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Reactivity of cyclometallated platinum complexes with chiral ligands

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Abstract

The reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with 3-substituted iminic thiophenes and 2-phenylpyridine gives platinum (II) [C,N] cyclometallated complexes which contain a labile ligand (SMe_2 or CH_3CN). Several platinum (II) complexes have been synthesized by substitution reactions with phosphine or sulfoxide ligands to introduce, in most cases, a second chiral center. The new complexes' reactions with methyl iodide were subsequently studied and showed results that are dependent on the steric and electronic effects of both the cyclometallated ligand and the ancillary phosphine or sulfoxide ligand. The structure of $[PtMe((R)\text{-}C_{10}H_7CHMeNCHC_4H_2S)(CH_3CN)]$, a synthetic precursor, is also reported.
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1. Introduction

Square-planar platinum (II) and specifically cyclometallated complexes are of interest for several reasons including their interesting photochemical and photophysical properties, their potential use as molecular devices, and more generally as products or intermediates in catalytic reactions [1]. In addition, oxidative addition reactions involving transition metals are fundamental steps in stoichiometric and catalytic processes [2]. We have recently focused attention on the stereoselectivity of oxidative addition of alkyl halides to chiral square-planar platinum (II) complexes. Following our results for the oxidative addition of methyl iodide to platinum (II) complexes with chiral imines derived from (*S*)-methylbenzylamine [3] and those derived from the more sterically demanding (*R*)-(1-naphthyl)ethylamine [4] we decided to undertake additional studies on analogous compounds but with other chiral ligands such as sulfoxides and phosphines. In view of the high degree of stereoselectivity for the oxidative addition reaction of methyl iodide to platinum (II) complexes containing chiral imines derived from (*R*)-(1-naphthyl)ethylamine we were interested as to how varying the fourth ligand in the coordination sphere would affect the oxidative addition results and the complexes' reactivity in general.

2. Results and discussion

Compound $[PtMe(PhCH_2NCHC_4H_2S)(SMe_2)]$ (**1a**) [5] and $[PtMe((R)\text{-}C_{10}H_7CHMeNCHC_4H_2S)(SMe_2)]$ (**2a**) [4] were prepared as previously reported.

Displacement of the dimethylsulfide ligand by dimethylsulfoxide or by racemic methyl(*para*-tolyl)sulfoxide were studied. While the reactions with dimethylsulfoxide took place at room temperature, those involving methyl(*para*-tolyl)sulfoxide required a twofold excess of methyl(*para*-tolyl)sulfoxide, and that the reaction mixture be refluxed for 4 h in acetone for the substitution reaction to take place.

In an attempt to more easily obtain the compounds with a methyl(*para*-tolyl)sulfoxide ligand, compound $[PtMe((R)\text{-}C_{10}H_7CHMeNCHC_4H_2S)(CH_3CN)]$ (**2b**) containing an acetonitrile ligand was prepared from the reaction of

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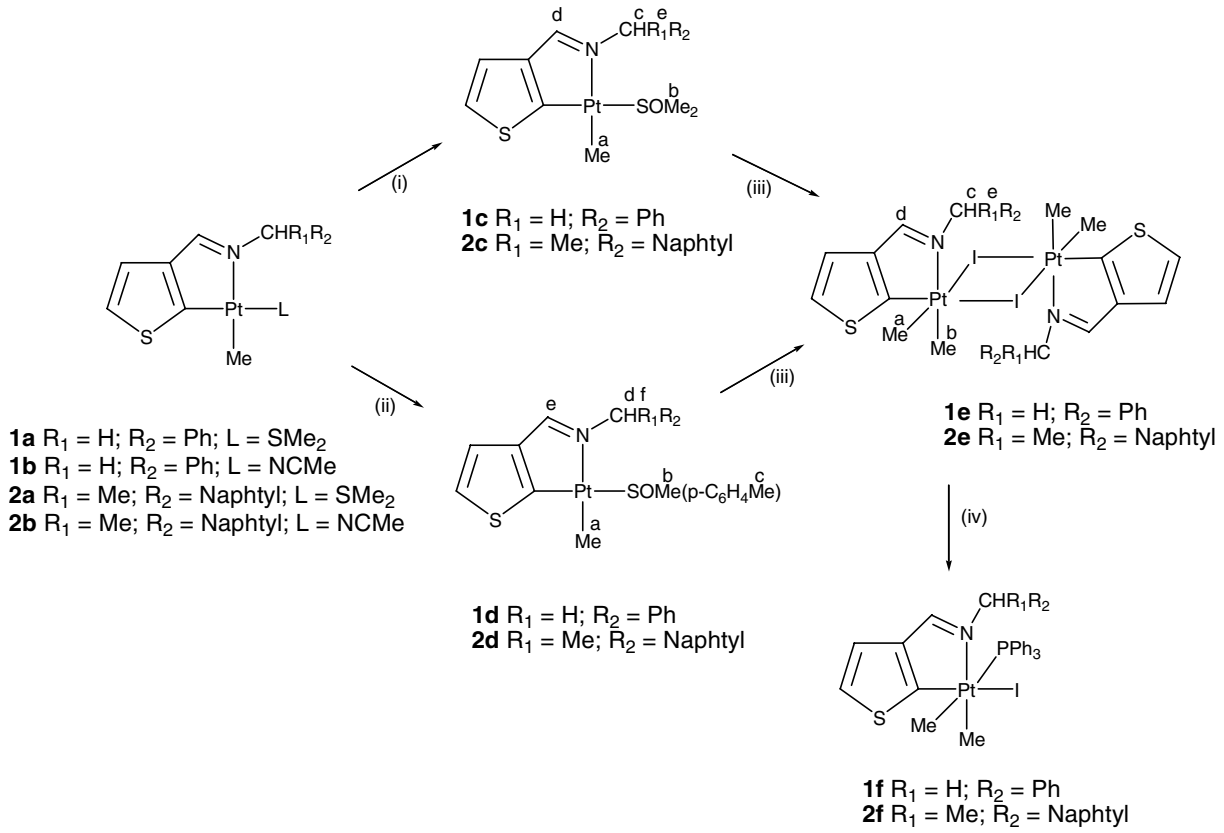
3-(*R*)-($C_{10}H_7$)CHMeNCHC$_4$H$_3$S and [$Pt_2Me_4(\mu\text{-}SMe_2)_2$], using acetonitrile as solvent, following a reported procedure for analogous compounds [6]. Acetonitrile was more easily displaced than SMe_2 and the substitution process did not require an excess of sulfoxide. The reaction of [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] with 3-PhCH$_2$NCH(C$_4H_3$S) was also carried out in acetonitrile at room temperature and gave a 1:1 mixture of [PtMe(PhCH$_2$NCHC$_4$H$_2$S)(SMe$_2$)] (**1a**) and [PtMe(PhCH$_2$NCHC$_4$H$_2$S)(CH$_3$CN)] (**1b**) but after refluxing the mixture in acetonitrile for 2 h, the substitution was complete. It is likely that the larger steric bulk of the dangling naphthyl moiety, compared to benzyl, facilitates the substitution of the dimethylsulfide for the less-sterically demanding acetonitrile ligand.

The compounds shown in Scheme 1 were characterized by NMR and elemental analyses. In the ^{1}H NMR spectra, only one set of resonances was observed for **1c**, **1d** and **2c**, while **2d** consists of two sets of signals of approximately equal intensity corresponding to two diastereomers (R_C,S_S) and (R_C,R_S). The reaction of **1a** with enantiomerically pure (*R*)-methyl(*para*-tolyl)sulfoxide ligand gave one isomer (R_C,R_S) only, which indicates that no racemization of the chiral ligand takes place upon coordination.

The presence of coordinated dimethylsulfoxide, in **1c** and **2c**, is evidenced by a resonance at 2.73 ppm coupled to platinum (^3J(H–Pt) = 20) which integrates to six hydrogens for **1c**, and by two resonances at 2.74 and 3.12 ppm coupled to platinum (^3J(H–Pt) = 19 and 22 Hz) and integrating to three hydrogens each for **2c**. The values of the coupling constants are consistent with coordinated *S*-dmso *trans* to a C atom [7]. For compound **1d**, and for the two isomers of **2d**, resonances corresponding to the sulfoxide methyl protons, which are coupled to platinum, and the *para*-tolyl substituents are observed. The ^{13}C NMR spectra of compounds **1c**, **1d** and **2c** were recorded and confirm the presence of coordinated sulfoxide.

The oxidative addition reaction of methyl iodide to compounds **1c** and **1d** was also studied in order to compare the results with those previously obtained for **1a** [5]. Additional interest arise from the fact that sulfoxide ligands may coordinate either through S or O atoms and the increase in the oxidation state of the platinum may promote the isomerization of these ligands. However, in both cases, compound [{PtMe$_2$(PhCH$_2$NCHC$_4$H$_2$S)}(μ-I)$_2$] (**1e**) is formed. The absence of coordinated *S*- or *O*-sulfoxides in both the IR and ^{1}H NMR spectra points to an iodide bridged platinum (IV) dimer, a structure which was confirmed by FAB-MS. Of the two methyl resonances the one at lower field is assigned to the equatorial methyl [8]; the ^2J(H–Pt) values (72 and 68 Hz) are smaller



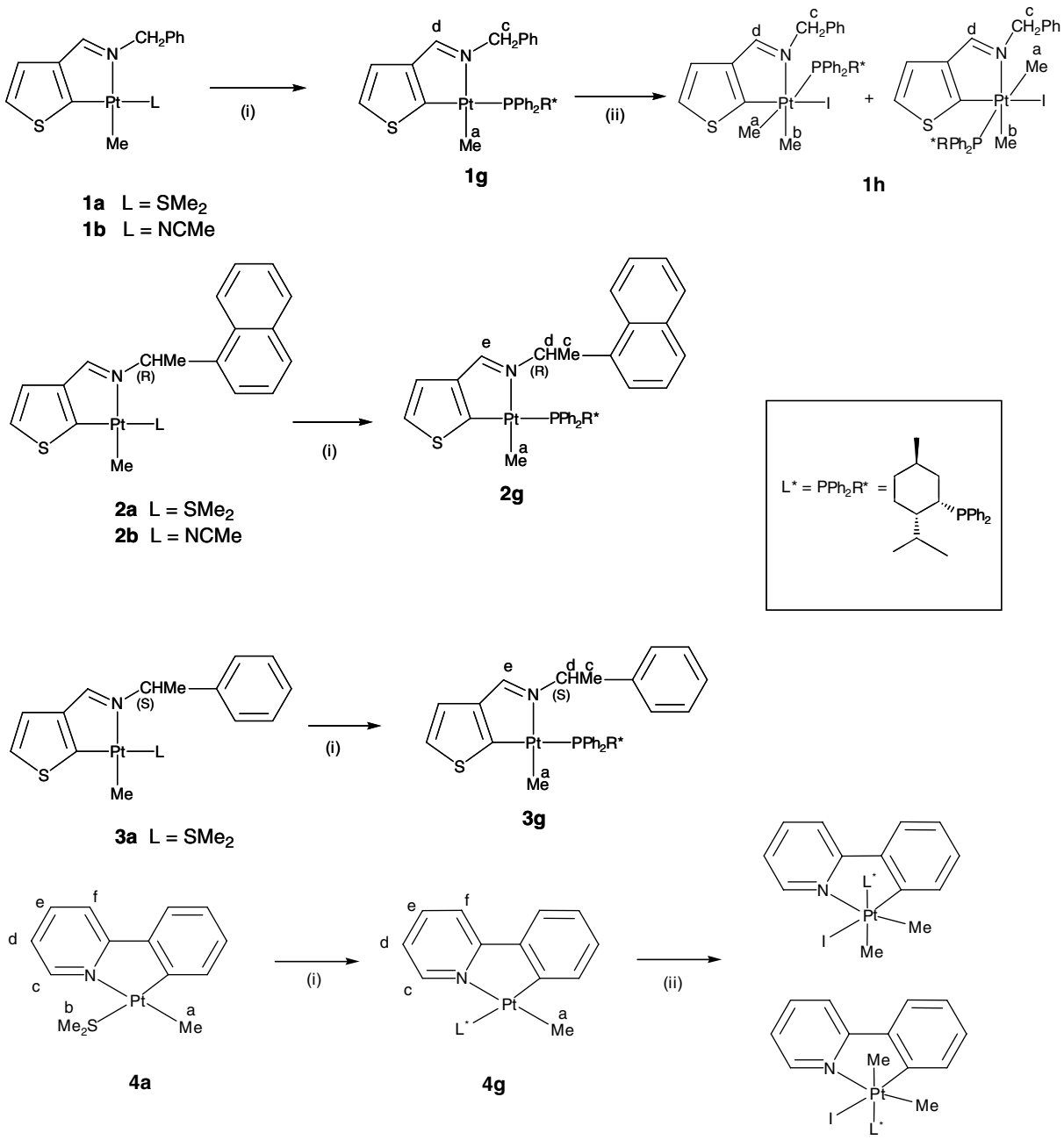
(i): + $SOMe_2$ (1:1) in CH_2Cl_2 at room temperature, 4h. (ii): + *rac*-SOMe(*p*-C_6H_4Me) (2:1 for **1a** and **2a** or 1:1 for **1b** and **2b**) in refluxing acetone, 4h. (iii): + MeI in CH_2Cl_2 at room temperature,1h. (iv): + PPh_3 (1:2) in $CDCl_3$.

Scheme 1.

than those observed for **1c** (79 Hz) and **1d** (80 Hz) which is consistent with the oxidation of the platinum center to platinum (IV) [1k,1n]. As previously reported [9] a low affinity of sulfoxide ligands for platinum (IV) may account for these results.

Analogous results were obtained upon oxidative addition of methyl iodide to compounds **2c** and **2d**, and the corresponding compound [{$PtMe_2$((*R*)-$C_{10}H_7$CHMe $NCHC_4H_2S$)}(μ-I)$_2$] (**2e**) was obtained and characterized by its ^{1}H NMR spectrum in solution. The reactions of compounds **1e** and **2e** with triphenylphosphine lead to formation of the corresponding platinum (IV) derivative **2e** [5] and **2f** [4], respectively.

In an attempt to study the effect that the fourth ligand in the coordination sphere has on the reaction with methyl iodide, complexes with the chiral ligand, (+)-neomenthyldiphenylphosphine were prepared. The chiral phosphine reacted with complex **1a** or **1b** to give [PtMe((*R*)-$C_{10}H_7$-CHMe$NCHC_4H_2S$)(PPh_2R^*)], **1g** (R^* = neomenthyl). Similar reactions were performed with complexes **2a/2b**, **3a**, and **4a** to give **2g**, **3g** and **4g**, respectively (Scheme 2). The precursor **4a** was prepared from [Pt_2Me_4(μ-SMe_2)$_2$]



(i) :+ L *= PPh_2R^* (1:1) in acetone at room temperature, 2h. (ii): + MeI in acetone at room temperature,1h

Scheme 2.

and phenylpyridine in acetone. An analogous cyclometallated compound derived from 2-phenylpyridine with dimethylsulfoxide has recently been reported [10]. The phosphine complexes were characterized in solution by NMR spectroscopy as they were always contaminated with small amounts of free phosphine ligand, however, one isomer was observed in all cases. The reactions of the phosphine complexes with methyl iodide were then studied in acetone solution. Complexes **1g** and **4g** gave similar results of oxidative addition that were monitored in solution by phosphorous NMR. The single peak for the platinum (II) species disappeared while two new peaks appeared due to the formation of two platinum (IV) diastereomers formed by the oxidative addition of the methyl iodide. The ratio of 1:1.2 for the pair of diastereomers was determined by the integration of the peaks in the phosphorous NMR. No subsequent products were observed therefore the compounds are concluded to have the stereochemistry indicated (Scheme 2), arising from *trans* oxidative addition followed by very fast isomerization of the phosphine. This places the bulky phosphine in a more favored axial position and allows *fac* stereochemistry for the three carbon donors [1k–5]. The reaction of methyl iodide with complexes **2g** and **3g** gave no platinum (IV) oxidative addition species; only decomposition products and dissociation of the phosphine were observed. This can be attributed to the combination of steric bulk of both the phosphine and the methyl/benzyl or naphthyl/ethyl moieties not allowing for the S_N2 oxidative addition to occur.

Suitable crystals of **2b** were obtained as orange crystals from acetonitrile solution. The crystal structure is shown in Fig. 1, and confirms the expected geometry. The molecules are held together in the crystal by van der Waals forces. The methyl ligand is *trans* to the nitrogen atom, the C=N group is included in the five-membered metallacycle, and the stereochemistry of the asymmetric carbon is *R*. Selected bond lengths and angles are listed in Table 1. These values are in the usual range for analogous compounds [3–5]. The angles between adjacent atoms in the coordination sphere of platinum lie in the range 78.97(8)–96.50(7)°, the smallest angle corresponding to the metallacycle and the largest to the N(2)–Pt–N(1) angle. The latter is smaller than N–Pt–P for the analogous compound [PtMe((*R*)-$C_{10}H_7CHMeNCHC_4H_2S$)(PPh_3)] (106.0(1)°) [4], which indicates a less congested molecule.

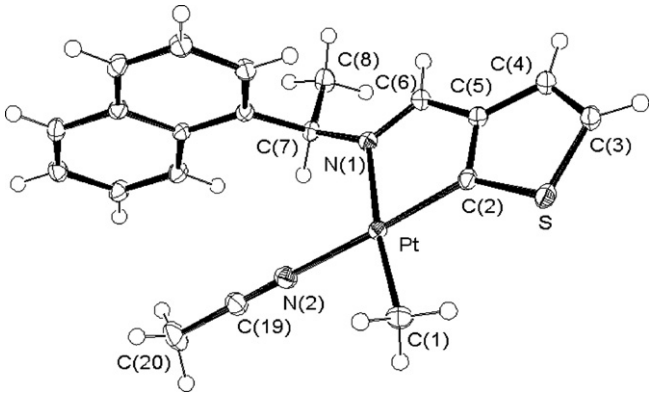


Fig. 1. Molecular structure of compound **2b**.

Table 1
Selected bond lengths (Å) and angles (°)[a] for **2b**

Pt–C(1)	2.046(2)		
Pt–C(2)	1.956(2)	C(2)–Pt–C(1)	94.48(10)
Pt–N(1)	2.1326(17)	C(1)–Pt–N(2)	90.02(9)
Pt–N(2)	2.048(2)	C(2)–Pt–N(1)	78.97(8)
N(1)–C(6)	1.296(3)	N(2)–Pt–N(1)	96.50(7)
C(5)–C(6)	1.444(3)		
C(2)–C(5)	1.394(3)		

[a] Estimated standard deviation in the least significant figure are given in parentheses.

Cyclometallated platinum (II) complexes with chiral sulfoxides and phosphines were readily prepared. The oxidative addition reactions of the complexes with methyl iodide revealed interesting results: (1) Dimethylsulfoxide readily dissociates from the harder platinum (IV) but not from the softer platinum (II). (2) As the bulk of the cyclometallated ligand increases, dissociation of chiral phosphine is enhanced as no six-coordinate platinum (IV) products are observed when the group bonded to the imine nitrogen is larger than benzyl, but products were readily seen when PPh_3 was used [4]. (3) Oxidative addition to platinum (II) usually gives trans products followed by isomerization to give apparent cis products [1n–5]. The products obtained for the large chiral phosphine above show only the final mixture of isomers and none of the initial trans products. This is contrary to results for the thiophene ligand system with PPh_3 previously reported [5]. The extra bulk [11] of the ligand most likely increases the rate of isomerization for the platinum (IV) complexes. Unfortunately, we were unable to determine the effect that two chiral centers as in **2g** and **3g** have on the oxidative addition reaction of methyl iodide.

3. Experimental

3.1. Instrumentation

^1H and ^{13}C NMR spectra were recorded at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona using Varian Gemini 200 (^1H, 200 MHz), Bruker 250 (^{13}C, 62.5 MHz) and Mercury 400 (^1H, 400 MHz; ^{13}C, 100 MHz) spectrometers, or Varian Mercury 300 MHz (^1H, 300 MHz; ^{31}P, 121.44 MHz) at the Department of Chemistry, Bard College and referenced to $SiMe_4$ (^1H, ^{13}C) and H_3PO_4 (^{31}P). δ values are given in ppm and *J* values in hertz. Microanalyses and mass spectra were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona. FAB-MS were carried out in a VG-Quattro spectrometer with a 3-nitrobenzyl alcohol matrix and ES-MS in a ZQ spectrometer using a CH_3CN/H_2O mixture as eluent.

3.2. Preparation of the compounds

Compounds $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ [12], **1a** [5], and **2a** [4] were prepared as reported. (+)-neomenthyldiphenylphosphine was purchased as technical grade 85% purity from Sigma–Aldrich.

$[PtMe(PhCH_2NCHC_4H_2S)(CH_3CN)]$ (**1b**) was obtained from the reaction of 70 mg of ligand $PhCH_2NCHC_4H_2S$ with 100 mg (1.74×10^{-4} mol) of compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in acetonitrile (10 mL). The mixture was stirred for 3 h at room temperature and an orange solid precipitated. The solid was filtered and was then refluxed in 10 mL of acetonitrile for 2 h. The resulting red solution was evaporated to *ca.* 5 mL and orange crystals were formed at room temperature after 4 h. Yield: 70 mg. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.04$ [s, ^2J(H–Pt) = 80.4, 3H, Me–Pt]; 1.89 [s, J(H–Pt) = 7.6, 3H, CH_3CN]; 5.05 [s, ^3J(H–Pt) = 10.4, 2H, CH_2]; {7.08 [d, ^4J(Pt–H) = 38, J(H–H) = 4.8, 1H]; 7.17 [d, J(H–H) = 4.8, 1H], thiophene}; 7.28–7.39 [m, Phenyl]; 8.30 [s, ^3J(H–Pt) = 54.8, 1H, CHN]. ES-MS: 436 [M−Me]. Anal. Found: C, 40.9; H, 4.1; N, 5.5; S, 7.7. Calc. for $C_{15}H_{16}N_2PtS$: C, 39.91; H, 3.57; N, 6.20; S, 7.10%.

$[PtMe\{C_{10}H_7CHMeNCHC_4H_2S\}(CH_3CN)]$ (**2b**) was obtained from the reaction of 93 mg of ligand $C_{10}H_7CHMeNCHC_4H_2S$ with 100 mg (1.74×10^{-4} mol) of compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in acetonitrile (10 mL). The mixture was stirred for 3 h at room temperature and an orange solid precipitated. The solid was filtered and dried under vacuum. Yield: 100 mg (56%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.99$ [s, ^2J(H–Pt) = 80, 3H, Me–Pt]; 1.25 [s, J(H–Pt) = 8, 3H, CH_3CN]; 1.82 [d, J(H–H) = 6.6, 3H, MeCH]; 5.91 [q, J(H–H) = 6.6, 1H, CHMe]; {7.09 [d, ^4J(Pt–H) = 38, J(H–H) = 4.8, 1H]; 7.19 [d, J(H–H) = 4.8, 1H], thiophene}; {7.44 [d, J(H–H) = 6.8, 1H]; 7.50 [t, J(H–H) = 7.6, 1H], 7.51 [t, J(H–H) = 7.2, 1H], 7.58 [t, J(H–H) = 8.0, 1H], 7.79 [d, J(H–H) = 8.4, 1H], 7.91 [d, J(H–H) = 7.8, 1H], 8.12 [d, J(H–H) = 8.8, 1H], naphthyl}; 8.44 [s, ^3J(H–Pt) = 57.2, 1H, CHN]. FAB-MS: 500 [M−CH_3], 474 [M−CH_3CN], 459 [M−CH_3−CH_3CN]. Anal. Found: C, 46.8; H, 4.1; N, 5.5; S, 6.4 Calc. for $C_{20}H_{20}N_2PtS$: C, 46.59; H, 3.91; N, 5.43; S, 6.22%.

$[PtMe(PhCH_2NCHC_4H_2S)(SOMe_2)]$ (**1c**) was obtained by treating a dichloromethane solution of compound **1a** (25 mg, 53×10^{-3} mmol) with an equimolar amount of $SOMe_2$. The mixture was stirred for 4 h at room temperature and the solvent was removed by evaporation. The residue was triturated with a small amount of water. The resulting solid was filtered and washed with hexane. Yield: 20 mg (77.4%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.85$ [s, $^2J(H^a\text{–}Pt) = 79$, 3H, Me^a]; 2.73 [s, $^3J(H^b\text{–}Pt) = 20$, 6H, Me^b]; 5.19 [s, $^3J(H^c\text{–}Pt) = 11$, 2H, H^c]; {7.21 [d, ^4J(Pt–H) = 33, J(H–H) = 5, 1H]; 7.29–7.33 [m, 6H], aromatics}; 8.41 [s, $^3J(H^d\text{–}Pt) = 60$, 1H, H^d]. ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = -19.79$ [$J(C^a\text{–}Pt) = 688$, C^a]; 43.04 [$J(C^b\text{–}Pt) = 50$, C^b]; 63.03 [C^c]; {127.15 [2C]; 128.38 [2C]; 138.29 [1C], Ph}; {125.23; 125.99 [J(C–Pt) = 49]; 148.16, thiophene}; 168.18 [$J(C^d\text{–}Pt) = 59$, C^d]. Anal. Found: C, 35.7; H, 3.8; N, 2.8. Calc. for $C_{15}H_{19}NOPtS_2$: C, 36.88; H, 3.92; N, 2.87%.

$[PtMe(C_{10}H_7CHMeNCHC_4H_2S)(SOMe_2)]$ (**2c**) was obtained from **2a** using the same procedure as for **1c**. Yield: 20 mg (77.7%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.90$ [s, $^2J(H^a\text{–}Pt) = 78$, 3H, Me^a]; 1.81 [d, J(H–H) = 6, 3H, Me^e]; 2.74 [s, $^3J(H^b\text{–}Pt) = 19$, 3H, Me^b]; 3.12 [s, $^3J(H^b\text{–}Pt) = 22$, 3H, Me^b]; 6.54 [q, J(H–H) = 6, H^c]; {7.10–7.13 [m]; 7.46–7.56 [m]; 7.81–7.86 [m]; 8.12 [d, J(H–H) = 8, 1H]}; 8.23 [s, $^3J(H^d\text{–}Pt) = 62$, 1H, H^d]. ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = -19.34$ [$J(C^a\text{–}Pt) = 694$, C^a]; 20.98 [C^e]; 43.37 [J(C–Pt) = 50, C^b]; 43.87 [J(C–Pt) = 52, C^b]; 60.09 [C^c]; {124.47; 125.19; 125.24; 125.61; 126.05; 126.76; 128.56; 128.71; 131.60; 134.24; 138.38; 149.58, aromatics}; 164.58 [$J(C^d\text{–}Pt) = 60$, C^d]. Anal. Found: C, 43.8; H, 4.0; N, 2.4. Calc. for $C_{20}H_{23}NOPtS_2$: C, 43.47; H, 4.20; N, 2.53%.

$[PtMe(PhCH_2NCHC_4H_2S)\{SOMe(p\text{-}C_6H_4Me)\}]$(**1d**) was obtained by adding *rac*-SOMe(p-C_6H_4Me) (16.3 mg, 0.105 mmol) to an acetone solution of compound **1a** (25 mg, 53×10^{-3} mmol). The mixture was refluxed for 4 h and the solvent was removed by evaporation. The residue was recrystallized from CH_2Cl_2/MeOH and the resulting solid was filtered. Yield: 20 mg (66.8%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.03$ [s, $^2J(H^a\text{–}Pt) = 80$, 3H, Me^a]; 2.38 [s, 3H, Me^c]; 3.10 [s, ^3J(H–Pt) = 19, 3H, Me^b]; {4.96 [J(H–H) = 15, ^3J(H–Pt) = 15]; 5.22 [J(H–H) = 15], 2H, *AB* quartet, H^d]; {7.64 [d, J(H–H) = 8, 2H]; 7.06–7.27 [m, 9H], aromatics}; 8.28 [s, $^3J(H^e\text{–}Pt) = 60$, 1H, H^e]. ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = -19.42$ [s, $J(C^a\text{–}Pt) = 689$, C^a]; 21.31 [s, C^c]; 44.11 [s, $J(C^b\text{–}Pt) = 58$, C^b]; 62.80 [s, C^d]; {126.00 [2C]; 128.41 [2C]; 128.58 [2C]; 129.99 [2C]; 123.99; 125.68; 126.29; 127.20; 130.46; 137.94; 142.90; 148.82], aromatics}; 167.86 [s, C^e]. Anal. Found: C, 43.7; H, 4.0; N, 2.6. Calc. for $C_{21}H_{23}NOPtS_2$: C, 44.67; H, 4.11; N, 2.48%.

$[PtMe(C_{10}H_7CHMeNCHC_4H_2S)\{SOMe(p\text{-}C_6H_4Me)\}]$ (**2d**) was obtained as a mixture of diastereomers following the same procedure as for **1d**, starting from **2a** (ratio *rac*-SOMe(p-C_6H_4Me): Pt = 2:1) or from **2b** (ratio *rac*-SOMe(p-C_6H_4Me): Pt = 1:1) or as a single isomer when (R)-SOMe(p-C_6H_4Me) was used. ^{1}H NMR (400 MHz, $CDCl_3$): isomer (Rc,Ss): $\delta = 1.18$ [s, ^2J(H–Pt) = 77.6, 3H, Me^a]; 1.36 [d, J(H–H) = 6.4, 3H, Me^f]; 2.47 [s, 3H, Me^c]; 3.30 [s, ^3J(H–Pt) = 18.8, 3H, Me^b]; 6.49 [q, J(H–H) = 6.4, H^d]; 7.86 [s, J(H–Pt) = 61.6, 1H, H^e]. Isomer (Rc,Rs): $\delta = 1.13$ [s, ^2J(H–Pt) = 79.2, 3H, Me^a]; 1.77 [d, J(H–H)= 6.8, 3H, Me^f]; 2.33 [s, 3H, Me^c]; 3.11 [s, ^3J(H–Pt) = 18.8, 3H, Me^b]; 6.30 [q, J(H–H) = 6.8, H^d]; 8.29 [s, 1H, J(H–Pt) = 61.6, H^e]. Aromatic region: 6.93 [d, J(H–H) = 5.0, 1H]; 6.97 [d, 2H, J(H–H) = 8.4]; 7.07 [d, 1H, J(H–H) = 4.8]; 7.16 [td, 2H, J(H–H) = 8.0; 1.5]; 7.24–7.29 [m, 3H]; 7.34 [td, 1H, J(H–H) = 7.0; 1.0]; 7.39 [d, 2H, J(H–H) = 8.4], 7.45–7.59 [m, 6H]; 7.65 [t, 2H, J(H–H) = 8.0]; 7.83 [d, 2H, J(H–H) = 8.0]; 8.07 [d, 2H,

J(H–H) = 8.4], 8.30 [d, 2H, J(H–H) = 8.4]. FAB-MS: 628 [M], 613 [M−CH_3], 474 [M−SOMe(p-C_6H_4Me)], 459 [M−CH_3−SOMe(p-C_6H_4Me)]. Anal. Found: C, 49.5; H, 4.3; N, 2.2; S, 9.9. Calc. for $C_{26}H_{27}NOPtS_2$: C, 49.67; H, 4.33; N, 2.23; S, 10.20%.

[{$PtMe_2(PhCH_2NCHC_4H_2S)$}(μ-I)$_2$] (**1e**) was obtained as a white solid upon treating 20 mg (41×10^{-3} mmol) of **1c** in dichloromethane with an excess of methyl iodide (0.2 mL). The mixture was stirred for 1 h at room temperature and the solvent was removed by evaporation. The residue was washed with a small amount of ether and dried *in vacuo*. Yield: 18 mg (79.6%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.12$ [s, $^2J(H^a–Pt) = 72$, 3H, Me^a]; 2.54 [s, $^2J(H^b–Pt) = 68$, 3H, Me^b]; 5.66 [m, 2H, H^c]; {7.10 [d, J(H–H) = 6, 2H]; 7.35–7.45 [m, 5H], aromatics}; 7.94 [s, $^3J(H^d–Pt) = 44$, 1H, H^d]. FAB(+)-MS, m/z: 1104 [M], 1056 [M−3Me], 1041 [M−4Me], 395 [Pt($PhCH_2NCHC_4H_2S$)]. Anal. Found: C, 31.1; H, 2.8; N, 2.3; S, 6.7. Calc. for $C_{28}H_{32}I_2N_2Pt_2S_2$: C, 30.44; H, 2.92; N, 2.53; S, 5.80%.

[{$PtMe_2(C_{10}H_7CHMeNCHC_4H_2S)$}(μ-I)$_2$] (**2e**) was characterized in solution upon treating 20 mg of **2c** in dichloromethane with an excess of methyl iodide. The mixture was stirred for 1 h at room temperature and the solvent was removed by evaporation. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.89$ [s, $^2J(H^a–Pt) = 73.6$, 3H, Me^a]; 1.94 [d, J(H–H) = 6.4, 3H, H^e]; 2.84 [s, $^2J(H^b–Pt) = 68.8$, 3H, Me^b]; 6.67 [q, J(H–H) = 6.4, 1H, H^c]; 8.61 [s, ^3J(H–Pt) = 44.8, 1H, H^d].

[$PtMe(C_6H_4NC_5H_4)(SMe_2)$] (**4a**) was prepared similarly to a precursor previously reported [10]. One equivalent of phenylpyridine dissolved in 5 ml of acetone was added to 100 mg of [Pt_2Me_4(μ-SMe_2)$_2$] dissolved in 20 mL of acetone. The solution was stirred for 16 h and the solvent removed by evaporation. The remaining oil was triturated with ether to give a solid that was washed with ether and pentane and dried *in vacuo*. Yield 65%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.07$ [s, $^2J(H^a–Pt) = 83$, 3H, Me^a]; 2.45 [s, $^3J(H^b–Pt) = 25$, 3H, Me^b]; {7.08–7.28 [m]; 7.60–7.64 [m]; 7.76–7.86 [m]; 8.90 [d, ^3J(H–H) = 6, $^3J(H^c–Pt) = 62$, 1H, H^c], aromatic protons}.

[$PtMe(C_6H_4NC_5H_4)(PC_{22}H_{26})$] (**4g**) was obtained from **4a** by reacting a 1:1 ratio of (+)-neomenthyldiphenylphosphine to platinum complex in acetone solution for 1 h. The solvent was removed by evaporation and the resulting crude product was washed with hexane but free ligand could not be entirely removed. Recrystallization in acetone/hexane, hexane, and methylene chloride failed. ^{31}P NMR (121.44 MHz, d^6-acetone): $\delta = 27.55$ [s, ^1J(P–Pt) = 2504].

[$PtMe(C_6H_5CH_2NCHC_4H_2S)(PC_{22}H_{26})$] (**1g**) was prepared similarly to **4g**. ^{31}PNMR (d^6-acetone) $\delta = 26.64$ [s, ^1J(Pt–P) = 2500].

[$PtMe(C_{10}H_7CHMeNCHC_4H_2S)(PC_{22}H_{26})$] (**2g**) was prepared similarly to **4g**. ^{31}PNMR ($CDCl_3$) $\delta = 29.91$ [s, ^1J(Pt–P) = 2503].

[$PtMe(C_6H_5CHMeNCHC_4H_2S)(PC_{22}H_{26})$] (**3g**) was prepared similarly to **4g**. ^{31}P NMR (121.44 MHz, d^6-acetone): $\delta = 27.55$ [s, ^1J(P–Pt) = 2504].

[$PtMe_2I(C_6H_5CH_2NCHC_4H_2S)(PC_{22}H_{26})$] (**1h**) was characterized by phosphorous NMR in d^6-acetone solution when following the oxidative addition reaction of **1g** with MeI. ^{31}P NMR (121.44 MHz, d^6-acetone): $\delta = -13.45$ [s, ^1J(P–Pt) = 942]; minor isomer: $\delta = -12.38$ [s, ^1J(P–Pt) = 958].

[$PtMe_2I(C_6H_4NC_5H_4)(PC_{22}H_{26})$] (**4h**) was characterized similarly to **1h**. ^{31}P NMR (121.44 MHz, d^6-acetone): major isomer: $\delta = -12.35$ [s, ^1J(P–Pt) = 938]; minor isomer: $\delta = -10.55$ [s, ^1J(P–Pt) = 947].

3.3. X-ray structure determination

X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα ($\lambda = 0.71073$ Å)) at 115 K. A suitable crystal was mounted in a nylon loop with Paratone-N cryoprotectant oil. During data examination and space group determination with XPREP, the $\sigma(I)$ values were normalized and multiplied by a factor of 0.5. The structure was solved using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.14) [13]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated posi-

Table 2
Crystal data, data collection, and refinement parameters for **2b**

Formula	$C_{20}H_{20}N_2PtS$
Habit, color	Parallelepiped, yellow
Size, mm	$0.23 \times 0.10 \times 0.05$
Lattice type	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	8.1945(1)
b (Å)	12.1261(2)
c (Å)	17.9478(2)
V (Å^3)	1783.42(4)
Z	4
Fwt. (g mol^{-1})	515.53
D_c (g cm^{-3})	1.920
μ (mm^{-1})	7.988
F(000)	992
θ Range (°)	2.03–36.32
Index ranges	$-13 \leqslant h \leqslant 13$, $-20 \leqslant k \leqslant 20$, $-28 \leqslant l \leqslant 29$
Reflections collected	38,820
Unique reflections	8628 ($R_{int} = 0.0393$)
Completeness to $\Phi = 36.32°$	99.9%
Abs correction	Empirical
Max., min. transmission	0.6908, 0.2609
Data, restraints, parameters	8628/0/221
R_1, wR_2 ($I > 2\sigma(I)$)	0.0179, 0.0385
R_1, wR_2 (all data)	0.0193, 0.0392
Goodness-of-fit (on F^2)	1.075
Largest difference in peak, hole (e Å^{-3})	1.036, −0.959
Abs structure parameter	0.004(4)

tions and were refined using a riding model. Crystal data and refinement details are presented in Table 2.

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Appendix A. Supplementary material

CCDC 614928 contains the supplementary crystallographic data for **2b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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