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Oxidative addition of alkyl halides to chiral cyclometallated platinum(II) complexes with thienyl imines. X-ray crystal structure of [PtMe{3-((*S*)-PhCHMeNCH)C_4H_2S}SMe_2]

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Abstract

The reaction of [Pt_2Me_4(μ-SMe_2)$_2$] with ligand 3-((*S*)-PhCHMeNCH)C_4H_3S (**1**) produced the chiral cyclometallated compound [PtMe{3-((*S*)-PhCHMeNCH)C_4H_2S}SMe_2] (**2**) which was characterized structurally. The reactions of **2** with phosphines gave compounds [PtMe{3-((*S*)-PhCHMeNCH)C_4H_2S}L] (L = PPh_3 (**3**), P(2-MeC_6H_4)$_3$ (**4**), $Ph_2PCH_2CH_2PPh_2$ (**5**)). The oxidative addition of methyl iodide to compounds **2** and **3** gave two diastereoisomers each of compounds [$PtMe_2$I{3-((*S*)-PhCHMeNCH)C_4H_2S}L] (L = SMe_2 (**6a**/**6a′**), PPh_3 (**7a**/**7a′**)) in a ratio 2.1:1 and 2.4:1, respectively. Subsequent isomerization gave, in each case, a new pair of diastereoisomers. Compounds **4** and **5** failed to react with methyl iodide, while platinum(II) compounds [PtX{3-((*S*)-PhCHMeNCH)C_4H_2S}PPh_3] (X = I (**8**), Br (**9**)) were obtained in the reactions of **3** with ethyl iodide or benzylbromide.

Keywords: Platinum; Thienylimines; Cyclometallation; Chirality; Crystal structure; Oxidative addition

1. Introduction

Oxidative addition reactions of organoplatinum complexes with nitrogen-donor ligands have been reviewed recently [1]. The reactions with organohalides usually give the products of *trans* oxidative addition. Sometimes, the *cis* isomer is formed by a competitive *cis* oxidative addition pathway, or it may be formed by *trans* oxidative addition with subsequent isomerization of the platinum(IV) product to the more stable *cis* isomer. In particular, cyclometallated platinum(II) compounds are good candidates in oxidative addition reactions of alkylhalides due to the presence of Pt–N and Pt–C σ bonds which increase the electron density at the metal center [2,3]. Square planar platinum(II) complexes are inherently achiral but due to increasing interest in chiral inorganic compounds related to enantiomeric catalysis, bioinorganic chemistry and supramolecular chemistry, the introduction of chirality in such compounds has been analyzed. This can be achieved when chiral ligands are involved, or when steric hindrance produced an helical distortion, as shown for *cis*-bis-cyclometallated compounds [4,5]. Studies of oxidative addition reactions to both types of chiral cyclometallated platinum(II) compounds have been reported recently [6–8].

We have studied previously the oxidative addition reactions of methyl iodide to compounds [PtMe{3-($PhCH_2$NCH)C_4H_2S}L] (L = SMe_2 or PPh_3), and the observed differences in the stereochemistry of the final products were explained by the different bulk of the ligand L [9]. In this paper we report the results obtained for the analogous chiral complexes [PtMe{3-((*S*)-PhCHMeNCH)C_4H_2S}L].

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2. Results and discussion

2.1. Syntheses and crystal structure of compound 2

Ligand 3-((*S*)-PhCHMeNCH)C_4H_3S (**1**) was prepared from the condensation reaction of 3-thiophenecarboxaldehyde and (*S*)-methylbenzylamine in ethanol. The reaction of this ligand with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ produced cyclometallated compound [PtMe{3-((*S*)-PhCHMeNCH)C_4H_2S}SMe_2] (**2**) as a single isomer 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 analogous systems [10,11].

Compound **2** was characterized by elemental analyses and ^{1}H-NMR spectroscopy. Three distinct resonances appeared in the methyl region corresponding to the methyl group bound to platinum (^2J(Pt–H) = 79 Hz), to the dimethylsulfide ligand (^2J(Pt–H) = 32 Hz), and to the methyl substituent of the benzyl group. The value of the coupling of the imine hydrogen to platinum (^2J(Pt–H) = 51 Hz) indicates the formation of a metallacycle [10,11], while the observed J(H–H) value for the mutual coupling of the thienyl hydrogens implies that the activation of the C–H bond took place at the α-position [12].

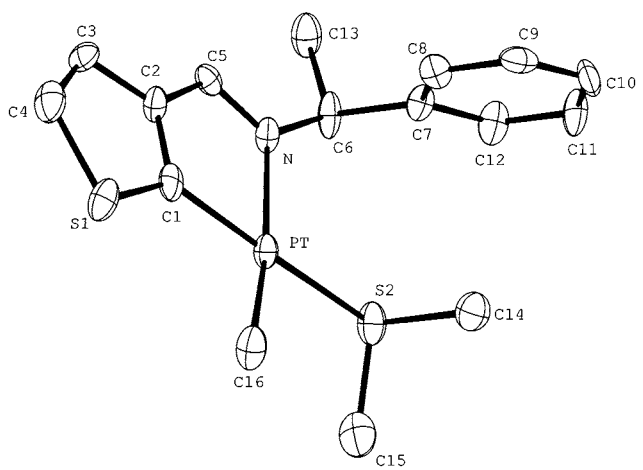


Fig. 1. Molecular structure of compound [PtMe{3-((*S*)-PhCHMeNCH)C_4H_2S}SMe_2] (**2**).

Table 1
Selected bond lengths (Å) and angles (°) in compound (**2**)

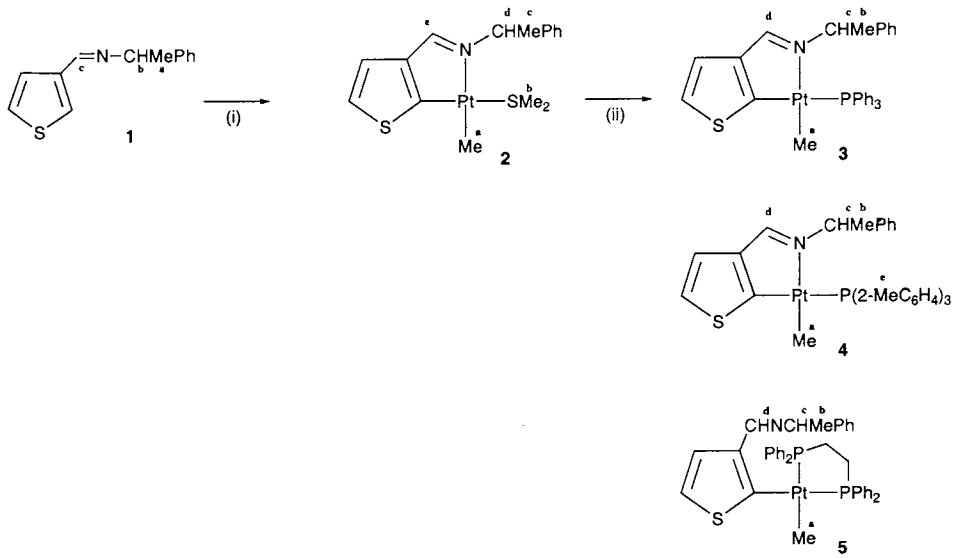
Bond lengths			
Pt–C	1.975(9)	Pt–C(16)	1.997(9)
Pt–N	2.143(7)	Pt–S(2)	2.336(3)
S(2)–C(15)	1.739(11)	S(2)–C(14)	1.801(10)
N–C	1.295(11)	N–C(6)	1.462(10)
C(1)–C(2)	1.322(13)	C(2)–C(5)	1.418(11)
C(6)–C(7)	1.519(12)	C(6)–C(13)	1.519(12)
Bond angles			
C(1)–Pt–C(16)	92.9(4)	C(1)–Pt–N	77.4(4)
C(16)–Pt–N	170.1(3)	C(1)–Pt–S(2)	171.3(3)
C(16)–Pt–S(2)	94.4(3)	N–Pt–S(2)	95.4(2)
C(15)–S(2)–C(14)	99.8(5)	C(15)–S(2)–Pt	109.9(4)
C(14)–S(2)–Pt	106.9(3)	C(5)–N–C(6)	121.9(8)
C(5)–N–Pt	112.2(6)	C(6)–N–Pt	125.8(6)
C(2)–C(1)–Pt	117.7(7)	C(1)–C(2)–C(5)	115.6(9)
N–C(5)C–(2)	117.0(8)	N–C(6)–C(7)	111.1(7)
N–C(6)–C(13)	114.1(7)	C(7)–C(6)–C(13)	108.9(8)

Suitable crystals of compound [PtMe{3-((*S*)-PhCHMeNCH)C_4H_2S}SMe_2] (**2**) were grown in acetone solution. The crystal structure is composed of discrete molecules separated by van der Waals interactions. The structure is shown in Fig. 1, and confirms the geometry expected. In particular, the methyl group is *trans* to the nitrogen atom, the C=N group is *endo* to the cycle and the stereochemistry of the asymmetric carbon is *S*. The imine adopts an (*E*)-configuration, the torsion angle C(6)–N–C(5)–C(2) being −176.4°. 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: Pt, 0.023; S(2), −0.055; N, 0.056; C(1), −0.075; C(16), 0.051. The metallacycle is approximately planar — the largest deviation from the mean plane determined by the five atoms is 0.018 Å for C(2) — and nearly coplanar with the coordination plane, the dihedral angle being 3.20°. Molecular dimensions are listed in Table 1. The angles between adjacent atoms in the coordination sphere of platinum lie in the range 77.4–95.4°, the smallest angle corresponding to the metallacycle. Bond lengths in the coordination sphere of the platinum and in the thiophene ring are in the usual range for analogous compounds [7,13–15]. The metallacycle is smaller than for compound [PtMe{3-($PhCH_2$NCH)C_4H_2S}PPh_3] [9] (perimeter 8.153 vs. 8.309 Å) which is consistent with the smaller size of SMe_2 versus PPh_3 ligand. Moreover, in the latter structure as well as in compound [PtMe{(*S*)-PhCHMeNCHC_6H_3F-2}PPh_3], the benzyl group lies away from the coordination plane in order to minimize the steric crowding in the coordination sphere of the platinum, whereas for **2**, the benzyl group lies towards the small SMe_2 ligand.

2.2. Reactions with phosphines

As shown in Scheme 1, the reaction of **2** with monodentate phosphines produced compounds [PtMe{3-((*S*)-PhCHMeNCH)C_4H_2S}L] (L = PPh_3 (**3**), P(2-MeC_6H_4)$_3$ (**4**)) which were characterized by elemental analysis and ^{1}H- and ^{31}P-NMR spectroscopies. The phosphine replaced the SMe_2 ligand, and even with an excess of phosphine, the metallacycle is not cleaved.

A single isomer is detected for compound **3** while compound **4** consists of two isomers (ratio 3:1), due to the hindered rotation of the *ortho*-tolyl groups. In all cases, the methylplatinum resonance appears as a dou-



Scheme 1. (i) Reaction with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in acetone; (ii) reaction with the corresponding phosphine in acetone.

blet due to coupling with the phosphorus atom and is also coupled to platinum. The imine hydrogen is coupled to platinum but not to phosphorus, which indicates a *cis* arrangement of the imine and the phosphine. For each isomer of compound **4**, three distinct resonances appear for the methyl groups of the *ortho*-tolylphosphine.

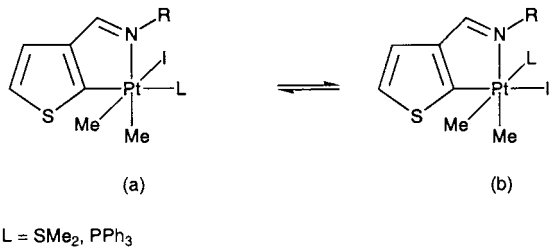
Due to the chelating nature of the diphosphine, a different result was obtained when the reaction of **2** with 1,2-bis(diphenylphosphino)ethane (dppe) was carried out under the same experimental conditions. In this case, both the SMe_2 ligand and the nitrogen of the imine ligand are displaced from the coordination sphere of the platinum. Consequently, the metallacycle is cleaved and the imine acts as a $[C^-]$ monodentate ligand. Compound $[PtMe\{3\text{-}((S)PhCHMeNCH)\text{-}C_4H_2S\}(Ph_2PCH_2CH_2PPh_2)]$ (**5**) was characterized by elemental analysis and ^1H- and ^{31}P-NMR. Spectral data are consistent with those for analogous compounds with chelating dppe [16]. The methylplatinum resonance is coupled with both phosphorus atoms and shows platinum satellites. The coupling of the imine hydrogen to platinum is considerably reduced ($J(Pt–H) = 8$ Hz). In the ^{31}P-NMR spectrum, two resonances due to the non-equivalent phosphorus atoms appear and $J(P–Pt)$ values (1660 and 2233 Hz) are consistent with the presence of carbon atoms *trans* to the phosphorus. The bigger value is assigned to the phosphorus *trans* to thiophene, due to the low *trans* influence of this group [9].

2.3. Oxidative addition reactions

It is generally accepted that the oxidative addition of alkyl halides to platinum(II) compounds give *trans* stereochemistry, although products arising from *cis* oxidative addition can be formed in a subsequent isomerization process [3,8]. There is an increasing interest for the potential stereoselectivity of oxidative addition of alkyl halides to chiral cyclometallated platinum(II) compounds. Compounds containing the cyclometallated chiral imine 3-((*S*)-PhCHMeNCH)C_4H_2S are adequate substrates for such a study since the platinum center is expected to have a high electronic density. Moreover, the results obtained when either a SMe_2 or a phosphine ligand complete the coordination sphere of the platinum could be compared.

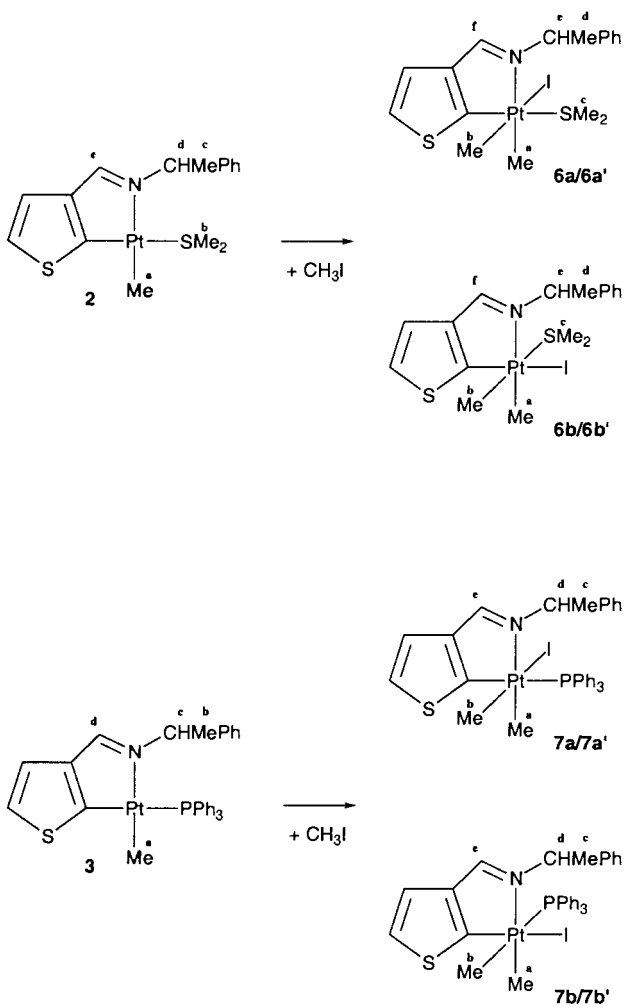
Assuming a *trans* addition, two diastereoisomers (C, S) and (A, S), in which C/A represents the absolute stereochemistry (clockwise and anticlockwise) at the platinum and *S* describes the chirality at carbon are possible. We have reported previously that the oxidative addition of methyl iodide to $[PtMe_2\{(S)\text{-}PhCHMeNCHC_5H_4N\}]$, containing a $[N, N']$ chelate ligand [17], and to the cyclometallated compound $[PtMe\{(S)\text{-}PhCHMeNCHC_6H_3F\text{-}2\}PPh_3]$ gave [7], in each case, two diastereoisomers in nearly equal amounts (1:1 and 1.25:1, respectively).

It has been reported previously for compounds $[PtMe\{3\text{-}(PhCH_2NCH)C_4H_2S\}L]$ ($L = SMe_2$, PPh_3), that the oxidative addition takes place with *trans* stereochemistry, and is followed by isomerization of the resulting platinum(IV) compound. The isomerization, shown in reaction (1), should proceed through a dissociative pathway to yield a five-coordinate intermediate, which rearranges in order to minimize steric effects in the final platinum(IV) compound. For the bulky PPh_3 ligand, isomerization is completed within a few hours, while for SMe_2, an equilibrium mixture of both isomers is attained. Such an isomerization should lead in this case to a new pair of diastereoisomers.



L = SMe_2, PPh_3

As shown in Scheme 2, the reaction of [PtMe{3-((*S*)-PhCHMeNCH)C_4H_2S}SMe_2] (**2**) with methyl iodide in acetone at room temperature gave a mixture of two pairs of diastereoisomers (**6a**/**6a**′ and **6b**/**6b**′) of the cyclometallated platinum(IV) compound [$PtMe_2I$\{3-((*S*)-PhCHMeNCH)C_4H_2S}SMe_2] (**6**). From the ^2J(H–Pt) values for the methyl groups, a *fac*-PtC_3 structure is assigned to all isomers. Isomers **6a**/**6a**′ differ from isomers **6b**/**6b**′ in having a methyl group *trans* to I or *trans* to SMe_2, respectively. In agreement with previous studies, the resonances at lower δ were assigned to axial methyl groups *trans* to iodide (isomers **6a**/**6a**′). When a ^{1}H-NMR was registered just after adding methyl iodide to a solution of **2** in deuterated acetone, the isomers **6a**/**6a**′ and **6b**/**6b**′ were detected in the same relative amounts as in the preparative synthesis and their ratio remained constant in solution. The mixture of isomers is composed as follows: **6a** (19.4%), **6a**′ (9.3%), **6b** (38.9%), and **6b**′ (32.4%). Thus, the main products are the pair of diastereoisomers **6b**/**6b**′ arising from isomerization of the initially formed **6a**/**6a**′. The ratio **6a**:**6a**′ = 2.1:1 indicates a significant degree of enantioselectivity in the initial *trans* oxidative addition, although subsequent isomerization yields nearly equal amounts of both diastereoisomers (**6b**:**6b**′ = 1.2:1).



Scheme 2.

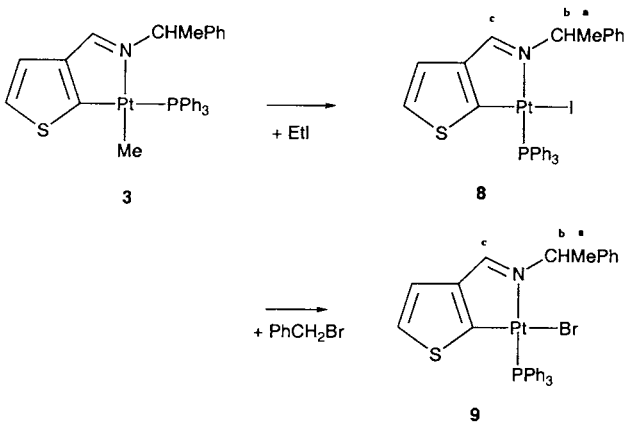
When a ^{1}H-NMR was registered just after adding methyl iodide to a solution of **2** in deuterated acetone, the isomers **6a**/**6a**′ and **6b**/**6b**′ were detected in the same relative amounts as in the preparative synthesis and their ratio remained constant in solution. The mixture of isomers is composed as follows: **6a** (19.4%), **6a**′ (9.3%), **6b** (38.9%), and **6b**′ (32.4%). Thus, the main products are the pair of diastereoisomers **6b**/**6b**′ arising from isomerization of the initially formed **6a**/**6a**′. The ratio **6a**:**6a**′ = 2.1:1 indicates a significant degree of enantioselectivity in the initial *trans* oxidative addition, although subsequent isomerization yields nearly equal amounts of both diastereoisomers (**6b**:**6b**′ = 1.2:1).

When the mixture of isomers **6b**/**6b**′ was treated with PPh_3 in acetone, the substitution reaction of SMe_2 for PPh_3 yielded isomers **7b**/**7b**′ in which the triphenylphosphine is *trans* to a methyl group, in the ratio 1.2:1, as confirmed by ^{31}P-NMR spectroscopy.

The reaction of racemic [PtMe{3-(PhCHMeNCH)C_4H_2S}SMe_2] (**2**′) with methyl iodide was also monitored by ^{1}H-NMR. Again, four sets of resonances in the same ratio as for chiral compound **2** are observed and assigned to the two pairs of diastereoisomers, each with its enantiomer.

The reaction of [PtMe{3-((*S*)-PhCHMeNCH)C_4H_2S}PPh_3] (**3**) with methyl iodide in acetone at room temperature was monitored by ^{1}H- and ^{31}P-NMR. In the early stages of the reaction, resonances assigned to a pair of diastereoisomers (**7a**/**7a**′) of the platinum(IV) compound [$PtMe_2I$\{3-((*S*)-PhCHMeNCH)C_4H_2S}-PPh_3] appeared in a ratio 2.4:1 in the ^{31}P-NMR, together with signals due to unreacted platinum(II) compound **3**. In the corresponding ^{1}H-NMR, only the resonances due to the major of these isomers could be assigned unambiguously. As the reaction proceeded, resonances due to a second set of platinum(IV) diastereoisomers (**7b**/**7b**′) appeared and fully replaced the former resonances within 4 h. The isomer **7a** (or **7a**′) displays two methylplatinum resonances which appear as doublets due to coupling to the phosphorus atom and with similar ^2J(HPt) values (67 and 68 Hz, respectively). As for analogous cyclometallated compounds reported previously, the resonance at higher fields is assigned to the axial methyl. A similar pattern is observed for isomers **7b**/**7b**′, except for the fact that a reduced coupling to platinum (^2J(HPt) = 60 Hz) is now observed for the axial methyl, which suggests a *trans* arrangement of the axial methyl and the PPh_3. ^{31}P-NMR supported the successive formation of two different isomers, since the initial resonances assigned to **7a**/**7a**′ decreased its intensity, while two new resonances due to the pair of diastereoisomers **7b**/**7b**′ grew. The intensities of the signals in both ^{1}H- and ^{31}P-NMR indicate that the ratio **7b**:**7b**′ is 2.2:1.

The reaction of racemic [PtMe{3-(PhCHMeNCH)C_4H_2S}PPh_3] (**3**′) with methyl iodide was also



Scheme 3.

monitored by ^{1}H- and ^{31}P-NMR and the results were identical to those observed for the chiral compound **3**.

Compounds [PtMe{3-((*S*)-PhCH$_2$NCH)C$_4$H$_2$S}P(2-MeC$_6$H$_4$)$_3$] (**4**) and [PtMe{3-((*S*)-PhCH$_2$NCH)C$_4$H$_2$S}-(Ph$_2$PCH$_2$CH$_2$PPh$_2$)] (**5**) failed to react with methyl iodide under the same experimental conditions used for the reactions of compounds **2** and **3**. The lack of reactivity of compound **4** can be related to the results reported for analogous iridium compounds [18], for which the crystal structure revealed that one of the *ortho* methyl groups in the phosphine is located above the coordination plane and isolates the central atom from attacking molecules. As for **5**, the decrease in electronic density at the platinum when the imine nitrogen is replaced by a phosphorus atom may account for the result obtained.

As shown in Scheme 3, the reactions of ethyl iodide and benzyl bromide with compound [PtMe{3-((*S*)-PhCHMeNCH)C$_4$H$_2$S}PPh$_3$] (**3**) produced platinum(II) compounds [PtI{3-((*S*)-PhCHMeNCH)C$_4$H$_2$S}PPh$_3$] (**8**) and [PtBr{3-((*S*)-PhCHMeNCH)C$_4$H$_2$S}PPh$_3$] (**9**), respectively. The formation of a small amount of metallic platinum indicates some degree of decomposition in this process. Although it is most likely that compounds **8** and **9** arise from oxidative addition of the alkyl halide followed by reductive elimination, the corresponding platinum(IV) compounds could not be detected when the reaction was monitored by ^{31}P-NMR.

In the ^{1}H-NMR of compounds **8** and **9**, the coupling of the imine nitrogen to phosphorus, within the same range as reported for analogous palladium compounds [19,20], indicates a *trans* arrangement of N and P atoms, which is also supported by the J(P–Pt) values.

In conclusion, a higher degree of stereoselectivity is obtained for the oxidative addition of methyl iodide to thienyl derivatives [PtMe{3-((*S*)-PhCHMeNCH)-C$_4$H$_2$S}L] (L = SMe$_2$, **6a**:**6a**′ = 2.1:1; PPh$_3$, **7a**:**7a**′ = 2.4:1) than for the phenyl analogues reported previously [7]. The bulk of ligand L does not significantly affect the ratio of the diastereoisomers formed initially but it is a decisive factor in the ratio of the diastereoisomers arising from the subsequent isomerization process. While for the bulky PPh$_3$ derivatives, the proportion of the diastereoisomers is practically maintained (**7b**:**7b**′ = 2.2:1), for SMe$_2$ an equilibration of the diastereoisomers occurs (**6b**:**6b**′ = 1.2:1).

The diastereomeric ratios obtained for **6a**/**6a**′ and **7a**/**7a**′ are similar to those reported for the oxidative addition of methyl iodide to compound [PtMe{*trans*-1-(N=CHC$_6$H$_4$)-2-(N=CHC$_6$H$_5$)C$_6$H$_{10}$}] containing a [C, N, N′] tridentate ligand [8], in spite of the fact that the compounds reported here have the chiral center in a dangling benzyl group two atoms away from the platinum center.

3. Experimental

3.1. Instrumentation

^{1}H- and ^{31}P{^{1}H}-NMR spectra were recorded by using Varian Gemini 200 (^{1}H, 200 MHz), Varian 500 (^{1}H, 500 MHz) and Bruker 250 (^{31}P, 101.25 MHz) spectrometers, and referenced to SiMe$_4$ (^{1}H) and H$_3$PO$_4$ (^{31}P). δ values are given in ppm and J values in Hz. IR spectra were recorded as KBr disks on a Nicolet 520 FTIR spectrometer. Microanalyses and mass spectra (CI and FAB) were performed by the Serveis Científico, Tècnics de la Universitat de Barcelona.

3.2. Preparation of the compounds

Compound [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] was prepared as reported [21].

3.2.1. Synthetic procedure for the compounds *1* and *2*

3-((*S*)-PhCHMeNCH)C$_4$H$_3$S (**1**) was prepared by the reaction of 0.5 g (4.46 mmol) of 3-tiophenecarboxaldehyde with the equimolar amount of (*S*)-methylbenzylamine (0.54 g) in refluxing ethanol. After 4 h, the solvent was removed in a rotary evaporator to yield a white solid. Yield 0.8 g (83%). Racemic 3-(PhCHMeNCH)C$_4$H$_3$S (**1**′) was prepared in an analogous way using (±)-methylbenzylamine. ^{1}H-NMR (200 MHz, CDCl$_3$: δ = 1.58 [d, J(H^a–H^b) = 7, H^a]; 4.48 [q, J(H^a–H^b) = 7, H^b]; {7.34 [m]; 7.60 [m, 1H], aromatics}; 8.38 [s, H^c].

[PtMe{(3-((*S*)-PhCHMeNCH)C$_4$H$_2$S}SMe$_2$] (**2**) was obtained by adding a solution of 75 mg (3.5×10^{-4} mol) of the imine **1** in acetone (10 ml) to a solution of 100 mg (1.74×10^{-4} mol) of compound [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] in acetone (10 ml). The mixture was stirred for 1 h and the acetone was removed in a rotary evaporator. The residue was washed with hexane and dried in

vacuum. Yield 120 mg (71%). Racemic [PtMe{(3-(PhCHMeNCH)C_4H_2S}SMe_2] (**2′**) was prepared from **1′** in an analogous way. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.09$ [s, ^2J(Pt–H) = 79, Me^a]; 1.71 [d, J(H^c–H^d) = 7, H^c]; 1.93 [s, ^3J(H^b–Pt) = 32, H^b]; 5.28 [q, J(H^c–H^d) = 6, H^d]; {7.18 [d, ^4J(Pt–H) = 35, J(H–H) = 5]; 7.30 [m], aromatics}; 8.49 [s, ^3J(Pt–He) = 51, He]. Anal. Found: C, 39.2; H, 4.3; N, 2.9. Calc. for $C_{16}H_{21}NPtS_2$: C, 39.50; H, 4.35; N, 2.88%.

3.2.2. Synthetic procedure for the phosphine derivatives

[PtMe{(3-((*S*)-PhCHMeNCH)C_4H_2S}PPh_3] (**3**) was obtained by the reaction of 50 mg (1.03×10^{-4} mol) of compound **2** with 25 mg (0.95×10^{-4} mol) of PPh_3 in acetone. After continuous stirring for 2 h, the solvent was removed in a rotary evaporator and the resulting yellow solid was filtered, washed with hexane, and diethylether and dried in vacuum. Yield 55 mg (78%). Racemic [PtMe{(3-(PhCHMeNCH)C_4H_2S}PPh_3] (**3′**) was prepared from **2′** in an analogous way. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 0.91$ [d, ^2J(Pt–H) = 80, ^3J(P–H) = 8, Me^a]; 1.05 [d, J(H–H) = 7, Me^b]; 4.40 [q, J(H–H) = 7, H^c]; {6.93 [m, 2H]; 7.18 [m, 5H], 7.33 [m, 10H]; 7.68 [m, 5H], aromatics}; 8.27 [s, ^3J(Pt–H^d) = 53, H^d]. ^{31}P-NMR (101.26 MHz, $CDCl_3$): $\delta = 31.29$ [J(Pt–P) = 2586]. Anal. Found: C, 55.8; H, 4.4; N, 2.1. Calc. for $C_{32}H_{30}NPPtS$: C, 55.97; H, 4.40; N, 2.04%.

[PtMe{(3-((*S*)-PhCHMeNCH)C_4H_2S}$P(2\text{-}MeC_6H_4)_3$] (**4**) was prepared in an analogous way using the corresponding phosphine. Yield 60 mg (80%). ^{1}H-NMR (200 MHz, $CDCl_3$): major isomer: $\delta = 0.05$ [d, ^3J(P–H) = 7, Me^b]; 0.99 [d, ^2J(Pt–H) = 82, ^3J(P–H) = 8, Me^a]; {1.60[s], 1.95[s], 2.97[s], He}; 4.65 [q, J(H–H) = 7, H^c]; 8.04 [s, ^3J(Pt–H^d) = 52, H^d]; 9.22 [dd, J(H–H) = 16; 7, H^{ar}]. ^{31}P-NMR (101.26 MHz, $CDCl_3$): $\delta = 25.17$ [J(Pt–P) = 2473]; minor isomer: $\delta = 0.96$ [d, ^2J(Pt–H) = 82, ^3J(P–H) = 8, Me^a]; 1.48 [d, ^3J(P–H) = 7, Me^b]; {1.57[s], 1.95[s], 2.81[s], H^e}; 8.37 [s, ^3J(Pt–H^d) = 52, H^d]; 9.15 [dd, J(H–H) = 16; 7, H^{ar}]. ^{31}P-NMR (101.26 MHz, $CDCl_3$): $\delta = 26.12$ [J(Pt–P) = 2479]. Anal. Found: C, 57.6; H, 4.9; N, 1.9. Calc. for $C_{35}H_{36}NPPtS$: C, 57.68; H, 4.98; N, 1.92%.

[PtMe{(3-((*S*)-PhCHMeNCH)C_4H_2S}$Ph_2PCH_2CH_2PPh_2$] (**5**) was obtained by the reaction of 50 mg (1.03×10^{-4} mol) of compound **2** with 41 mg (1.03×10^{-4} mol) of dppe in acetone. After continuous stirring for 6 h, the solvent was removed in a rotary evaporator and the resulting white solid was filtered, washed with hexane, and diethylether and dried in vacuum. Yield 60 mg (71%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 0.64$ [t, ^2J(Pt–H) = 69, ^3J(P–H) = 7, Me^a]; 1.39 [d, J(H–H) = 7, Me^b]; 2.25 [m, CH_2P], 4.09 [q, J(H–H) = 7, H^c]; {7.21 [m]; 7.35 [m], 7.49 [m]; 7.72 [m], aromatics}; 8.38 [s, ^3J(Pt–H^d) = 8, H^d]. ^{31}P-NMR (101.26 MHz, $CDCl_3$): $\delta = 47.38$ [J(Pt–P) = 2233], 44.28 [J(Pt–P) = 1660]. Anal. Found: C, 58.2; H, 4.8; N, 1.6. Calc. for $C_{40}H_{39}NP_2PtS$: C, 58.39; H, 4.78; N, 1.70%.

3.2.3. Synthetic procedures for the oxidative addition reactions

An excess of methyl iodide (0.1 ml) was added to solutions of 50 mg of the compounds **2** and **3** in acetone. The mixtures were stirred for 4 h, and the solvent was removed under vacuum to yield light yellow solids.

*[PtMe$_2$I{(3-((S)-PhCHMeNCH)C_4H_2S}SMe_2] (**6a**/**6a′**/**6b**/**6b′**).* Yield 50 mg (77%). ^{1}H-NMR (500 MHz, acetone-d_6): (**6a**/**6a′**), major isomer: $\delta = 0.59$ [s, ^2J(Pt–H) = 68, Me^b]; 1.41 [s, ^2J(Pt–H) = 68, Me^a]; 1.73 [d, J(H–H) = 7, H^d]; 5.71 [qd, J(H–H) = 7, J(H–H) = 1.5, H^e]; 8.67 [d, ^3J(Pt–H) = 45, J(H–H) = 1.5, H^f]; minor isomer: $\delta = 0.81$ [s, ^2J(Pt–H) = 68, Me^b]; 1.54 [s, ^2J(Pt–H) = 68, Me^a]; 1.83 [d, J(H–H) = 7, H^d]; 5.61 [q, J(H–H) = 7, H^e]; 8.10 [d, ^3J(Pt–H) = 45, J(H–H) = 1, H^f]. (**6b**/**6b′**), major isomer: $\delta = 1.35$ [s, ^2J(Pt–H) = 70, Me^b]; 1.63 [s, ^2J(Pt–H) = 68, Me^a]; 1.74 [d, J(H–H) = 7, H^d]; 6.14 [q, J(H–H) = 7, H^e]; 8.40 [d, ^3J(Pt–H) = 44, J(H–H) = 2, H^f]; minor isomer: $\delta = 1.15$ [s, ^2J(Pt–H) = 70, Me^b]; 1.61 [s, ^2J(Pt–H) = 68, Me^a]; 1.76 [d, J(H–H) = 7, H^d]; 1.98 [s, ^3J(Pt–H) = 12, H^c]; 2.14 [s, ^3J(Pt–H) = 13, H^c]; 6.22 [q, J(H–H) = 7, J(Pt–H) = 6.5, H^e]; 8.52 [d, ^3J(Pt–H) = 45, J(H–H) = 1, H^f]. Anal. Found: C, 32.4; H, 3.8; N, 2.2. Calc. for $C_{17}H_{24}INPtS_2$: C, 32.49; H, 3.85; N, 2.23%.

*[PtMe$_2$I{(3-((S)-PhCHMeNCH)C_4H_2S}PPh_3] (**7b**/**7b′**).* Yield 45 mg (74%). Major isomer: ^{1}H-NMR (500 MHz, acetone-d_6): $\delta = 0.82$ [d, ^2J(Pt–H) = 60, J(H–P) = 7, Me^b]; 1.60 [d, ^2J(Pt–H) = 69, J(H–P) = 7, Me^a]; 1.05 [d, J(H–H) = 7, H^c]; 6.02 [q, J(H–H) = 7, J(Pt–H) = 7, H^d]; {6.54 [d, J(H–H) = 7], 7.10 [d, J(H–H) = 5.5, J(H–Pt) = 25], aromatics}, 8.75 [d, ^3J(Pt–H) = 48, J(H–H) = 2, H^e]. ^{31}P-NMR (101.26 MHz, acetone-d_6): $\delta = -10.45$ [J(Pt–P) = 983]. Minor isomer: ^{1}H-NMR (500 MHz, acetone-d_6): $\delta = 1.35$ [d, ^2J(Pt–H) = 60, J(H–P) = 7, Me^b]; 1.69 [d, ^2J(Pt–H) = 70, J(H–P) = 8, Me^a]; 1.82 [d, J(H–H) = 7, H^c]; 5.72 [q, J(H–H) = 6, H^d]; {6.98 [d, J(H–H) = 5], 7.03 [d, J(H–H) = 5], aromatics}, 7.78 [s, ^3J(Pt–H) = 45, H^e]. ^{31}P-NMR (101.26 MHz, acetone-d_6): $\delta = -10.60$ [J(Pt–P) = 1012]. Anal. Found: C, 47.4; H, 4.0; N, 1.9. Calc. for $C_{33}H_{33}INPtS$: C, 47.83; H, 4.01; N, 1.69%.

The reactions of compounds **2** and **3** with methyl iodide were monitored by NMR in the following way; 10 ml 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.

*[PtMe$_2$I{(3-((S)-PhCHMeNCH)C_4H_2S}PPh_3] (**7a**/**7a′**).* [PtMe$_2$I{(3-((*S*)-PhCHMeNCH)C_4H_2S}PPh_3] (**7a**/**7a′**) was characterized spectroscopically in solution. Major isomer: ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 0.21$ [d, ^2J(Pt–H) = 66, J(H–P) = 7, Me^b]; 1.46 [d,

Table 2
Crystallographic data and details of the refinements for compound **2**

Formula	$C_{16}H_{21}NPtS_2$
Formula weight	486.55
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	11.191(2)
b (Å)	11.974(7)
c (Å)	12.321(8)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	1651(2)
D_{calc} (g cm^{-3})	2.076
Z	4
$F(000)$	936
Crystal size (mm^3)	$0.1\times0.1\times0.2$
λ(Mo–K$_\alpha$) (Å)	0.71069
T (K)	293(2)
Reflections collected	2321
$R[I>2\sigma(I)]$	0.0321
$R_w(F^2)$	0.0673
Refined parameters	183
max. shift/estimated S.D.	0.0
max. and min. difference peaks (e Å^{-3})	0.681 and −0.680

^2J(Pt–H) = 68, J(H–P) = 7, Me[a]; 1.55 [d, J(H–H) = 7, H[c]; 5.35 [m, H[d]; 6.63 [d, J(H–H) = 6, aromatics], 8.66 [d, ^3J(Pt–H) = 46, H[e]. ^{31}P-NMR (101.26 MHz, acetone-d_6): $\delta = -6.03$ [J(Pt–P) = 1544]. Minor isomer: ^{31}P-NMR (101.26 MHz, acetone-d_6): $\delta = -3.92$ [J(Pt–P) = 1553].

An excess of ethyl iodide or benzylbromide (0.1 ml) was added to solutions of 50 mg of compound **3** in acetone. The mixtures were stirred for 48 h, and the solvent was removed under vacuum to yield yellow solids.

*[PtI{(3-((S)-PhCHMeNCH)C$_4$H$_2$S}PPh$_3$] (**8**).* ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 1.73$ [d, ^2J(H–H) = 7, Me[a]; 6.81 [m, H[b]; {7.35–7.50[m]; 7.71–7.82[m], aromatics}; 7.95 [d, ^3J(H–Pt) = 89, J(H–P) = 9.5, H[c]. ^{31}P-NMR (101.26 MHz, acetone-d_6): $\delta = 13.65$ [J(Pt–P) = 3786]. Anal. Found: C, 46.5; H, 3.6; N, 1.7. Calc. for $C_{31}H_{27}INPPtS$: C, 46.63; H, 3.41; N, 1.75%.

*[PtBr{(3-((S)-PhCHMeNCH)C$_4$H$_2$S}PPh$_3$] (**9**).* ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 1.75$ [d, ^2J(H–H) = 7, Me[a]; 6.50 [m, H[b]; {7.26–7.46[m]; 7.70–7.76[m], aromatics}; 7.95 [d, ^3J(H–Pt) = 90, J(H–P) = 9.5, H[c]. ^{31}P-NMR (101.26 MHz, acetone-d_6): $\delta = 15.02$ [J(Pt–P) = 3836].

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 ($12 < \theta < 21°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo–K$_\alpha$ radiation, using $\omega/2\theta$ scan-technique. 2321 reflections were measured in the range $2.37 < \theta < 29.95°$; 2299 were non-equivalent by symmetry and 2083 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 SHELXS computer program [22], and refined by the full-matrix least-squares method, with the SHELX-93 computer program [23] using 2249 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w\left||F_o|^2 - |F_c|^2\right|^2$, where $w = [\sigma^2(I) + (0.0326P)_2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from international tables of X-ray crystallography [24]. The chirality of the structure was defined from the Flack coefficient [25], which is equal to 0.03(2) for the given results. All hydrogen atoms were computed 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 has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 140492 for compound **2**. 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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References

[1] L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.
[2] G. van Koten, Pure Appl. Chem. 61 (1989) 1681.
[3] A. von Zelewsky, A.P. Suckling, H. Stoeckli-Evans, Inorg. Chem. 32 (1993) 4585.
[4] U. Knof, A. von Zelewsky, Angew. Chem. Int. Ed. Engl. 38 (1999) 302.
[5] M. Gianini, A. von Zelewsky, H. Stoeckly-Evans, Inorg. Chem. 36 (1997) 6094.
[6] M. Gianini, A. Forster, P. Haag, A. von Zelewsky, H. Stoeckli-Evans, Inorg. Chem. 35 (1996) 4889.

[7] M. Crespo, X. Solans, M. Font-Bardia, Polyhedron 17 (1998) 3927.
[8] C.R. Baar, H.A. Jenkins, J.J. Vittal, G.P.A. Yap, R.J. Puddephatt, Organometallics 17 (1998) 2805.
[9] C.M. Anderson, M. Crespo, A. Klein, M. Font-Bardia, J. Organomet. Chem. 601 (2000) 22.
[10] C.M. Anderson, M. Crespo, M.C. Jennings, A.J. Lough, G. Ferguson, R.J. Puddephatt, Organometallics 10 (1991) 2672.
[11] M. Crespo, M. Martinez, J. Sales, X. Solans, M. Font-Bardia, Organometallics 11 (1992) 1288.
[12] O. Meth-Cohn, in: D. Barton, W.D. Ollis (Eds.), Comprehensive Organic Chemistry, Part 19, vol. 4, Pergamon Press, Oxford, 1979, p. 793.
[13] T.J. Giordano, P.G. Rasmussen, Inorg. Chem. 14 (1975) 1628.
[14] T.J. Giordano, W.M. Butler, P.G. Rasmussen, Inorg. Chem. 17 (1978) 1917.
[15] M. Crespo, X. Solans, M. Font-Bardia, Organometallics 14 (1995) 355.
[16] M. Crespo, X. Solans, M. Font-Bardia, J. Organomet. Chem. 483 (1994) 187.
[17] M. Crespo, Polyhedron 15 (1996) 1981.
[18] R. Brady, W.H. DeCamp, B.R. Flynn, M.L. Schneider, J.D. Scott, L. Vaska, M.F. Werneke, Inorg. Chem. 14 (1975) 2669.
[19] J. Albert, M. Gomez, J. Granell, J. Sales, X. Solans, Organometallics 9 (1990) 1405.
[20] J. Albert, R.M. Ceder, M. Gomez, J. Granell, J. Sales, Organometallics 11 (1992) 1536.
[21] J.D. Scott, R.J. Puddephatt, Organometallics 2 (1983) 1643.
[22] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[23] G.M. Sheldrick, A computer program for determination of crystal structures, University of Göttingen, Germany, 1994.
[24] International tables of X-ray crystallography, vol. IV, Kynoch, Birmingham, 149, 1974, pp. 89–100.
[25] H.D. Flack, Acta Crystallogr. Sect A 39 (1983) 876.