

# Cyclometallated platinum complexes with thienyl imines. X-ray crystal structure of [PtMe{3-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}PPh<sub>3</sub>]

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## Abstract

The reaction of [Pt<sub>2</sub>Me<sub>4</sub>(μ-SMe<sub>2</sub>)<sub>2</sub>] with ligands 3-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S (**2a**) and 3-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S (**2b**) produced cyclometallation at the α-position of the thiophene ring to give the platinum(II) complexes [PtMe{3-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}] (**4a**) and [PtMe{3-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}SMe<sub>2</sub>] (**4b**), containing [C,N,N'] or [C,N] ligands, respectively. The reaction of these compounds with triphenylphosphine produced [PtMe{3-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}PPh<sub>3</sub>] (**5a**) and [PtMe{3-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}PPh<sub>3</sub>] (**5b**). Compound **5b** was structurally characterized. Attempts to achieve the cyclometallation of the ligands 2-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S (**2c**) and 2-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S (**2d**) were unsuccessful and only compounds [PtMe<sub>2</sub>{2-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S}] (**3c**) and [PtMe<sub>2</sub>{2-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S}SMe<sub>2</sub>] (**3d**), in which the imine behaves as a [N,N'] or [N]-donor ligand, respectively, could be obtained. The electrochemical properties of the compounds based on cyclic voltammetry or square-wave voltammetry were studied at various temperatures. Reversible one-electron reductions, assigned to ligand-centered processes, were observed at room temperature for **5b** and at lower temperatures for **4a**, **4b** and **5a**. The reversibility varies with the ligand *trans* to the thienyl moiety. The one-electron oxidations always occurred in an irreversible manner and were assigned to oxidation at the platinum center. Oxidative addition of methyl iodide to **4a** yielded [PtMe<sub>2</sub>I{3-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}] (**6a**), while the reactions of methyl iodide with **4b** and **5b** each gave mixtures of isomers, arising from oxidative addition with *trans* stereochemistry followed by isomerization of the resulting platinum(IV) compounds. The reaction of methyl iodide with compound **5a** yielded a complex mixture of compounds. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Platinum; Thienylimines; Cyclometallation; Crystal structure; Electrochemistry; Oxidative addition

## 1. Introduction

Hydrodesulfurization of heterocycles such as thiophenes has been the subject of much research [1,2]. Models for this process and studies of the related C–H or C–S bond activation by transition-metal complexes have been reported [3–14]. Moreover, thiophene-based chromophores [15] and bimetallic materials with oligothiophene systems [16,17] have been studied in relation to their nonlinear optical properties.

The binding modes of thiophenes to metal centers [18–20] and the coordination behavior of thiophene-based macrocycles [21,22], ketimines [23] or phosphines [24–28] have also been analyzed. Ligand 2-(2'-thienyl)pyridine [29–31] acts as a monodentate N-donor in gold, palladium or platinum species, as a cyclometallated [C,N] ligand in palladium [32] and platinum compounds [33–35] or as a bidentate [N,S] in ruthenium chemistry. Several bonding modes, such as bidentate [N,N'], terdentate [N,N',S] or terdentate cyclometallated [N,N',C] have also been reported for ligand 6-(2''-thienyl)2,2'-bipyridine in ruthenium and rhodium complexes [36,37], while the reactions with gold compounds give dimers in which this ligand acts as a bridge [38].

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Intramolecular C–H bond activation of benzene rings has been achieved at platinum [39,40], therefore we decided to study the activation of such bonds in thiophenes using a similar strategy. This will allow us to compare the reactivity and aromatic characteristics of thiophene with those of benzene. The reactions of  $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$  with imine ligands derived from 2- or 3-thiophenecarboxaldehyde and benzylamine or *N,N*-dimethylethylenediamine are reported, as well as the reactivity and properties of the corresponding resulting compounds. Cyclic voltammetry experiments were carried out on the platinum complexes in order to gain insight into their electronic properties and to establish a comparison with analogous phenyl derivatives [41,42].

## 2. Results and discussion

### 2.1. Ligands derived from 3-thiophenecarboxaldehyde

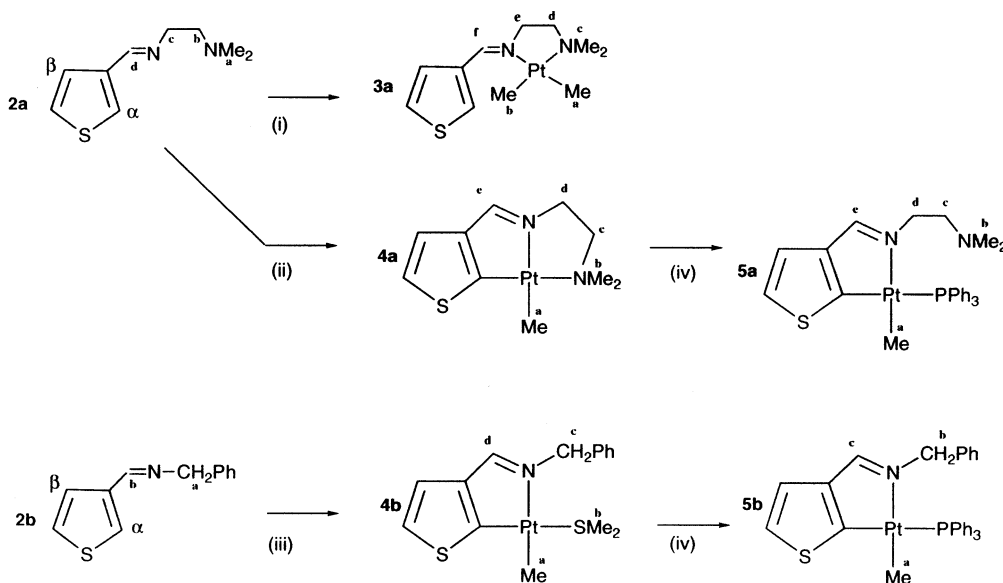
The ligands 3-( $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NCH}$ ) $\text{C}_4\text{H}_3\text{S}$  (**2a**) and 3-( $\text{PhCH}_2\text{NCH}$ ) $\text{C}_4\text{H}_3\text{S}$  (**2b**) were prepared from the condensation reactions of 3-thiophenecarboxaldehyde and *N,N*-dimethylethylenediamine or benzylamine carried out in refluxing ethanol. The resulting imines were characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra and their reactions with  $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$  (**1**), shown in Scheme 1, were carried out in acetone.

The reactions produce cyclometallated compounds  $[\text{PtMe}\{3\text{-(Me}_2\text{NCH}_2\text{CH}_2\text{NCH})\text{C}_4\text{H}_2\text{S}\}]$  (**4a**) and  $[\text{PtMe}\{3\text{-(PhCH}_2\text{NCH})\text{C}_4\text{H}_2\text{S}\}\text{SMe}_2]$  (**4b**) in which the imine ligand acts as a tridentate [C,N,N'] or as a bidentate [C,N] ligand, respectively. Both compounds are formed

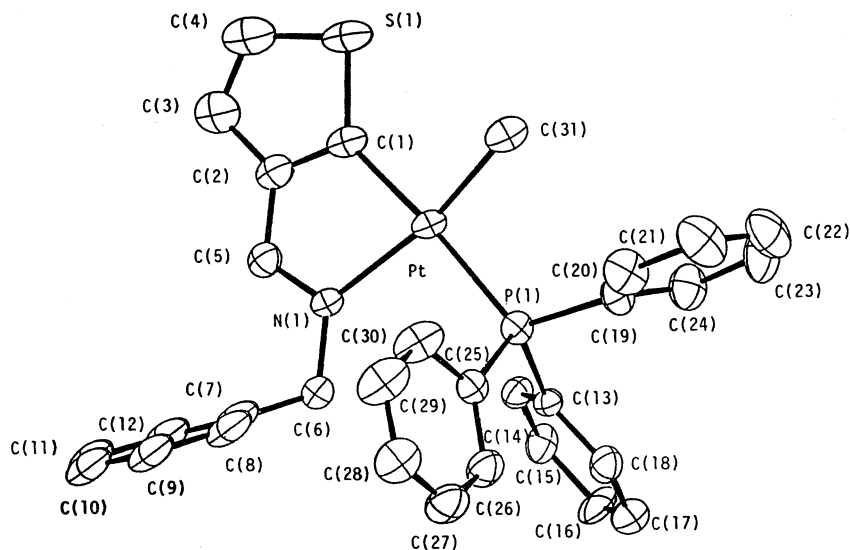
as single isomers arising from intramolecular activation of a C–H bond of the thiophene ring, followed by methane elimination, in a similar process to that reported for other aryl systems [39,40,43].

As observed for the activation of C–H bonds in benzene groups [40], the strong tendency to form metallacycles containing the imine group (endocycles) precludes the formation of an exocycle, which could in principle be formed by the activation of a C–H bond of the benzyl group in ligand **2b**.

Moreover, ligands **2a** and **2b** could in principle afford two different metallacycles arising from activation of either of the two non-equivalent C–H bonds *ortho* to the imine ( $\alpha$  and  $\beta$  to the sulfur atom). The value of the coupling constant  $J(\text{H-H})$  for the remaining two hydrogens in the thienyl group is a valuable tool to elucidate the activated position. Coupling constants in the range 4.90–5.80 Hz have been reported for adjacent hydrogens, while smaller values (3.20–3.65 Hz) are expected for the coupling between two  $\alpha$  hydrogens [13,44]. From the value obtained for the mutual coupling of the thienyl hydrogens in compounds **4a** and **4b** ( $J(\text{H-H}) = 5$  Hz), it can be concluded that exclusive activation of the  $\alpha$  C–H bond takes place. This fact is not unexpected, since it is well established that the predominant reactivity of thiophene occurs at the carbon atom adjacent to, and activated by, the sulfur atom to yield regiospecifically 2-thienyl derivatives [11,45,46]. The cyclometallated compounds **4a** and **4b** have been characterized by elemental analyses, and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra. All spectral parameters are in good agreement with the results obtained for analogous aryl cyclometallated compounds [39,40]. A downfield shift of the methyl–platinum resonance could be tentatively



Scheme 1. (i), (ii) and (iii) Reactions with  $[\text{Pt}_2\text{Me}_4(\text{SMe}_2)_2]$  (**1**) in acetone, (i) 15 min; (ii) 16 h,  $-\text{CH}_4$ ; (iii) 1 h,  $-\text{CH}_4$ . (iv) Reaction with  $\text{PPh}_3$  in acetone, 2 h.

Fig. 1. Molecular structure of compound **5b**.

explained by an interaction of the methyl group with the sulfur atom of the thiophene ring, since an analogous shift has been reported for methyl groups displaying a through-space interaction with fluorine or chlorine substituents on the aryl rings [47].

When the reaction of  $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$  with ligand **2a** was monitored by  $^1\text{H-NMR}$ , compound  $[\text{PtMe}_2\{3\text{-(Me}_2\text{NCH}_2\text{CH}_2\text{NCH)C}_4\text{H}_3\text{S}\}]$  (**3a**) was detected as an intermediate that yielded **4a** in a further step. A similar experiment for ligand **2b** showed the straightforward formation of **4b**. Previous results [39,40] indicate that coordination of the imine ligand to platinum is a preceding step to the cyclometallation process, and that the corresponding coordination compounds are easily detected for chelate dinitrogen ligands. For imines containing one single nitrogen, such compounds could only be observed when the metallation step is either hindered as for the ligand  $\text{PhCH}_2\text{NCH}(2,4,6\text{-C}_6\text{H}_2\text{Me}_3)$  [40], or hampered by bulky groups as for  $\text{PhCH}_2\text{NCH}(3,5\text{-C}_6\text{H}_2\text{Cl}_2)$  [47]. Since an increased reactivity is expected for thiophene when compared with benzene [45], the cyclometallation step is probably even faster for the ligand **2b** than for previously studied phenyl derivatives, thus preventing the detection of a coordination compound. At no stage in the reactions of  $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$  with ligands **2a** and **2b** was coordination of the thiophene sulfur atom to platinum(II) detected.

The reactions of compounds **4a** and **4b** with  $\text{PPh}_3$  were also carried out and produced compounds  $[\text{PtMe}\{3\text{-(Me}_2\text{NCH}_2\text{CH}_2\text{NCH)C}_4\text{H}_2\text{S}\}\text{PPh}_3]$  (**5a**) and  $[\text{PtMe}\{3\text{-(PhCH}_2\text{NCH)C}_4\text{H}_2\text{S}\}\text{PPh}_3]$  (**5b**), which were characterized by elemental analysis, and  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR. The phosphine replaces either the  $\text{SMe}_2$  ligand or the  $\text{NMe}_2$  moiety of the tridentate ligand, and even with an excess of  $\text{PPh}_3$  the metallacycles are not cleaved. The values obtained for  $J(\text{P-Pt})$  in compounds

**5a** and **5b** ( $J(\text{P-Pt}) = 2594$  and  $2593$  Hz) are larger than those obtained for analogous phenyl compounds such as  $[\text{PtMe}\{2\text{-ClC}_6\text{H}_4\text{CH}_2\text{NCH)C}_6\text{H}_4\}\text{PPh}_3]$  ( $J(\text{P-Pt}) = 2175$  Hz) [48]. A smaller *trans* influence of the thienyl group, which may be related to the inductive effect of the sulfur atom, is deduced.

## 2.2. Crystal structure of compound **5b**

Suitable crystals were grown from acetone solution. The crystal structure is composed of discrete molecules separated by van der Waals interactions. There are two molecules in the asymmetric unit that are related by a non-crystallographic pseudo-center of symmetry. Inspection of these two molecules shows that there are no major differences between them, and the bond lengths and bond angles are very similar and are within experimental error ( $3\sigma$ ). A view of one of these molecules is shown in Fig. 1. Selected bond lengths and angles are given in Table 1.

Table 1

Selected bond lengths (Å) and bond angles (°) for compound **5b**, with estimated S.D.

| Bond lengths  |           |           |           |
|---------------|-----------|-----------|-----------|
| Pt–C(1)       | 2.021(9)  | Pt–C(31)  | 2.032(10) |
| Pt–N          | 2.168(7)  | Pt–P      | 2.294(2)  |
| S–C(1)        | 1.702(9)  | S–C(4)    | 1.737(14) |
| N–C(5)        | 1.311(11) | N–C(6)    | 1.462(10) |
| C(1)–C(2)     | 1.363(14) | C(2)–C(5) | 1.462(10) |
| C(3)–C(4)     | 1.34(2)   | C(2)–C(3) | 1.431(13) |
| Bond angles   |           |           |           |
| C(1)–Pt–C(31) | 91.3(4)   | C(1)–Pt–N | 78.0(4)   |
| C(31)–Pt–N    | 168.5(4)  | C(1)–Pt–P | 175.3(3)  |
| C(31)–Pt–P    | 92.8(3)   | N–Pt–P    | 98.2(0)   |
| C(5)–N–C(6)   | 117.1(8)  |           |           |

As expected from spectroscopic characterization, the methyl group is *trans* to the nitrogen atom, the C=N group is *endo* to the cycle and the imine adopts an *E* configuration. The platinum atom displays a tetrahedral distorted planar coordination and the following displacements (Å) are observed from the least-squares plane of the coordination sphere (molecule A): Pt, −0.0099; P(1), −0.0469; N(1), 0.0618; C(1), −0.0656; and C(31), 0.0607. The metallacycle is approximately planar; the largest deviation from the mean plane determined by the five atoms is −0.0103 Å for Pt. The metallacycle is nearly coplanar with the coordination plane, the dihedral angle being 2.97°. The angles between adjacent atoms in the coordination sphere of platinum lie in the range 78.0–98.0°, the smallest angle corresponding to the metallacycle. Bond lengths in the coordination sphere of the platinum and in the thiophene are in the usual range for analogous compounds [29,30,43,49]. In particular, the Pt–P bond length is within the range obtained for compounds with substituted phenyl groups in spite of the lower *trans* influence of the thienyl group.

### 2.3. Ligands derived from 2-thiophenecarboxaldehyde

The ligands 2-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S (**2c**) and 2-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S (**2d**) were prepared from the condensation reactions of 2-thiophenecarboxaldehyde and *N,N*-dimethylethylenediamine or benzylamine carried out in refluxing ethanol and they were characterized by <sup>1</sup>H-NMR spectra.

Interest in these ligands arises from the fact that they might display several modes of coordination to platinum, as reported in the literature for ligands 2-(2'-thienyl)pyridine and 6-(2'-thienyl)2,2'-bipyridine. However, activation of the C–H bond in these ligands would only be possible at the less reactive β position of the thiophene.

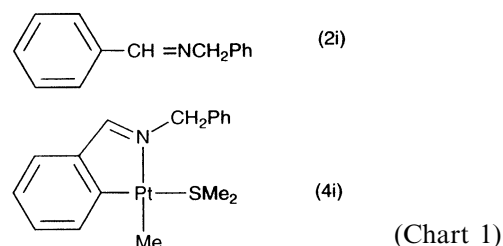
The reaction of [Pt<sub>2</sub>Me<sub>4</sub>(μ-SMe<sub>2</sub>)<sub>2</sub>] (**1**) with ligand **2c** under the same conditions used for the cyclometallation of ligand **2a**, produced compound [PtMe<sub>2</sub>{2-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S}] (**3c**) as shown in Scheme 2. This compound was characterized using elemental ana-

lysis and <sup>1</sup>H-NMR spectra. Spectral data were fully consistent with coordination through both nitrogen atoms. Ligand **2d** reacted with [Pt<sub>2</sub>Me<sub>4</sub>(μ-SMe<sub>2</sub>)<sub>2</sub>] (**1**) to yield unstable compound [PtMe<sub>2</sub>{2-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S}SMe<sub>2</sub>] (**3d**), which could not be isolated in a pure form and could only be characterized in solution by <sup>1</sup>H-NMR. Spectral parameters are consistent with coordination through the imine nitrogen atom only. In contrast to dialkylsulfides SR<sub>2</sub>, thiophene is a very weak sulfur-donor ligand, and few S-bound thiophene complexes are actually known [18]. For instance, it has been shown that imines [(SC<sub>4</sub>H<sub>3</sub>)CR=N]C<sub>2</sub>H<sub>4</sub> coordinate to soft metals such as Ag(I) or Cu(I) through nitrogen atoms without any evidence of interaction of the sulfur atom [23]. Further evidence of the low nucleophilicity of thiophene is the fact that no sulfonium salt is produced upon reaction of thiophene with methyl iodide [44].

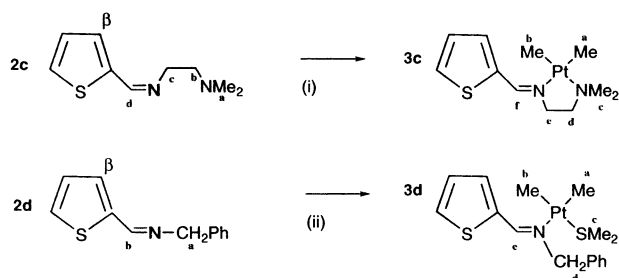
Attempts to achieve the cyclometallation of ligands **2c** and **2d** in a range of solvents and conditions were unsuccessful and led to decomposition with formation of metallic platinum. Since cycloplatination of ligand 2-(2'-thienyl)pyridine [29] has been described, the failure to obtain cyclometallated compounds from ligands **2c** and **2d** cannot only be explained by the lower reactivity of the β-positions of thiophene; other factors such as the design of the ligands and the nucleophilic character of the platinum substrate [Pt<sub>2</sub>Me<sub>4</sub>(μ-SMe<sub>2</sub>)<sub>2</sub>] (**1**) should be taken into account.

### 2.4. Electrochemical measurements

Electrochemical data are summarized in Table 3, together with those for previously reported compounds **2i** and **4i** (see Chart 1) [50].



In the cyclic voltammogram of the non-cyclometallated complex **3c**, measured at ambient temperature in THF solution, one reduction wave and one oxidation wave were observed. The reduction potential is lower compared with that of the free ligand. Although a reoxidation wave is discernible and allows us to calculate a half-wave potential, the ratio of the peak currents  $I_{pa}/I_{pc} = 0.19$  indicates that the reduction wave is not reversible. The ratio  $I_{pa}/I_{pc}$  grows with decreasing temperature up to 0.46 at 268 K. The oxidation wave was observed at a rather low potential and is irreversible, even at temperatures down to 248 K and at high scan rates (5000 mV s<sup>−1</sup>).



Scheme 2. (i) and (ii) Reactions with [Pt<sub>2</sub>Me<sub>4</sub>(μ-SMe<sub>2</sub>)<sub>2</sub>] (**1**) in acetone, (i) 16 h; (ii) 15 min.

Both of the cyclometallated complexes **4a** and **4b** exhibit one reduction wave and two oxidation waves. An additional second reduction process was observed for **4b**. The potential of the first reduction is also lowered compared with the free ligands. The potentials are in the same range, but under identical conditions **4a** (with the terdentate [C,N,N'] ligand) showed a higher degree of reversibility than **4b**. They are both reversible at 268 K ( $I_{pa}/I_{pc} = 1$ ). Both showed two irreversible oxidation processes, **4b** at a higher potential than **4a**.

The triphenylphosphine complexes **5a** and **5b** exhibited very similar electrochemical behavior compared with their analogues **4a** and **4b**. The oxidation and reduction potentials were in the same range as those for **4a** and **4b**, but the degree of reversibility of the reduction reactions was generally higher.

The first reduction process for all the platinum compounds contains one electron, which was checked by comparative measurement of a weighed sample of ferrocene. The currents for the first oxidation wave were of comparable size.

From comparison with previous studies on such cyclometallated complexes [41,42], it is reasonable to assume that the reduction reactions take place in essentially ligand-centered orbitals. The oxidation reaction on the other hand is metal centered and leads to very unstable platinum(III) species.

Electrochemical oxidation and reduction of thiophenes is generally followed by fast chemical reactions. Polythiophenes are formed after oxidation and polymeric, often paramagnetic, material after reduction [51]. The cyclovoltammetric responses are therefore irreversible. Coordination of the ligand to a platinum fragment as in **3c** leads to a lower reduction potential compared with the free ligand and to some degree a re-oxidation wave can be observed. Therefore the decomposition reactions that follow the electron uptake are still present but slowed down. The effect can be increased with lower temperature. The cyclometallation reaction yielding the complexes **4a**, **4b**, **5a** or **5b** does not give rise to further lowering of the reduction potentials, but markedly enhances the stability of the mono-reduced state. We assume that the cyclometallation hinders some of the decomposition pathways. An increase in stability, in the series **4b** < **4a** < **5a** < **5b** can be derived from the  $I_{pa}/I_{pc}$  ratio. Obviously  $PPh_3$  has the strongest stabilizing effect, most probably due to its  $\pi$ -acceptor properties. Moreover, the  $NMe_2$ -chelate ligand in **4a** gives better stabilization than  $SMe_2$  in **4b**. It is also worth noting that the lowering of the reduction potential and the stabilizing effect on the radical anionic species is less pronounced for these thiophene complexes than for the analogues that contain a phenyl moiety. The cyclometallated complex **4i** showed a reversible reduction wave at  $-2.59$  V that is 380 mV lower than for the free ligand while on going from **2b** to

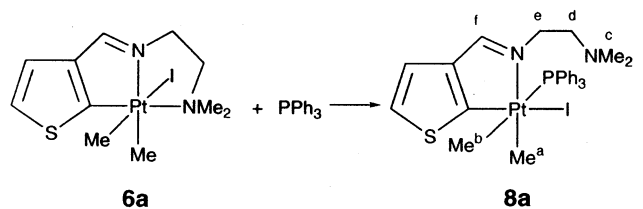
**4b** the potential changes by only 240 mV. If we attribute the stabilizing effect to the enlargement of the heterocyclic ring system to a 10-electron  $\pi$ -system [41], platinaisindole in **4i** is more favored than thieno[2,3]-platinapyrrole in **4b**. The reason might be related to the lower aromaticity of the thiophene system.

## 2.5. Oxidative addition reactions

It is generally accepted that the oxidative addition of alkyl halides to platinum(II) compounds gives *trans* stereochemistry. Compounds with *cis* stereochemistry may be formed in a subsequent isomerization process [52,53]. In order to assess the influence of different ligands *trans* to the thienyl carbon, the study of the oxidative addition of methyl iodide to cyclometallated compounds **4a**, **4b** and **5b** was undertaken (Scheme 3).

Valuable information concerning the electronic structure of these compounds can be obtained from  $^{195}Pt$ -NMR and UV-vis spectroscopies. In agreement with the reported trends [54], the chemical shift  $\delta(^{195}Pt)$  moves to higher fields in the order **4a** < **4b** < **5b**, indicating an increased shielding of the platinum nucleus as the covalency increases from N-donor (**4a**) to S-donor (**4b**) to P-donor (**5b**). The reactivity of square-planar complexes with respect to oxidative addition has been found to be related to the energies of the lowest-energy electronic transitions in the UV-vis spectra [55]. For the compounds under study, the band at lowest energy, assigned to a metal-to-ligand charge transfer (MLCT) transition, increases its energy in the order **4a** < **4b** < **5b** as the electron density at the metal center decreases. Therefore, we can anticipate that the reactivity with respect to oxidative addition should follow the order **4a** > **4b** > **5b**. This trend is fully consistent with the electrochemical studies, which show that the oxidation potential increase in the order **4a** < **4b** < **5b**.

The reaction of  $[PtMe\{3-(Me_2NCH_2CH_2NCH)C_4H_2S\}]$  (**4a**) with methyl iodide in acetone at room temperature gave the platinum(IV) compound  $[PtMe_2I\{3-(Me_2NCH_2CH_2NCH)C_4H_2S\}]$  (**6a**) arising from *trans*-oxidative addition of the alkyl halide. The reaction of **6a** with  $PPh_3$  produced the displacement of the  $NMe_2$  group for the phosphine ligand according to Reaction (1) in which **8a** is formed. Both  $J(Me-Pt)$  and  $J(P-Pt)$  values suggest a *trans* arrangement of the phosphine and the methyl group [39], which indicates that an isomerization process takes place.



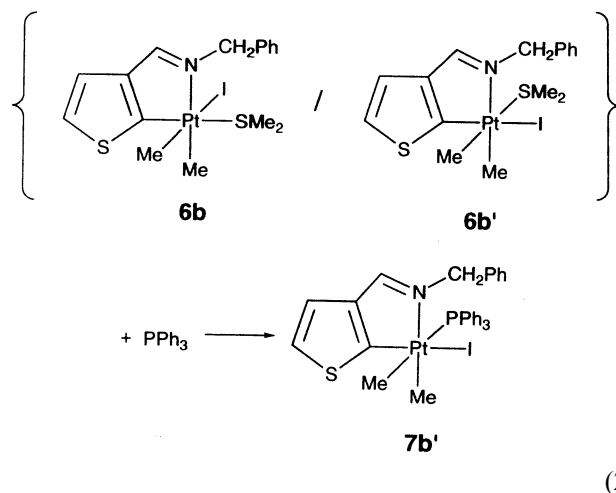
(1)

The reaction of  $[\text{PtMe}\{3-(\text{PhCH}_2\text{NCH})\text{C}_4\text{H}_2\text{S}\}\text{SMe}_2]$  (**4b**) with methyl iodide in acetone at room temperature gave a mixture of two isomers of the cyclometallated platinum(IV) compound  $[\text{PtMe}_2\text{I}\{3-(\text{PhCH}_2\text{NCH})\text{C}_4\text{H}_2\text{S}\}\text{SMe}_2]$  (**6b** and **6b'**) as evidenced from the presence of two sets of signals in a 2:1 ratio in the  $^1\text{H}$ -NMR spectrum. From the  $^2J(\text{H-Pt})$  values for the methyl groups, a *fac*- $\text{PtC}_3$  structure is assigned to both the isomers, which differ only in having a methyl group *trans* to iodide or *trans* to  $\text{SMe}_2$ . When the reaction was monitored by  $^1\text{H}$ -NMR, the 2:1 ratio of products was seen immediately and remained constant.

When the reaction of  $[\text{PtMe}\{3-(\text{PhCH}_2\text{NCH})\text{C}_4\text{H}_2\text{S}\}\text{PPh}_3]$  (**5b**) with methyl iodide was monitored by  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR spectra, resonances assigned to platinum(IV) compound  $[\text{PtMe}_2\text{I}\{3-(\text{PhCH}_2\text{NCH})\text{C}_4\text{H}_2\text{S}\}\text{PPh}_3]$  (**7b**) appeared in the early stages of the reaction together with signals due to unreacted platinum(II) compound **5b**. As the reaction proceeded, the intensity of the latter decreased, while resonances due to a second platinum(IV) isomer **7b'** appeared. Within 24 h, the spectra showed that the isomerization of **7b** to **7b'** was complete. A reduced coupling to platinum is observed for the axial methyl in **7b'**, which suggests a *trans* arrangement of the axial methyl and the  $\text{PPh}_3$ . The  $J(\text{P-Pt})$  values are in the range expected for platinum(IV) compounds, which is considerably reduced from that of the platinum(II) compound, but for **7b**, the value is greater than for the phenyl analogue due to the low *trans* influence of the thienyl group.

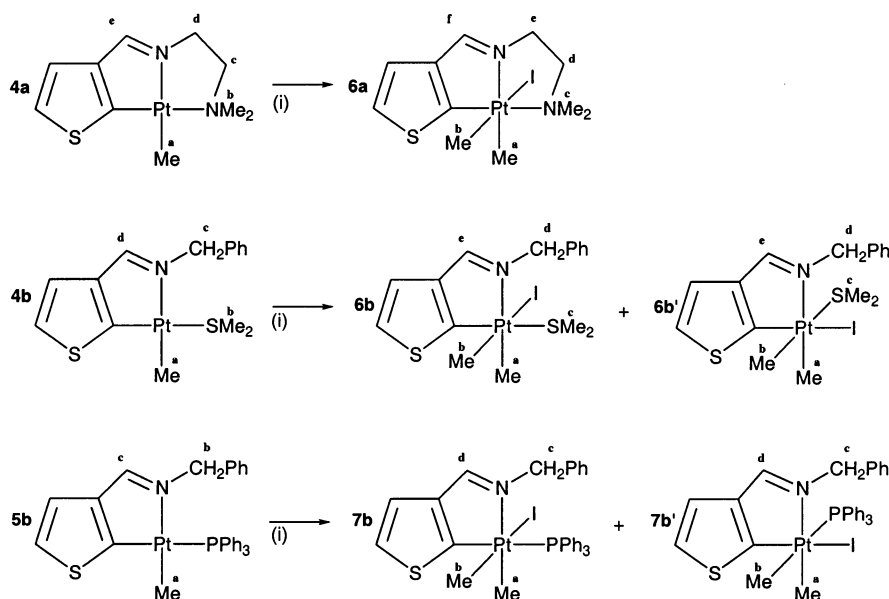
Furthermore, when the mixture of isomers **6b/6b'** was treated with  $\text{PPh}_3$  in acetone, the substitution reaction

of  $\text{SMe}_2$  for  $\text{PPh}_3$  yielded only isomer **7b'** in which the triphenylphosphine is *trans* to a methyl group, as shown in Reaction (2).



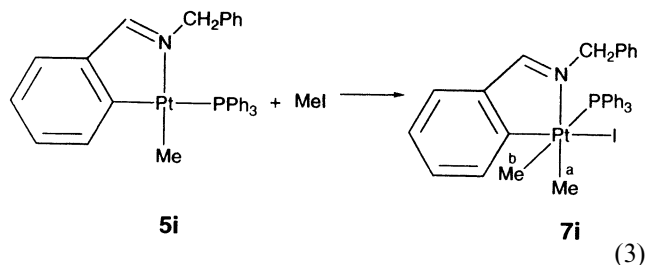
The results obtained for **4b** and **5b** indicate that: (1) the oxidative addition takes place with *trans* stereochemistry and is followed by isomerization of the resulting platinum(IV) compound; (2) the oxidative addition is slower for the phosphine derivative **5b** than for the  $\text{SMe}_2$  derivative **4b**, as expected from considering both steric and electronic factors and (3) while isomers **6b** and **6b'** have a similar stability, isomer **7b'** with the  $\text{PPh}_3$  *trans* to methyl is more stable than **7b**. The latter result can be related with the greater bulk of the phosphine ligand.

The reaction of the analogous platinum(II) phenyl metallated complex  $[\text{PtMe}\{(\text{PhCH}_2\text{NCH})\text{C}_6\text{H}_4\}\text{PPh}_3]$  (**5i**) [48] with methyl iodide was monitored by NMR for

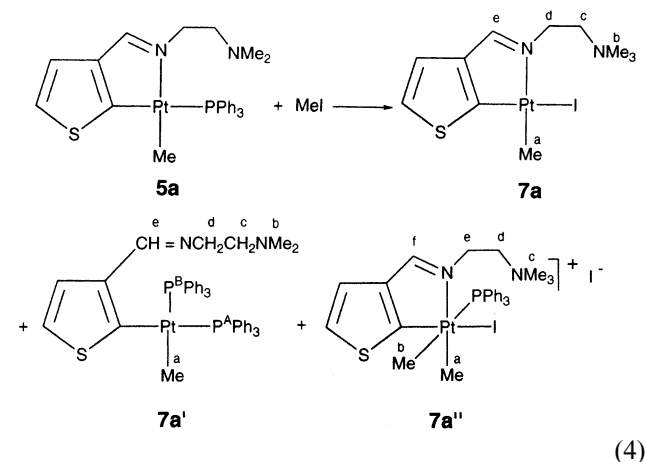


Scheme 3. (i) Reactions with MeI in acetone, r.t.

comparison with **5b** (Reaction (3)). Compound **5i** gave a single isomer of  $[\text{PtMe}_2\text{I}\{\text{(PhCH}_2\text{NCH)}\text{C}_6\text{H}_4\}\text{PPh}_3]$  with  $\text{PPh}_3$  *trans* to the axial methyl group, based on NMR data. The higher rate of the isomerization process can be attributed to the higher *trans* influence of the phenyl when compared with the thienyl group.

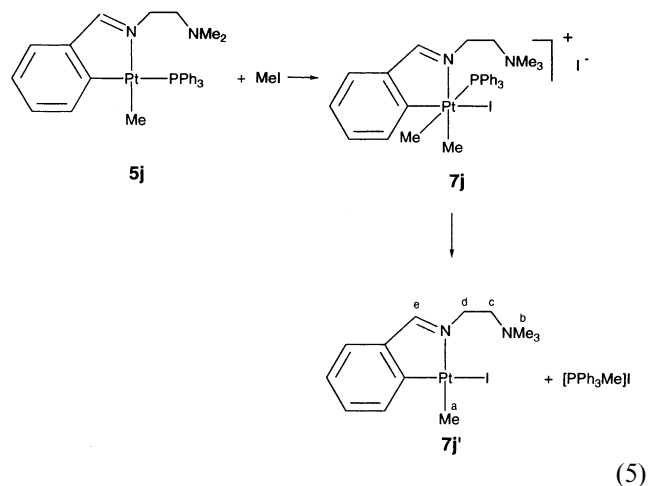


The reaction of methyl iodide with compound  $[\text{PtMe}\{3\text{-(Me}_2\text{NCH}_2\text{CH}_2\text{NCH)}\text{C}_4\text{H}_2\text{S}\}(\text{PPh}_3)]$  (**5a**), in which the  $\text{NMe}_2$  fragment is not coordinated to the platinum is more complex (Reaction (4)). The  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR spectra show the presence of several compounds.  $[\text{PtMeI}\{3\text{-(Me}_3\text{NCH}_2\text{CH}_2\text{NCH)}\text{C}_4\text{H}_2\text{S}\}]$  (**7a**) was detected in the  $^1\text{H}$ -NMR spectrum by the presence of a methylplatinum group appearing as a singlet, indicating dissociation of the  $\text{PPh}_3$  ligand, and a corresponding resonance integrating nine hydrogens assigned to an  $\text{NMe}_3$  moiety. The  $^{31}\text{P}$ -NMR spectrum showed the presence of a platinum(II) compound containing two non-equivalent  $\text{PPh}_3$  ligands *trans* to C-donors, for which the structure  $[\text{PtMe}\{3\text{-(Me}_2\text{NCH}_2\text{CH}_2\text{NCH)}\text{C}_4\text{H}_2\text{S}\}(\text{PPh}_3)_2]$  (**7a'**) was assigned. In the  $^{31}\text{P}$ -NMR, a minor resonance at  $\delta = -9.93$  [ $J(\text{P-Pt}) = 1031$  Hz] corresponding to a platinum(IV) compound was tentatively assigned to **7a''**, since the  $J(\text{Ppt})$  value is in the same range, but not identical to that of compound **8a**.



After several hours in solution, the only compounds detected were **7a**, characterized as above, and  $[\text{PPh}_3\text{Me}]\text{I}$ , for which  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR data are consistent with the values given in the literature [56,57].

Interestingly, the analogous platinum(II) compound  $[\text{PtMe}\{3\text{-(Me}_2\text{NCH}_2\text{CH}_2\text{NCH)}\text{C}_6\text{H}_4\}(\text{PPh}_3)]$  (**5j**) [39] containing a phenyl instead of a thienyl group gave initially only one product when reacted with methyl iodide, a platinum(IV) compound **7j**. After several hours the reaction yielded  $[\text{PPh}_3\text{Me}]\text{I}$  and a platinum(II) compound **7j'** exclusively, as shown in Reaction (5).



Although the reactions of **5a** and **5j** with methyl iodide are not entirely similar, in both cases the addition of methyl iodide to the dangling  $\text{NMe}_2$  moiety competes with addition at the metal center.

In conclusion, while intramolecular C–H activation at the less reactive  $\beta$  position of the thiophene ring could not be achieved, activation at the  $\alpha$  position allows the preparation of new cyclometallated platinum compounds containing two or three fused five-membered rings. The electrochemical properties and the reactivity of these compounds appear to be modulated by the ligands in the coordination sphere of the platinum center.

### 3. Experimental

#### 3.1. Instrumentation

$^1\text{H}$ -,  $^{13}\text{C}$ -,  $^{31}\text{P}$ - $\{^1\text{H}\}$  and  $^{195}\text{Pt}$ -NMR spectra were recorded by using Varian Gemini 200 ( $^1\text{H}$ , 200 MHz), Varian 300 ( $^{13}\text{C}$ , 75 MHz) and Bruker 250 ( $^{31}\text{P}$ , 101.25 MHz;  $^{195}\text{Pt}$ , 54 MHz) spectrometers, and referenced to  $\text{SiMe}_4$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ),  $\text{H}_2\text{PtCl}_6$  in  $\text{D}_2\text{O}$  ( $^{195}\text{Pt}$ ), and  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ).  $\delta$  values are given in ppm and  $J$  values in Hz. IR spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Microanalyses and mass spectra (CI and FAB) were performed by the Serveis Científic-Tècnics de la Universitat de Barcelona. UV–vis spectra were recorded in a Shimadzu UV-160A spectrophotometer.

Cyclic voltammetry and square-wave voltammetry experiments were carried out using a three-electrode configuration (glassy carbon working electrode, platinum counter electrode, Ag | AgCl reference) and a PAR 273 potentiostat and function generator with PAR M270/250 software. As internal standard the ferrocene | ferrocenium couple ( $\text{FeCp}_2^{+/0}$ ) was used. Ferrocene was added in equimolar amount so as to estimate the electrochemical reversibility and the effects of uncompensated resistance. The temperature was adjusted using a FRYKA FT08-64 cryostat, temperature tolerance was  $\pm 1^\circ\text{C}$ . The electrochemical experiments were carried out under an argon atmosphere in dried and deaerated solvents using tetrabutylammoniumhexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) as the supporting electrolyte.

### 3.2. Preparation of the compounds

The complex  $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$  was prepared as reported [58].

#### 3.2.1. Synthetic procedure for compounds 2

Compounds **2** were prepared by the reaction of 0.5 g (4.4 mmol) of the corresponding aldehyde (2- or 3-thiophenecarboxaldehyde) with an equimolar amount of *N,N*-dimethylethylenediamine (0.39 g), or *N*-benzylamine (0.48 g) in refluxing ethanol. After 4 h, the solvent was removed in a rotary evaporator to yield yellow or red oils. Yield 80–85%.

**3.2.1.1. 3-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S (2a).** <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.30 [s, H<sup>a</sup>]; 2.62 [t, <sup>3</sup>*J*(H<sup>b</sup>–H<sup>c</sup>) = 7, H<sup>b</sup>]; 3.69 [td, <sup>3</sup>*J*(H<sup>c</sup>–H<sup>b</sup>) = 7, <sup>4</sup>*J*(H<sup>c</sup>–H<sup>d</sup>) = 1, H<sup>c</sup>]; {7.30 [dd, *J*(H–H) = 5; 3]; 7.51 [dd, *J*(H–H) = 5; 1]; 7.59 [dd, *J*(H–H) = 3; 1], aromatics}; 8.32 [s, 1H, H<sup>d</sup>]. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 45.90 [s, C<sup>a</sup>]; {59.90; 60.13, C<sup>b</sup>, C<sup>c</sup>}; {125.66; 126.24; 128.24; 140.39, thiophene}; 156.08 [s, C<sup>d</sup>].

**3.2.1.2. 3-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S (2b).** <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.78 [s, H<sup>a</sup>]; {7.32 [m]; 7.57 [dt, *J*(H–H) = 5; 1]; 7.64 [dd, *J*(H–H) = 3; 1], aromatics}; 8.40 [s, H<sup>b</sup>]. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 65.01 [s, C<sup>a</sup>]; {125.77; 126.33; 126.91; 139.09, thiophene}; {127.92; 128.41; 128.56, aromatics}; 156.20 [s, C<sup>b</sup>].

**3.2.1.3. 2-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S (2c).** <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.30 [s, H<sup>a</sup>]; 2.63 [t, <sup>3</sup>*J*(H<sup>b</sup>–H<sup>c</sup>) = 7, H<sup>b</sup>]; 3.71 [td, <sup>3</sup>*J*(H<sup>c</sup>–H<sup>b</sup>) = 7, <sup>4</sup>*J*(H<sup>c</sup>–H<sup>d</sup>) = 1, H<sup>c</sup>]; {7.06 [dd, *J*(H–H) = 5; 4]; 7.29 [dd, *J*(H–H) = 4; 1]; 7.39 [dt, *J*(H–H) = 5; 1], aromatics}; 8.41 [d, <sup>4</sup>*J*(H<sup>d</sup>–H<sup>c</sup>) = 1, H<sup>d</sup>].

**3.2.1.4. 2-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S (2d).** <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.79 [s, H<sup>a</sup>]; {7.06 [dd, *J*(H–H) = 4; 3.5]; 7.33 [m]; 7.39 [dt, *J*(H–H) = 4; 1], aromatics}; 8.44 [s, H<sup>b</sup>].

#### 3.2.2. Synthetic procedure for compounds 3

Compound **3c** was obtained by adding a solution of  $3.5 \times 10^{-4}$  mol of the imine in acetone (10 ml) to a solution of 100 mg ( $1.74 \times 10^{-4}$  mol) of compound **1** in acetone (10 ml). The mixture was stirred for 16 h and, upon cooling, orange crystals were formed. These were filtered, washed with hexane and dried in vacuum.

**3.2.2.1. [PtMe<sub>2</sub>{2-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S}] (3c).** Yield 100 mg (70%). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.48 [s, <sup>2</sup>*J*(Pt–H) = 91, Me<sup>a</sup>]; 0.64 [s, <sup>2</sup>*J*(Pt–H) = 84 Me<sup>b</sup>]; 2.64 [m, H<sup>d</sup>]; 2.81 [s, <sup>3</sup>*J*(H–Pt) = 21, H<sup>c</sup>]; 4.05 [m, H<sup>e</sup>]; {7.03 [dd, *J*(H–H) = 5; 4]; 7.62 [dd, *J*(H–H) = 5; 2]; 8.06 [dt, *J*(H–H) = 4; 2], aromatics}; 8.96 [s, <sup>3</sup>*J*(Pt–H) = 47, H<sup>f</sup>]. Anal. Found: C, 32.4; H, 5.0; N, 7.0. Calc. for C<sub>11</sub>H<sub>20</sub>N<sub>2</sub>S<sub>2</sub>Pt: C, 32.27; H, 4.92; N, 7.33%.

Compounds **3a** and **3d** were characterized by the following procedure: a 20.0 mg (0.035 mmol) amount of complex **1** and 0.07 mmol of the corresponding imine were dissolved in 0.6 ml of acetone-*d*<sub>6</sub>, and the <sup>1</sup>H-NMR spectrum was recorded within a period of 15 min.

**3.2.2.2. [PtMe<sub>2</sub>{3-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S}] (3a).** <sup>1</sup>H-NMR (200 MHz, acetone-*d*<sub>6</sub>):  $\delta$  = 0.20 [s, <sup>2</sup>*J*(Pt–H) = 92, Me<sup>a</sup>]; 0.41 [s, <sup>2</sup>*J*(Pt–H) = 85 Me<sup>b</sup>]; 2.66 [m, H<sup>d</sup>]; 2.71 [s, <sup>3</sup>*J*(H–Pt) = 22, H<sup>c</sup>]; 4.01 [m, H<sup>e</sup>]; {7.79 [dd, *J*(H–H) = 2; 1]; 8.28 [dd, *J*(H–H) = 5; 1]; 8.58 [m], aromatics}; 9.02 [s, <sup>3</sup>*J*(Pt–H) = 49, H<sup>f</sup>].

**3.2.2.3. [PtMe<sub>2</sub>{2-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S}]SMe<sub>2</sub> (3d).** <sup>1</sup>H-NMR (200 MHz, acetone-*d*<sub>6</sub>):  $\delta$  = 0.31 [s, <sup>2</sup>*J*(Pt–H) = 87, Me]; 0.37 [s, <sup>2</sup>*J*(Pt–H) = 83, Me]; 1.75 [s, <sup>3</sup>*J*(H–Pt) = 24, H<sup>c</sup>]; 5.10 [m, H<sup>d</sup>]; 9.25 [s, <sup>3</sup>*J*(Pt–H) = 52, H<sup>e</sup>].

#### 3.2.3. Synthetic procedure for compounds 4

Compound **4a** was obtained by the reaction of 100 mg ( $1.74 \times 10^{-4}$  mol) of compound **1** with 64 mg ( $3.52 \times 10^{-4}$  mol) of compound **2a** in acetone (20 ml). After continuous stirring during 16 h, the solvent was removed in a rotary evaporator and the resulting orange solid was filtered, washed with hexane and dried in vacuum.

**3.2.3.1. [PtMe{3-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>3</sub>S}] (4a).** Yield 90 mg (66%). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.05 [s, <sup>2</sup>*J*(Pt–H) = 78, Me<sup>a</sup>]; 2.86 [s, <sup>3</sup>*J*(Pt–H) = 25, Me<sup>b</sup>]; 3.19 [t, *J*(H–H) = 6, H<sup>c</sup>]; 4.00 [t, *J*(H–H) = 6, H<sup>d</sup>]; {7.01 [d, <sup>4</sup>*J*(Pt–H) = 34, *J*(H–H) = 5]; 7.13 [d, *J*(H–H) = 5], aromatics}; 8.37 [s, <sup>3</sup>*J*(Pt–H<sup>e</sup>) = 57, H<sup>e</sup>]. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = –17.74 [*J*(Pt–C) = 736, Me<sup>a</sup>]; 49.18 [Me<sup>b</sup>]; {51.81 [*J*(Pt–C) = 27]; 68.67, C<sup>c</sup>, C<sup>d</sup>}; {122.79 [*J*(Pt–C) = 60]; 125.22 [*J*(Pt–C) = 57]; 149.18 [*J*(Pt–C) = 51]; 153.96 [*J*(Pt–C) = 1325], thiophene}; 160.17 [*J*(Pt–C) = 76, C<sup>e</sup>]. <sup>195</sup>Pt-NMR (54

MHz, acetone- $d_6$ ):  $\delta = -3668.6$  [s]. UV–vis (acetone):  $\lambda = 389$  nm ( $\epsilon = 1122$  M $^{-1}$  cm $^{-1}$ ). Anal. Found: C, 30.3; H, 4.2; N, 6.9. Calc. for C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>SPt: C, 30.69; H, 4.12; N, 7.16%.

An analogous procedure with a reaction time of 1 h yielded compounds **4b**.

3.2.3.2. *[PtMe{3-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}SMe<sub>2</sub>] (4b)*. Yield 120 mg (73%). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 1.10$  [s, <sup>2</sup>*J*(Pt–H) = 78, Me<sup>a</sup>]; 1.98 [s, <sup>3</sup>*J*(Pt–H) = 32, Me<sup>b</sup>]; 5.09 [s, <sup>3</sup>*J*(H<sup>c</sup>–Pt) = 14, H<sup>c</sup>]; {7.18 [d, <sup>4</sup>*J*(Pt–H) = 35, *J*(H–H) = 5]; 7.30 [m], aromatics}; 8.41 [s, <sup>3</sup>*J*(Pt–H<sup>d</sup>) = 52, H<sup>d</sup>]. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = -20.18$  [*J*(Pt–C) = 719, Me<sup>a</sup>]; 19.86 [Me<sup>b</sup>]; 62.18 [C<sup>c</sup>]; {124.75; 125.19; 137.68; 147.45, thiophene}; {127.53; 128.48; 137.25, aromatics}; 167.69 [*J*(Pt–C) = 66, C<sup>d</sup>]. <sup>195</sup>Pt NMR (54 MHz, acetone- $d_6$ ):  $\delta = -4040.0$  [s]. UV–vis (acetone):  $\lambda = 378$  nm ( $\epsilon = 3147$  M $^{-1}$  cm $^{-1}$ ). Anal. Found: C, 38.1; H, 4.1; N, 2.9. Calc. for C<sub>15</sub>H<sub>19</sub>NS<sub>2</sub>Pt: C, 38.13; H, 4.05; N, 2.96%.

### 3.2.4. Synthetic procedure for compounds **5**

Compounds **5** were obtained by the reaction of 50 mg of the corresponding compound **4** with the equimolar amount of PPh<sub>3</sub> in acetone. After continuous stirring during 2 h, the solvent was removed in a rotary evaporator and the resulting yellow solid was filtered, washed with hexane and diethyl ether and dried in vacuum.

3.2.4.1. *[PtMe{3-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}PPh<sub>3</sub>] (5a)*. Yield 70 mg (84%). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 0.86$  [d, <sup>2</sup>*J*(Pt–H) = 82, <sup>3</sup>*J*(P–H) = 8, Me<sup>a</sup>]; 1.85 [s, Me<sup>b</sup>]; 1.77 [t, *J*(H–H) = 7, H<sup>c</sup>]; 3.15 [t, *J*(H–H) = 7, H<sup>d</sup>]; {7.42 [m]; 7.68 [m], aromatics}; 8.40 [s, <sup>3</sup>*J*(Pt–H<sup>e</sup>) = 52, H<sup>e</sup>]. <sup>31</sup>P-NMR (101.26 MHz, CDCl<sub>3</sub>):  $\delta = 30.78$  [*J*(Pt–P) = 2594]. Anal. Found: C, 51.0; H, 4.8; N, 4.2. Calc. for C<sub>28</sub>H<sub>31</sub>N<sub>2</sub>PSPt: C, 51.45; H, 4.78; N, 4.29%.

3.2.4.2. *[PtMe{3-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}PPh<sub>3</sub>] (5b)*. Yield 60 mg (84%). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 0.89$  [d, <sup>2</sup>*J*(Pt–H) = 81, <sup>3</sup>*J*(P–H) = 8, Me<sup>a</sup>]; 4.13 [s, *J*(Pt–H) = 10, H<sup>c</sup>]; {6.80 [m]; 7.19 [m], 7.36 [m], 7.67 [m], aromatics}; 8.09 [s, <sup>3</sup>*J*(Pt–H<sup>d</sup>) = 52, H<sup>d</sup>]. <sup>31</sup>P-NMR (101.26 MHz, CDCl<sub>3</sub>):  $\delta = 30.55$  [*J*(Pt–P) = 2593]. <sup>195</sup>Pt NMR (54 MHz, acetone- $d_6$ ):  $\delta = -4328.1$  [d, *J*(Pt–P) = 2614]. UV–vis (acetone):  $\lambda = 373$  nm ( $\epsilon = 2546$  M $^{-1}$  cm $^{-1}$ ). Anal. Found: C, 55.7; H, 4.2; N, 2.1. Calc. for C<sub>31</sub>H<sub>28</sub>NPSPt: C, 55.35; H, 4.20; N, 2.08%.

### 3.2.5. Synthetic procedure for compounds **6**, **7** and **8**

An excess of methyl iodide (0.1 ml) was added to solutions of 50 mg of the corresponding compounds **4a**, **4b** and **5b** in acetone. The mixtures were stirred for 3 h, and the solvent was removed under vacuum to yield light yellow solids.

3.2.5.1. *[PtMe<sub>2</sub>I{3-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}] (6a)*. Yield 50 mg (73%). <sup>1</sup>H-NMR (200 MHz, acetone- $d_6$ ):  $\delta = 0.78$  [s, <sup>2</sup>*J*(Pt–H) = 71, Me<sup>b</sup>]; 1.24 [s, <sup>2</sup>*J*(Pt–H) = 64, Me<sup>a</sup>]; {2.66 [s, <sup>3</sup>*J*(Pt–H) = 19], 3.22 [s, <sup>3</sup>*J*(Pt–H) = 19], Me<sup>c</sup>]; 4.20 [m, H<sup>d</sup>–H<sup>e</sup>]; {7.11 [m, *J*(H–H) = 5], 7.22 [m, *J*(H–H) = 5], aromatics}; 8.47 [s, <sup>3</sup>*J*(Pt–H<sup>f</sup>) = 48, H<sup>f</sup>]. Anal. Found: C, 25.3; H, 4.0; N, 5.2. Calc. for C<sub>11</sub>H<sub>19</sub>IN<sub>2</sub>SPt: C, 24.77; H, 3.59; N, 5.25%.

3.2.5.2. *[PtMe<sub>2</sub>I{3-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}SMe<sub>2</sub>] (6b/6b')*. Yield 50 mg (77%). <sup>1</sup>H-NMR (200 MHz, acetone- $d_6$ ): **6b**:  $\delta = 0.66$  [s, <sup>2</sup>*J*(Pt–H) = 69, Me<sup>b</sup>]; 1.41 [s, <sup>2</sup>*J*(Pt–H) = 67, Me<sup>a</sup>]; 8.45 [s, <sup>3</sup>*J*(Pt–H<sup>e</sup>) = 45, H<sup>e</sup>]; **6b'**:  $\delta = 1.21$  [s, <sup>2</sup>*J*(Pt–H) = 70, Me<sup>b</sup>]; 1.59 [s, <sup>2</sup>*J*(Pt–H) = 68, Me<sup>a</sup>]; 2.06 [s, <sup>3</sup>*J*(Pt–H) = 14 Me<sup>c</sup>]; 5.37 [m, H<sup>d</sup>]; {7.36 [m], 7.57 [m], aromatics}; 8.46 [s, <sup>3</sup>*J*(Pt–H<sup>e</sup>) = 45, H<sup>e</sup>]. Anal. Found: C, 31.8; H, 3.6; N, 2.3. Calc. for C<sub>16</sub>H<sub>22</sub>INS<sub>2</sub>Pt: C, 31.28; H, 3.61; N, 2.28%.

3.2.5.3. *[PtMe<sub>2</sub>I{3-(PhCH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}PPh<sub>3</sub>] (7b/7b')*. Yield 45 mg (74%). <sup>1</sup>H-NMR (200 MHz, acetone- $d_6$ ): **7b**:  $\delta = 0.35$  [s, <sup>2</sup>*J*(Pt–H) = 67, <sup>3</sup>*J*(P–H) = 7, Me<sup>b</sup>]; 1.50 [s, <sup>2</sup>*J*(Pt–H) = 68, <sup>3</sup>*J*(P–H) = 7, Me<sup>a</sup>]; {4.84 [d], 4.99 [d], *J*(H–H) = 15, *AB* pattern, H<sup>c</sup>], 8.19 [s, <sup>3</sup>*J*(Pt–H<sup>e</sup>) = 45, H<sup>d</sup>]; <sup>31</sup>P-NMR (101.26 MHz, acetone- $d_6$ ):  $\delta = -5.45$  [s, *J*(Pt–P) = 1564]. **7b'**:  $\delta = 1.15$  [s, <sup>2</sup>*J*(Pt–H) = 60, <sup>3</sup>*J*(P–H) = 8, Me<sup>b</sup>]; 1.69 [s, <sup>2</sup>*J*(Pt–H) = 68, <sup>3</sup>*J*(P–H) = 7, Me<sup>a</sup>]; {4.46 [d], 5.40 [d], *J*(H–H) = 15, *AB* pattern, H<sup>c</sup>]; 7.92 [s, <sup>3</sup>*J*(Pt–H<sup>d</sup>) = 44, H<sup>d</sup>]; <sup>31</sup>P-NMR (101.26 MHz, acetone- $d_6$ ):  $\delta = -10.53$  [s, *J*(Pt–P) = 1016]. Anal. Found: C, 46.6; H, 4.2; N, 1.7. Calc. for C<sub>32</sub>H<sub>31</sub>INSPt: C, 47.18; H, 3.84; N, 1.72%.

The reactions of these compounds and of **5a**, **5i** and **5j** with methyl iodide were monitored by NMR in the following way: 10  $\mu$ l of methyl iodide were added to 20 mg of the corresponding compound dissolved in 0.6 ml of acetone- $d_6$  in a 5 mm NMR tube and spectra were taken.

3.2.5.4. *[PtMe<sub>2</sub>I{PhCH<sub>2</sub>NCHC<sub>6</sub>H<sub>5</sub>}PPh<sub>3</sub>] (7i)*. <sup>1</sup>H-NMR (200 MHz, acetone- $d_6$ ):  $\delta = 1.12$  [s, <sup>2</sup>*J*(Pt–H) = 62, <sup>3</sup>*J*(P–H) = 8, Me<sup>b</sup>]; 1.56 [s, <sup>2</sup>*J*(Pt–H) = 70, <sup>3</sup>*J*(P–H) = 7, Me<sup>a</sup>]; {4.61 [d], 5.64 [d], *J*(H–H) = 16, *AB* pattern, H<sup>c</sup>]; {6.58 [*J*(Pt–H) = 43, *J*(H–H) = 8], 6.91 [dd, *J*(H–H) = 8; 1.5], 7.02 [t, *J*(H–H) = 8], 7.32 [m], 7.46 [m], aromatics}; 8.13 [s, <sup>3</sup>*J*(Pt–H<sup>e</sup>) = 49, H<sup>d</sup>]; <sup>31</sup>P-NMR (101.26 MHz, acetone- $d_6$ ):  $\delta = -8.72$  [s, *J*(Pt–P) = 1017].

3.2.5.5. *[PtMeI{3-(Me<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}] (7a)*. <sup>1</sup>H-NMR (200 MHz, acetone- $d_6$ ):  $\delta = 1.18$  [s, <sup>2</sup>*J*(Pt–H) = 72, Me<sup>a</sup>]; 3.46 [s, Me<sup>b</sup>]; {4.3 [m]; 4.7 [m], H<sup>c</sup>, H<sup>d</sup>]; {7.10 [d], 7.21 [d], aromatics}; 8.64 [s, <sup>3</sup>*J*(Pt–H<sup>e</sup>) = 40, H<sup>e</sup>].

Table 2

Crystallographic and refinement data for compound **5b**

|                                                       |                                            |
|-------------------------------------------------------|--------------------------------------------|
| Empirical formula                                     | C <sub>31</sub> H <sub>28</sub> NPPtS      |
| Formula weight                                        | 672.66                                     |
| Crystal system                                        | Monoclinic                                 |
| Space group                                           | P2 <sub>1</sub> /a                         |
| Unit cell dimensions                                  |                                            |
| <i>a</i> (Å)                                          | 12.151(10)                                 |
| <i>b</i> (Å)                                          | 24.417(8)                                  |
| <i>c</i> (Å)                                          | 18.286(4)                                  |
| $\alpha$ (°)                                          | 90                                         |
| $\beta$ (°)                                           | 99.42(3)                                   |
| $\gamma$ (°)                                          | 90                                         |
| <i>V</i> (Å <sup>3</sup> )                            | 5352(5)                                    |
| <i>D</i> <sub>calc</sub> (g cm <sup>−3</sup> )        | 1.670                                      |
| <i>Z</i>                                              | 8                                          |
| <i>F</i> (000)                                        | 2640                                       |
| Crystal size (mm <sup>3</sup> )                       | 0.1 × 0.1 × 0.2                            |
| $\lambda$ (Mo–K $\alpha$ ) (Å)                        | 0.71069                                    |
| Temperature (K)                                       | 293(2)                                     |
| Reflections collected                                 | 16 102                                     |
| Independent reflections                               | 15 571 [ <i>R</i> <sub>int</sub> = 0.0343] |
| <i>R</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]        | 0.0588                                     |
| <i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> )       | 0.1295                                     |
| Number of refined parameters                          | 640                                        |
| Max. shift/estimated S.D.                             | 0.00                                       |
| Largest difference peak and hole (e Å <sup>−3</sup> ) | 0.626 and −0.521                           |

3.2.5.6. [PtMe{3-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}(PPh<sub>3</sub>)<sub>2</sub>] (**7a'**). <sup>1</sup>H-NMR (200 MHz, acetone-*d*<sub>6</sub>):  $\delta$  = 0.38 [dd, <sup>2</sup>*J*(Pt–H) = 65, *J*(PH) = 8.6; 6.6, Me<sup>a</sup>; 9.09 [s, H<sup>e</sup>]; <sup>31</sup>P-NMR (101.26 MHz, acetone-*d*<sub>6</sub>):  $\delta$  = 24.22 [d, *J*(Pt–P) = 1839, *J*(PP) = 14]; 26.16 [d, *J*(Pt–P) = 2279, *J*(P–P) = 14].

3.2.5.7. [PtMe<sub>2</sub>I{3-(Me<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}PPh<sub>3</sub>]I (**7a''**). <sup>31</sup>P-NMR (101.26 MHz, acetone-*d*<sub>6</sub>):  $\delta$  = −9.93 [s, *J*(Pt–P) = 1031].

3.2.5.8. [PtMe<sub>2</sub>I{Me<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>NCHC<sub>6</sub>H<sub>4</sub>}PPh<sub>3</sub>]I (**7j**). <sup>31</sup>P-NMR (101.26 MHz, acetone-*d*<sub>6</sub>):  $\delta$  = −8.57 [s, *J*(Pt–P) = 1028].

3.2.5.9. [PtMeI{Me<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>NCHC<sub>6</sub>H<sub>4</sub>}] (**7j'**). <sup>1</sup>H-NMR (200 MHz, acetone-*d*<sub>6</sub>):  $\delta$  = 1.12 [s, <sup>2</sup>*J*(Pt–H) = 74, Me<sup>a</sup>]; 3.48 [s, Me<sup>b</sup>]; {4.4[m]; 4.9[m], H<sup>c</sup>, H<sup>d</sup>}; {7.01[m], 7.18[m], 7.55[m], aromatics}; 9.00 [s, <sup>3</sup>*J*(Pt–H<sup>e</sup>) = 42, H<sup>e</sup>].

3.2.5.10. [PtMe<sub>2</sub>I{3-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCH)C<sub>4</sub>H<sub>2</sub>S}PPh<sub>3</sub>] (**8a**). This was obtained by the reaction of 50 mg of compound **6a** with the equimolar amount of PPh<sub>3</sub> in acetone. After continuous stirring during 2 h, the solvent was removed in a rotary evaporator and the resulting yellow solid was filtered, washed with hexane and diethyl ether and dried in vacuum. Yield 60 mg (80%). <sup>1</sup>H-NMR (200 MHz, acetone-*d*<sub>6</sub>):  $\delta$  = 1.22 [d, <sup>2</sup>*J*(Pt–H) = 61, *J*(P–H) = 8, Me<sup>b</sup>]; 1.67 [d, <sup>2</sup>*J*(Pt–H) =

68, *J*(P–H) = 8, Me<sup>a</sup>]; 2.08 [s, Me<sup>c</sup>]; {2.15[m], 3.90[m], H<sup>d</sup>, H<sup>e</sup>}; 8.15 [s, <sup>3</sup>*J*(Pt–H<sup>f</sup>) = 45, H<sup>f</sup>]; <sup>31</sup>P-NMR (101.26 MHz, acetone-*d*<sub>6</sub>):  $\delta$  = 10.38 [*J*(Pt–P) = 1011]. Anal. Found: C, 43.8; H, 4.4; N, 3.4. Calc. for C<sub>29</sub>H<sub>34</sub>IN<sub>2</sub>PSPt: C, 43.78; H, 4.31; N, 3.52%.

### 3.3. X-ray structure analysis

#### 3.3.1. Data collection

A prismatic crystal was selected and mounted on an Enraf–Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ( $12^\circ < \theta < 21^\circ$ ) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo–K $\alpha$  radiation, using the  $\omega/2\theta$  scan technique. 16 102 reflections were measured in the range  $2.01^\circ < \theta < 29.98^\circ$ , 15 571 of which were non-equivalent by symmetry. 8727 were assumed as observed applying the condition  $I > 2\sigma(I)$ . Three reflections were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz polarization and absorption corrections were made. Further details are given in Table 2.

#### 3.3.2. Structure solution and refinement

The structure was solved by direct methods, using the SHELXS-97 computer program [59], and refined by the full-matrix least-squares method, with the SHELXL-97 computer program [59] using 15 445 reflections (very negative intensities were not assumed). The function minimized was  $\sum w||F_o|^2 - |F_c|^2|^2$ , where  $w = [\sigma^2(I) + (0.0725P)^2 + 12.610P]^{-1}$ , and  $P = (|F_o|^2 + 2|F_c|^2)/3$ . *f*, *f'* and *f''* were taken from the International Tables of X-Ray Crystallography [60]. 2H were located from a difference synthesis and refined with an overall isotropic temperature factor using a riding model. Further details are given in Table 2.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 136782 for compound **5b**. 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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Table 3

Electrochemical data of free ligands and platinum complexes <sup>a</sup>

| Compound  | $E_{\text{pa}}$ Ox2 | $E_{\text{pa}}$ Ox1 | $E_{1/2}$ Red1 ( $\Delta E_{\text{pp}}$ ) | $I_{\text{pa}}/I_{\text{pc}}$ <sup>b</sup> | $E_{\text{pc}}$ Red2 | $T$ (°C) |
|-----------|---------------------|---------------------|-------------------------------------------|--------------------------------------------|----------------------|----------|
| <b>2a</b> | 1.02                | 0.47                | −3.03 irr.                                |                                            |                      | 298      |
| <b>2b</b> |                     | 1.36                | −3.00 irr.                                |                                            |                      | 298      |
| <b>2c</b> | 1.06                | 0.47                | −2.83 irr.                                |                                            |                      | 298      |
| <b>2i</b> |                     | 1.24                | −2.97 irr.                                |                                            |                      | 298      |
| <b>3c</b> |                     | 0.08                | −2.56(92)                                 | 0.19                                       |                      | 298      |
| <b>3c</b> |                     | 0.09                | −2.48(82)                                 | 0.21                                       |                      | 288      |
| <b>3c</b> |                     | 0.10                | −2.47(72)                                 | 0.46                                       |                      | 268      |
| <b>4a</b> | 1.07                | 0.40                | −2.74(92)                                 | 0.84                                       |                      | 298      |
| <b>4a</b> | 1.20                | 0.51                | −2.74(82)                                 | 1.00                                       |                      | 268      |
| <b>4b</b> | 1.42                | 0.56                | −2.76(91)                                 | 0.79                                       | −3.08 irr.           | 298      |
| <b>4b</b> | 1.45                | 0.59                | −2.71(82)                                 | 1.00                                       | −3.55 irr.           | 268      |
| <b>4i</b> |                     | 0.52                | −2.59(78)                                 | 1                                          | −3.52 irr.           | 298      |
| <b>5a</b> |                     | 0.65 <sup>c</sup>   | −2.74(82)                                 | 0.92                                       | −3.56 irr.           | 298      |
| <b>5a</b> |                     | 0.68 <sup>c</sup>   | −2.74(68)                                 | 1.00                                       | −3.35 irr.           | 288      |
| <b>5b</b> | 1.38                | 0.64                | −2.67(84)                                 | 0.99                                       | −3.29 irr.           | 298      |
| <b>5b</b> | 1.42                | 0.68                | −2.67(84)                                 | 1.00                                       | −3.29 irr.           | 288      |

<sup>a</sup> Data from cyclic voltammetric or square-wave voltammetric experiments in 0.1 M THF–Bu<sub>4</sub>NPF<sub>6</sub> solutions; anodic peak potentials  $E_{\text{pa}}$  for irreversible oxidations, cathodic peak potentials  $E_{\text{pc}}$  for irreversible reductions, half-wave potentials  $E_{1/2}$  (in V), peak potential differences  $\Delta E_{\text{pp}}$  in parentheses (in mV).

<sup>b</sup> The ratio of cathodic peak current  $I_{\text{pc}}$  for reduction waves to anodic peak current  $I_{\text{pa}}$  for reoxidation waves is used to assign observed waves as fully reversible ( $I_{\text{pa}}/I_{\text{pc}} = 1.0$ ) or partly reversible ( $I_{\text{pa}}/I_{\text{pc}} < 1$ ).

<sup>c</sup> Followed by a shoulder at +0.83 V.

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