) = 1, 1H], 8.51 [s, 1H, H¹⁰], 9.59 [s, ³J(Pt–H) = 21, H^g]. 7.43–7.52 (m, 3H of **2b-(E)** and 4H of **2b'-(Z)**). **2b''-(E)**: δ = –0.31 [s, ²J(Pt–H) = 72, Me^a], 0.34 [s, ²J(Pt–H) = 74], 0.73 [s, ²J(Pt–H) = 71], Me^{b,c}}, {2.45 [s, ³J(H–H) = 15, 3H], 2.91 [s, ³J(Pt–H) = 9, 3H], H^d}, {2.77–2.81 [m, 1H], 3.25–3.28 [m, 1H], H^e}, {4.12–4.14 [m, 1H], 4.61–4.65 [m, 1H], H^f}, {7.43–7.45 [m, 2H, H^{3,6}], 7.57 [td, ³J(H–H) = 8, ⁴J(H–H) = 2, ⁴J(H–H) = 1, 2H, H^{2,7}], 7.94 [d, ³J(H–H) = 9, 2H, H^{4,5}], 8.25 [dd, ³J(H–H) = 8, ⁴J(H–H) = 1, 2H, H^{1,8}], 8.48 [s, 1H, H¹⁰], 9.58 [s, ³J(Pt–H) = 33, H^g]. ¹⁹⁵Pt NMR (CDCl₃, 54 MHz): δ = –2601.1 [s, **2b-(E)**], –2547.7 [s, **2b''-(Z)**]. FAB(+)-

MS (NBA, m/z): 516 [M–I]⁺, 471 [M–I–3Me]⁺. Anal. Found: C, 40.6; H, 4.5; N, 4.3. Calc. for C₂₂H₂₉N₂IPt: C, 41.06; H, 4.54; N, 4.35%.

Reaction with CD₃I: An excess of CD₃I (0.05 mL) was added at –40 °C to an NMR tube containing a solution of **1b** (5 mg) in acetone-d₆. ¹H NMR (500 MHz) spectra were recorded at –40, –20, 0, 10 and 20 °C as the solution was warmed.

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 11813 (**2a''**) and 8800 (**2b**) reflections (3° < θ < 31°) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation. 18605 (**2a''**) and 15585 (**2b**) reflections were measured in the range 1.09° < θ < 28.36° (**2a''**), or 1.92° < θ < 28.40° (**2b**). 5353 (**2a''**) and 2420 (**2b**) reflections were assumed as observed applying the condition I > 2σ(I). Lorentz polarisation and absorption corrections were made. Further details are given in Table 2.

3.3.2. Structure solution and refinement

The structures were solved by direct methods using SHELXS computer program [21] and refined by the full-matrix least-squares method, with the SHELXL-97 computer program using 7846 (**2a''**) and 3702 (**2b**) reflections (very negative intensities were not assumed). The function minimised was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0688 P)^2]^{-1}$ (**2a''**), or $w = [\sigma^2(I) + (0.0925 P)^2]^{-1}$ (**2b**) and $P = (|F_o|^2 + 2|F_c|^2)/3$. *f*, *f'* and *f''* were taken from International Tables of X-ray crystallography [22]. 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.

3.4. Computational details

All DFT calculations have been performed using the GAUSSIAN-03 [19] package of programs at the Becke3-LYP computational level [23]. The basis set has been chosen as follows: an effective core potential was used to replace the 68 innermost electrons of Pt and the 36 innermost electrons of I; for these atoms, the LANL2DZ [24] basis was used. In the case of N, C and H, the 6-31G basis was used [25]; for iodine, nitrogen and the carbon atoms bonded to the platinum centre, polarization functions [26] were added. All the geometry optimisations have been performed without imposing any symmetry restriction.

Table 2
Crystallographic and refinement data

	Compound 2a''	Compound 2b
Formula	C ₂₂ H ₂₉ IN ₂ Pt	C ₂₂ H ₂₉ IN ₂ Pt
<i>F</i> _w	643.46	643.46
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Orthorhombic, <i>P</i> bca
<i>a</i> (Å)	15.4000(10)	14.3810(10)
<i>b</i> (Å)	15.5260(10)	14.4430(10)
<i>c</i> (Å)	20.0990(10)	21.2410(10)
β , (°)	111.73	90.0
<i>V</i> (Å ³); <i>Z</i>	4464.2(5); 8	4411.9(5); 8
<i>d</i> _{calcd} (mg/m ³)	1.915	1.937
Absorption coefficient (mm ⁻¹)	7.677	7.768
<i>F</i> (000)	2448	2448
Number of reflections collected/unique	18,605/7846 [<i>R</i> _{int}] = 0.0396]	15,585/3702 [<i>R</i> _{int}] = 0.0515]
Data/restraints/parameters	7846/0/469	3702/0/235
Goodness-of-Fit on <i>F</i> ²	0.975	0.990
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0319	0.0454
<i>wR</i> ₂ (all data)	0.1048	0.1387
Peak and hole (e ⁺ Å ⁻³)	0.941 and -0.805	0.802 and -0.645

Table 3
Relative energies (kcal/mol) for compounds **1a**, **1b**, **2a**, **2a''**, **2b** and **2b''**

Compound	Relative energy ^a	Compound	Relative energy ^b
1a (<i>E</i>)	3.1	2a	4.5
1a (<i>Z</i>)	0.0	2a'' (δ)	0.0
1b (<i>E</i>)	9.6	2a'' (λ)	1.7
1b (<i>Z</i>)	5.8	2b (δ)	13.2
		2b (λ)	12.8
		2b''	8.2

^a Energy relative to **1a** (*Z*).

^b Energy relative to **2a''** (δ).

The semiempirical calculations were carried out at the PM3(tm) level, using the Spartan 5.0 suite of programs [20] implemented on a Silicon Graphics workstation (Indigo-2 Power XZ).

4. Supplementary material

The crystallographic data of compounds **2a''** and **2b** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 244279 and 244280. 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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