

Platinum(II) and Palladium(II) Compounds Containing Chiral Thioimines

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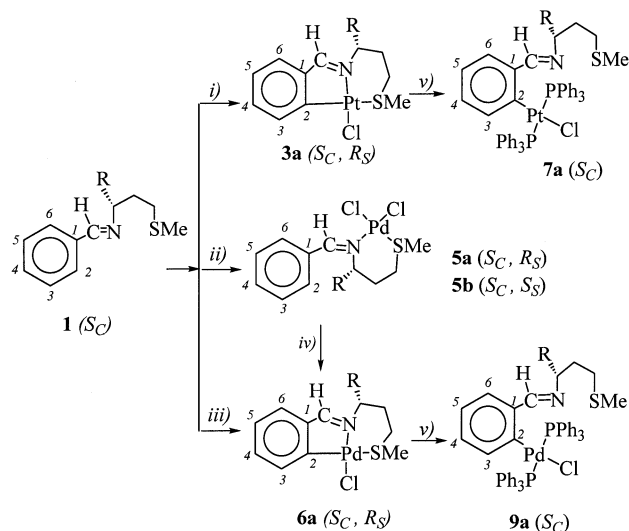
A comparative study of the reactivity of the optically pure thioimine: (*S_C*)-(–)-C₆H₅–CH=N–CH(CO₂Me)–CH₂–CH₂–SMe (**1**) versus platinum(II) and palladium(II) salts is reported. The reaction of **1** with *cis*-[PtCl₂(dmsO)₂] leads to the cycloplatinated derivative (*S_C*,*R_S*)-(+)-[Pt{C₆H₄–CH=N–CH(CO₂Me)–CH₂–CH₂–SMe}Cl] (**3a**). The absolute configuration of **3a** has been established unambiguously by X-ray diffraction: orthorhombic, with *a* = 8.979 (4), *b* = 9.605(9), *c* = 18.205(6) Å, *α* = *β* = *γ* = 90.0°, space group *P*2₁2₁2₁. Compound **3a** contains a [6.5.6] tricyclic system generated by the fusion of a phenyl ring, a five-membered platinacycle and a six-membered chelate ring formed by the coordination of the

nitrogen and sulfur to the platinum. When **1** was treated with Na₂[PdCl₄] in methanol at room temperature a (7.9:1) mixture of the two diastereomers {(*S_C*,*R_S*)-**5a** and (*S_C*,*S_S*)-**5b**} of *cis*-[Pd{C₆H₅–CH=N–CH(CO₂Me)–CH₂–CH₂–SMe}Cl₂] (**5**) was formed. However, when the reaction was performed in the presence of sodium acetate, the activation of the σ(*C_{sp}²*,*phenyl*–H) bond took place giving the cyclopalladated complex: (*S_C*,*R_S*)-(+)-[Pd{C₆H₄–CH=N–CH(CO₂Me)–CH₂–CH₂–SMe}Cl] (**6a**). In **6a**, the ligand acts as a monoanionic (C,*N*,*S*)[–] terdentate group. The study of the reactivity of **3a** and **6a** with PPh₃ is also reported.

Introduction

An important area of organometallic chemistry is that of cyclopalladated and cycloplatinated compounds.^[1] Interest in such compounds has increased exponentially due to their applications in several areas.^[2–12] Among the cyclometallated complexes described, those derived from optically pure N-donor ligands have attracted additional interest, since they can be used for the resolution of mono- or bidentate ligands^[10–11] as well as in chiral discrimination processes.^[12] As a part of a project directed towards the design of new optically pure cyclometallated complexes derived from Schiff bases of general formula: C₆H₅–CH=N–CH(R)R' or [(η⁵-C₅H₅)Fe{(η⁵-C₅H₄)–CH=N–CH(R)R'}] {R = alkyl, R' = phenyl, benzyl, or naphthyl groups}^[11c,12–14] we attempted to elucidate whether the replacement of the R' group by a pendant arm containing a prochiral atom with good donor abilities (i.e. N, O, S, or P) could determine, not only the diastereoselectivity of the coordination of the ligand to the palladium(II) or platinum(II), but also the nature of the final product formed in the cyclometallation process. The incorporation of a sulfur atom, which according to Pearson's concept^[15] is a softer base, in the backbone of the ligand may strengthen the binding to the palladium or platinum. In addition, the activation of the *ortho* σ(C–H) bond of the ligand may produce metallacycles with a (C,*N*,*S*)[–] terdentate group, which

are uncommon in the literature.^[16–17] Furthermore, optically pure platina- or palladacycles containing this sort of environment are very scarce.^[18] With these aims we prepared the Schiff base: (*S_C*)-(–)-C₆H₅–CH=N–CH(CO₂Me)–CH₂–CH₂–SMe (**1**) (Scheme 1) and studied its reactivity towards platinum and palladium(II) salts.



Scheme 1. R = CO₂Me. i) *cis*-[PtCl₂(dmsO)₂] in refluxing methanol. ii) Na₂[PdCl₄] in methanol at room temperature. iii) Na₂[PdCl₄] and NaAcO in refluxing methanol. iv) NaAcO in refluxing methanol. v) PPh₃ in CDCl₃ at room temperature

Results and Discussion

Ligand **1** was prepared according to the general procedure described for most arylaldimines.^[19] The ¹H and

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$^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** (Exp. Section) suggested that only one isomer (*E*-form) was present in solution. When **1** was treated with $\text{K}_2[\text{PtCl}_4]$ at room temperature, the reaction produced a yellow solid. Its ^1H NMR spectrum was complex and three signals assigned to the imine proton were detected at $\delta \approx 9.15$, 9.26, and 8.30. The ^{195}Pt NMR spectrum showed three singlets at ca. $\delta = -3029$, -3059 , and -3832 {of relative intensities: 2:0.3:3}. This indicated that the crude material contained at least three platinum(II) compounds. The position of signals at $\delta = -3029$ and -3059 was similar to those reported for: $[\text{Pt}(\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{SEt})\text{Cl}_2]$,^[17] $[\text{Pt}(\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{SEt})\text{Cl}_2]$,^[20] and for related compounds containing a “Pt(N,S)Cl₂” core.^[21] This result suggested that two isomers of *cis*- $[\text{Pt}\{\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}\text{Cl}_2]$ may be present in solution. The chemical shift of the third signal was similar to that of $[\text{Pt}\{\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{SMe}\}\text{Cl}]$ (**2**),^[17] $[\text{Pt}\{(\eta^5-\text{C}_5\text{H}_5)\text{Fe}[(\eta^5-\text{C}_5\text{H}_3)-\text{CH}(\text{R})-\text{NMe}_2]\text{Cl}(\text{dmsO})]$,^[22] and related compounds.^[21,23] Unfortunately, attempts to separate the major components of the mixture by either column chromatography or fractional crystallization failed due to the formation of metallic platinum during these experiments. More satisfactory results were obtained when the reaction was carried out using *cis*- $[\text{PtCl}_2(\text{dmsO})_2]$ ^[24] as starting material under refluxing conditions for 12 h. The slow evaporation of the solvent yielded single crystals suitable for X-ray diffraction. Elemental analyses of this material agreed with those expected for $[\text{Pt}\{\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}\text{Cl}]$ (**3**). The two-dimensional heteronuclear $\{^1\text{H}-^{13}\text{C}\}$ NMR spectrum suggested that the activation of the $\sigma(\text{C}_{\text{sp}^2,\text{phenyl}}-\text{H})$ bond had taken place. The position of the signal detected in the ^{195}Pt NMR spectrum was similar to that reported for **2**^[17] and for related platinum(II) compounds with a “Pt(C,N,S,Cl)” core.^[21]

Recent studies have shown that for optically pure organic imines or amines, such as: $\text{R}^1-\text{CH}=\text{N}-\text{CH}(\text{Me})-\text{R}^2$ { R^1 = phenyl or ferrocenyl groups and R^2 = phenyl or naphthyl groups} or $\text{C}_{10}\text{H}_7-\text{CH}(\text{R}^1)-\text{NR}^2\text{R}^3$ { R^1 , R^2 , R^3 = alkyl groups} the formation of the metallacycle through the activation of the $\sigma(\text{C}_{\text{sp}^2,\text{aryl}}-\text{H})$ bond does not modify the absolute configuration of the stereogenic centre of the ligand.^[11a,11c,25] Consequently, since **1** contains a stereogenic carbon and a prochiral sulfur atom, **3** may consist of a mixture of two diastereomers: $\{(S_C,R_S)$ or (S_C,S_S) hereinafter referred to as **3a** and **3b**. The use of molecular models and the SPARTAN 4.0 computer program^[26] indicated that in **3a**, where the $-\text{CO}_2\text{Me}$ and the Me group bound to the sulfur are on opposite sides of the coordination plane, the steric hindrance is clearly smaller than in the (S_C,S_S) isomer (**3b**). Thus, the formation of **3a** is expected to be strongly preferred to that of **3b**. ^1H and ^{13}C NMR spectra indicated that only one of the diastereomers of **3** was present in solution and its absolute configuration was determined by X-ray diffraction. An ORTEP diagram of **3a** is shown in Figure 1.

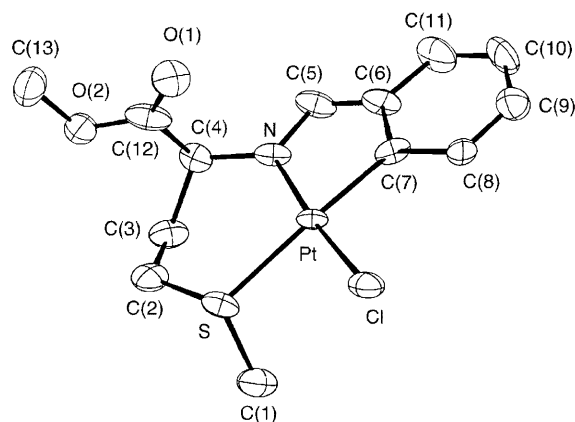


Figure 1. ORTEP diagram of the crystal structure of $(S_C,R_S)-(+)-[\text{Pt}\{\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}\text{Cl}]$ (**3a**). Selected bond lengths [in Å]: Pt–N, 1.984(11); Pt–S, 2.349(3); Pt–Cl, 2.308(4); Pt–C(7), 1.954(14); N–C(5), 1.954(14). Selected bond angles [in deg.]: C(7)–Pt–Cl, 94.0(4); N–Pt–S, 99.2(3); Cl–Pt–S, 85.84(13); N–Pt–Cl, 174.8(3); Pt–N–C(5), 114.9(11); N–C(5)–C(6) 119.6(16)

The structure consists of discrete molecules of $[\text{Pt}\{\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}]$ separated by van der Waals interactions. The platinum atom is bound to the chloride, the sulfur, the imine nitrogen and the *ortho*-carbon {C(7)} of the phenyl ring in a slightly distorted square-planar environment. The molecule contains a [6.5.6] tricyclic system derived from the fusion of the six-membered chelate ring, formed by the coordination of the sulfur and the nitrogen to the platinum(II), a five-membered platinacycle and the phenyl ring.

The metallacycle, which is formed by the atoms: Pt, N, C(5), C(6), and C(7), is practically planar and contains the $>\text{C}=\text{N}-$ functional group. The $>\text{C}=\text{N}-$ bond length is in the range described for related five-membered platinacycles derived from imines.^[27] The ligand adopts the *anti*-conformation [*E*-form] and the phenyl ring forms an angle of 6.27° with the plane of the platinacycle.

The six-membered chelate ring formed by the platinum and the “N–CH(CO₂Me)–CH₂–CH₂–S–” moiety exhibits a chair-conformation in which the atoms C(3) and Pt deviate from the mean plane -0.6148 and $+0.0928$ Å, respectively.

The comparison of the bond lengths and angles involving the platinum(II) atom in **3a** and in **2**,^[17] which contains a [6.5.5] tricyclic system, shows that in **3a** the Pt–C(7) bond length [1.954(14) Å] is clearly shorter than in **2** [2.012(8) Å]. However, this variation does not significantly affect the length of the Pt–S bond in a *trans* position [2.349(3) Å in **3a** and 2.334(10) Å in **2**]. In contrast, an increase in the size of the chelate ring [a five-membered ring in **2** and a six-membered ring in **3a**] introduces significant differences in the angles involving the pair of atoms Pt and Cl. For instance, in **2**, the angles: C–Pt–Cl and Cl–Pt–S are bigger than in **3a**. This finding, together with the higher value of

the Pt–Cl bond length in **3a** compared with **2**, suggests that the environment of the chlorine is more crowded in **3a**.

The absolute configuration of the molecule is determined by the chirality of the carbon atom (S_C) and the relative arrangement of the Me bound to the sulfur towards the $-\text{CO}_2\text{Me}$ group. In **3a**, these groups face opposite sides of the coordination plane of the palladium [the torsion angle $\text{C}(1)-\text{S}-\text{C}(4)-\text{C}(12)$ is 166.81°]. As mentioned above, if these substituents were on the same side a strong steric hindrance would arise. This arrangement of groups on the stereogenic centres of **3a** is formally identical to that found in $[\text{Pd}_2\{(\text{C}_4\text{H}_3\text{S})-\text{CH}=\text{N}-\text{C}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}_2\text{Cl}_2]$ (**4**).^[18]

The comparison of the results obtained in the reaction of $\text{cis}[\text{PtCl}_2(\text{dmsO})_2]$ with **1** or $\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{SEt}$ ^[17] shows that cycloplatination of **1** occurs easily, leading to one of the two diastereomers. These differences may be attributed to the presence of a bulky group^[28] in the proximity of the imine nitrogen.

When **1** was treated with $\text{Na}_2[\text{PdCl}_4]$ in methanol at ca. 20°C $\text{cis}[\text{Pd}\{\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}\text{Cl}_2]$ (**5**) was obtained. The ^1H NMR spectrum of **5** showed two superimposed sets of signals of relative intensities 7.9:1.0, which suggested the presence of two species in solution. $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic studies also confirmed these results. Complex **5** could also consist of different isomers which may differ in *a*) the conformation of the ligand (*E*- or *Z*-forms) and/or *b*) the chirality of the sulfur atom in the complex (R_S or S_S). Previous NMR spectroscopic studies of palladium(II) and platinum(II) compounds containing imines have shown that the chemical shift of the methinic proton indicates the conformation of the ligand.^[13,17,29,30] The ^1H NMR spectrum of **5** showed two singlets assigned to the imine protons at lower fields ($\delta = 8.41$ and 8.38) than in **1**, thus suggesting that in the two species the imine had the (*Z*) form. Consequently, the two isomers may have a different origin, which might be related to the presence of the prochiral sulfur atom in **1**. The formation of the six-membered chelate ring by coordination of the N and S atoms to the palladium(II) may produce two diastereomers [(S_C, R_S) and (S_C, S_S)]. On this basis we assumed that the complexity of the ^1H and ^{13}C NMR spectra of **5** could be due to the presence of the two diastereomers [(S_C, R_S) , **5a** and (S_C, S_S) , **5b**]. Attempts to separate them by crystallization or SiO_2 -column chromatography failed due to the low solubility of **5**.

The use of molecular models and the SPARTAN 4.0 computer program^[26] also suggested that the less hindered isomer corresponds to the (S_C, R_S) diastereomer (**5a**). Thus, we assume that the absolute configuration of the main component is (S_C, R_S) .

In order to examine whether the activation of the $\sigma(\text{C}_{\text{sp}^2, \text{phenyl}}-\text{H})$ bond of **1** could be promoted by palladium(II) salts, more drastic reaction conditions were used (i.e. refluxing methanol and reaction periods of up to 7 days). However, no evidence of the formation of any palladacycle was detected by NMR spectroscopy. Better results were obtained when the reaction was carried out under re-

flux in the presence of NaAcO, which yielded a bright yellow solid. Its elemental analyses agreed with those expected for the complex $[\text{Pd}\{\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}\text{Cl}]$ (**6**). Its ^1H , $^{13}\text{C}\{^1\text{H}\}$, and the two dimensional heteronuclear $\{^1\text{H}-^{13}\text{C}\}$ NMR spectra suggested the formation of a palladacycle with a $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{phenyl}}-\text{H})$ bond and the presence of only one of the two diastereomers of **6** in solution. In the view of the results obtained from the SPARTAN 4.0 program^[26] and from the X-ray crystal structure of the platinum(II) analogue (see above) we assume that the absolute configuration of the isolated material is (S_C, R_S) .

Compound **6a** could also be isolated by treatment of **5** with the stoichiometric amount of NaOAc in refluxing methanol. The transformation of **5** to **6a** requires the isomerization (*Z*) $\rightarrow$ (*E*) of the ligand and the formation of the $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{aryl}})$ bond.

Potentially terdentate chelating ligands $[\text{N}, \text{C}, \text{X}]^-$ {where $\text{X} = \text{N}, \text{P}, \text{O}$, or S } may adopt different binding modes and hapticities which is relevant to catalytic processes. As a first approach to explore whether the mode of binding or the hapticity of **1** could be modified under mild experimental conditions, the reactions of **3a** and **6a** with PPh_3 were studied in solution. When PPh_3 was added to a solution of **3a** {Pt: PPh_3 molar ratio equals to 1:2} in CDCl_3 at 20°C , a pale yellow solution was obtained. Its ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra suggested the formation of $[\text{Pt}\{\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}\text{Cl}(\text{PPh}_3)_2]$ (**7a**). Its ^{195}Pt NMR spectroscopic data is consistent with the values reported for platinum(II) compounds having a *trans*-“Pt(C, Cl, P_2)” core.^[31]

This result is in sharp contrast with that reported for **2**, for which the addition of large excesses of PPh_3 did not produce the cleavage of the Pt–N bond^[17] and suggests a higher lability of the Pt–N bond in complex **3a**. The use of the SPARTAN 4.0 computer program^[26] for the diastereomer $(S_C)-[\text{Pt}\{\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}\text{Cl}(\text{PPh}_3)]$ (**8a**) reveals that the environment around the metal is very crowded and at least one of the phenyl rings of the PPh_3 ligand is very close to the atoms of the $-\text{CO}_2\text{Me}$ group. This would increase the steric hindrance and reduce the stability of the molecule which may be related to the higher proclivity of **3a** {compared with **2**} to undergo a ring-opening process. The cleavage of the Pt–N bond would permit the free rotation around the N–C* bond, leading to a larger separation between the aryl rings and the “ CO_2Me ” fragment.

When the reaction was performed in identical experimental conditions, but using **6a** and PPh_3 , $[\text{Pd}\{\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}\text{Cl}(\text{PPh}_3)_2]$ (**9a**) was formed in solution and its ^{31}P NMR spectrum suggested a *trans*- arrangement of the PPh_3 ligands.

Since the formation of **7a** and **9a** involves the cleavage of the M–S bond (in **3a** and **6a**, respectively), the absolute configuration of these derivatives is expected to be S_C .

To sum up, the results reported in this work show the importance of the presence of a bulky and electron-withdrawing group on the stereogenic carbon atom of **1** in the

diastereoselectivity of the reactions under study. The preferential formation of **5a** versus **5b** (*d.e.* = 77.5%) may be attributed to steric effects. In **5a**, where the $-\text{CO}_2\text{Me}$ group and the Me bound to the sulfur are pointing towards opposite sides of the coordination plane of the metal, the steric hindrance is clearly smaller than in **5b**. A similar argument can be used to explain the formation of the metallacycles **3a** and **6a**. These findings suggest that the absolute configuration of the stereogenic carbon in **1** induces a high degree of diastereoselectivity in the coordination of the prochiral sulfur.

Several authors have postulated that the presence of an electron-withdrawing group favours the metallation of aliphatic carbon atoms.^[1,18,32] On this basis, for **1**, which contains an electron-withdrawing group^[28] at the stereogenic carbon, the activation of a ($\text{C}_{\text{sp}^2, \text{phenyl}}-\text{H}$) or a ($\text{C}_{\text{sp}^3}^*-\text{H}$) bond, in principal, could be expected. However, for **1**, the metallation of the phenyl ring is strongly preferred and no evidence of the presence of the metallacycles with a $\sigma(\text{M}-\text{C}_{\text{sp}^3}^*)$ bond was detected by NMR spectroscopy. These findings are in sharp contrast with those obtained in the cyclopalladation of $[(\text{C}_4\text{H}_5\text{S})-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}]^{[18]}$ which produced: $[\text{Pd}_2\{(\text{C}_4\text{H}_5\text{S})-\text{CH}=\text{N}-\text{C}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}_2\text{Cl}_2]$ (**4**) through activation of the $\sigma(\text{C}_{\text{sp}^3}^*-\text{H})$ bond.^[18] Consequently, the results presented here reveal the importance of the group bound to the imine carbon in determining the type of the $\sigma(\text{M}-\text{C})$ bond to be formed [$\sigma(\text{M}-\text{C}_{\text{sp}^2, \text{aryl}})$ or $\sigma(\text{M}-\text{C}_{\text{sp}^3}^*)$] in the cyclometallation process. Besides that, compounds **3a** and **6a** have an additional interest since they may be potentially useful in a wide variety of processes, i.e. as chiral recognition compounds or discriminators, or as precursors for the asymmetrical synthesis of novel organic or organometallic derivatives.

Experimental Section

Materials and Synthesis: Benzaldehyde was obtained from standard sources and purified by vacuum distillation before use. (*S_C*)-Methionine methyl ester hydrochloride was obtained from Janssen Chimica and transformed into the free amine before use. *cis*- $[\text{PtCl}_2(\text{dmsO})_2]$ was prepared as previously described.^[24] All the solvents used in this study were HPLC grade.

Elemental analyses (C, H, N, and S) were carried out at the Serveis Científics de la Universitat de Barcelona and at the Serveis de Recursos Científics (Universitat Rovira i Virgili, Tarragona). Infrared spectra were obtained with a Nicolet Impact 400 instrument using NaCl discs for **1** and KBr pellets for the solid samples. ^1H and the two dimensional $\{^1\text{H}-^{13}\text{C}\}$ heteronuclear NMR experiments were run using a Varian VXR-500 or a Bruker Avance 500DMX instrument. The solvents and references used are specified in the characterization section of each compound. $^{13}\text{C}\{^1\text{H}\}$ - and ^{195}Pt NMR spectra were recorded with a Bruker-250DXR instrument. The ^{195}Pt chemical shifts are referred to a $\text{Na}_2[\text{PtCl}_6]$ solution in D_2O as external reference. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained with a Bruker-250DXR instrument using CDCl_3 as solvent and $\text{P}(\text{OMe})_3$ as reference ($\delta^{31}\text{P}[\text{P}(\text{OMe})_3] = 140.17$). The

chemical shifts (δ) are given in ppm and the coupling constants (*J*) in Hz. – The optical rotations were determined in CH_2Cl_2 using a Perkin–Elmer 241MC-polarimeter. – FAB^+ mass spectra were obtained with a VG-Quatro Fisions instrument using 3-nitrobenzyl alcohol as matrix.

Preparation of (*S_C*)-(-)- $\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}$ (1**):** Benzaldehyde (304 mg, $2.86 \cdot 10^{-3}$ mol) was added to a solution of $\text{H}_2\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}$ (467 mg, $2.86 \cdot 10^{-3}$ mol) in 15 mL of methanol. The mixture was refluxed for 3 h. Then, the solution was concentrated to dryness giving a whitish oil. (Yield 601 mg, 82%). – IR: $\nu(\text{CO})$: 1736 and $\nu(>\text{C}=\text{N}-)$: 1644 cm^{-1} . – ^1H NMR (in CDCl_3):^[33] $\delta = 2.09$ (s, 3 H, $-\text{SMe}$), 2.18–2.35 (m, 2 H, $-\text{CH}_2-$), 2.46–2.60 (m, 2 H, $-\text{SCH}_2-$), 3.75 (s, 3 H, $-\text{OMe}$), 4.22 (m, 1 H, $>\text{CH}-$), 7.43 (m, 1 H, H^4), 7.45 (m, 2 H, H^3 and H^5), 7.80 (d, 2 H, H^2 and H^6), 8.33 (s, 1 H, $-\text{CH}=\text{N}-$). – $^{13}\text{C}\{^1\text{H}\}$ NMR (in CDCl_3):^[33] $\delta = 16.2$ ($-\text{SMe}$), 30.2 ($-\text{SCH}_2-$), 31.9 ($-\text{CH}_2-$), 52.3 ($-\text{OMe}$), 71.2 ($>\text{CH}-$), 135.4 (C^1), 128.5 (C^2 and C^6), 128.5 (C^3 and C^5), 131.2 (C^4), 164.3 ($-\text{CH}=\text{N}-$), 172.1 ($>\text{CO}_2$). $[\alpha]_{24}^\circ \text{C}$ ($c = 0.05$ g/100 mL) = -24.12 .

Preparation of (*S_C,R_S*)-(+)- $[\text{Pt}\{\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}\text{Cl}]$ (3a**):** To a hot solution formed by *cis*- $[\text{PtCl}_2(\text{dmsO})_2]$ (100 mg, $2.36 \cdot 10^{-4}$ mol) and 20 mL of methanol, **1** (59 mg, $2.35 \cdot 10^{-4}$ mol) was added. The suspension was refluxed for 12 h and filtered out. Then, the filtrate was concentrated to ca. 5 mL on a rotary evaporator. The slow evaporation of the solvent at ca. 20 °C produced golden crystals, which were collected and air-dried. (Yield 92 mg, 81.0%). – $\text{C}_{13}\text{H}_{16}\text{ClNO}_2\text{SPT}$: calcd. (found) C 32.5 (32.5), H 3.3 (3.3), N 2.9 (3.0), S 6.7 (6.7). – IR: $\nu(\text{CO})$: 1739 cm^{-1} and $\nu(>\text{C}=\text{N}-)$: 1594 cm^{-1} . – ^1H NMR (in CDCl_3):^[33] $\delta = 2.55$ [s, 3 H, $-\text{SMe}$, $^3J(\text{Pt}-\text{H}) = 20$], 2.62 and 2.79 (m, 2 H, $-\text{SCH}_2-$), 2.30 and 2.60 (m, 2 H, $-\text{CH}_2-$), 3.74 (s, 3 H, $-\text{OMe}$), 4.52 [m, 2 H, $>\text{CH}-$, $^3J(\text{Pt}-\text{H}) = 52$], 7.31 (d, 1 H, H^3), 7.09 (t, 1 H, H^4), 7.28 (t, 1 H, H^5), 7.95 [d, 1 H, H^6 , $^4J(\text{Pt}-\text{H}) = 39$], 8.27 [s, 1 H, $-\text{CH}=\text{N}-$, $^3J(\text{Pt}-\text{H}) = 133$]. – $^{13}\text{C}\{^1\text{H}\}$ NMR (in CDCl_3):^[33] $\delta = 21.2$ (Me), 27.7 ($-\text{SCH}_2$), 31.4 ($-\text{CH}_2-$), 53.3 ($-\text{OMe}$), 66.3 ($>\text{CH}-$), 143.0 (C^1), 152.1 (C^2), 128.2 (C^3), 124.3 (C^4), 133.4 (C^5), 132.2 (C^6), 181.9 ($-\text{CH}=\text{N}-$), 170.0 ($-\text{CO}_2$). – ^{195}Pt NMR (in CDCl_3): -3832 . $[\alpha]_{24}^\circ \text{C}$ ($c = 0.1$ g/100 mL) = $+73.9$. FAB^+ (selected data): 481 $[\text{M} + \text{H}]^+$, 445 $[\text{M} - \text{Cl}]^+$.

Preparation of *cis*- $[\text{Pd}\{\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{CH}(\text{CO}_2\text{Me})-\text{CH}_2-\text{CH}_2-\text{SMe}\}\text{Cl}_2]$ (5**):** Ligand **1** (157 mg, $6.25 \cdot 10^{-4}$ mol) was dissolved in 15 mL of methanol. A solution formed by $\text{Na}_2[\text{PdCl}_4]$ (184 mg, $6.25 \cdot 10^{-4}$ mol) and 10 mL of methanol was then added. The mixture was stirred at ca. 20 °C for 3 h. The solid formed was collected, washed with methanol (3·2 mL) and air-dried. (Yield 143 mg, 53.3%). – $\text{C}_{13}\text{H}_{17}\text{Cl}_2\text{NO}_2\text{SPd}$: calcd. (found) C 36.5 (36.3), H 4.0 (4.0), N 3.3 (3.1), S 7.5 (7.45). – IR: $\nu(\text{CO})$: 1740 cm^{-1} and $\nu(>\text{C}=\text{N}-)$ = 1624 cm^{-1} . – ^1H NMR spectroscopic data (in CDCl_3):^[33] *Major isomer, 5a* ($\{(\text{S}_{\text{C}},\text{R}_{\text{S}})\}$): $\delta = 2.63$ (s, 3 H, $-\text{SMe}$), 2.50 and 2.55 (m, 2 H, $-\text{SCH}_2-$), 3.40 and 3.90 (m, 2 H, $-\text{CH}_2-$), 3.88 (s, 3 H, $-\text{OMe}$), 4.22 (m, 1 H, $>\text{CH}-$), 7.69–7.82 (m, 3 H, H^3 , H^4 and H^5), 8.38 (s, 1 H, $-\text{CH}=\text{N}-$) and 9.23 (d, 2 H, H^2 and H^6). *Minor isomer, 5b* ($\{(\text{S}_{\text{C}},\text{S}_{\text{S}})\}$): $\delta = 2.52$ (s, 3 H, SMe), 2.60 and 2.45 (m, 2 H, $-\text{SCH}_2-$), 3.40 and 3.90 (m, 2 H, $-\text{CH}_2-$), 3.81 (s, 3 H, $-\text{OMe}$), 4.02 (m, 1 H, $>\text{CH}-$), 7.69 (m, 3 H, H^3 , H^4 and H^5), 8.41 (s, 1 H, $-\text{CH}=\text{N}-$), 9.05 (d, 2 H, H^2 and H^6). – ^1H NMR spectroscopic data (in $[\text{D}_6]\text{DMSO}$):^[33] *Major isomer, 5a* ($\{(\text{S}_{\text{C}},\text{R}_{\text{S}})\}$): $\delta = 2.88$ (s, 3 H, $-\text{SMe}$), 2.96–3.11 (m, 2 H, $-\text{SCH}_2-$), 3.40–3.90 (m, 2 H, $-\text{CH}_2-$), 4.07 (s, 3 H, $-\text{OMe}$), 4.96 (m, 1 H, $>\text{CH}-$), 7.69–7.82 (m, 3 H, H^3 , H^4 , and H^5), 8.38 (s, 1 H, $-\text{CH}=\text{N}-$), 9.23 (d, 2 H, H^2 and H^6). – $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic

data (in $[D_6]DMSO$):^[33] *Major isomer, 5a* $\{(S_C, R_S)\}$: δ = 21.1 (–SMe), 29.3 (–SCH₂–), 30.7 (–CH₂–), 53.2 (OMe), 70.5 (>CH–), 132.0 (C¹), 132.3 (C² and C⁴), 129.2 (C³ and C⁵), 134.7 (C⁴), 168.4 (–CO₂), 178.3 (–CH=N–).

Preparation of (S_C, R_S) -(+)-[Pd{C₆H₄–CH=N–CH(CO₂Me)–CH₂–CH₂–SMe}Cl] (6a): This complex was isolated by two different procedures using either compounds **1** or **5** [methods (a) and (b), respectively] as starting materials.

Method A: A 100 mg amount ($3.98 \cdot 10^{-4}$ mol) of **1** was dissolved in 10 mL of methanol. Na₂[PdCl₄] (117 mg, $3.98 \cdot 10^{-4}$ mol) and NaOAc (33 mg, $4.0 \cdot 10^{-4}$ mol) were then added and the mixture was refluxed for 2 h. The solid formed was removed by filtration and discarded. Slow evaporation of the filtrate produced the precipitation of a yellow solid, which was filtered out and air-dried. (Yield 87 mg, 56).

Method B: Compound **5** (98 mg, $2.28 \cdot 10^{-4}$ mol) was suspended in methanol (15 mL), and a solution of NaOAc (19 mg, $2.31 \cdot 10^{-4}$ mol) and 10 mL of methanol was added. The mixture was refluxed for 2 h and filtered out. The filtrate was allowed to evaporate at ca. 20 °C and the solid formed was collected by filtration and air-dried. (Yield 58 mg, 68%). C₁₃H₁₆ClNO₂PdS: calcd. (found) C 39.8 (39.8), H 4.1 (4.2), N 3.6 (3.6), S 8.2 (8.3). – IR: ν (–CO): 1736 cm^{–1} and ν (>C=N–): 1601 cm^{–1}. – ¹H NMR spectroscopic data (in CDCl₃):^[33] δ = 2.51 (s, 3 H, –SMe), 2.22–2.70 (m, 2 H, –SCH₂–), 2.58–2.72 (m, 2 H, CH₂–), 3.80 (s, 3 H, –OMe), 4.42

(m, 1 H, >CH–), 8.06 (s, 1 H, –CH=N–), 7.33 (d, 1 H, H³), 7.09 (t, 1 H, H⁴), 7.21 (t, 1 H, H⁵), 7.94 (t, 1 H, H⁶). – ¹³C{¹H} NMR spectroscopic data (in CDCl₃):^[33] δ = 19.9 (–SMe), 27.6 (–SCH₂–), 30.4 (–CH₂–), 53.1 (–OMe), 66.6 (>CH–), 179.8 (–CH=N–), 169.2 (–CO₂), 144.0 (C¹), 160.1 (C²), 128.2 (C³), 124.9 (C⁴), 131.6 (C⁵), 134.7 (C⁶). – $[\alpha]_{24}^{25}$ (c = 0.05 g/100 mL) = –51.6. – FAB⁺(selected data): 391 [M + H]⁺, 357 [M – Cl]⁺.

Preparation of (S_C) -[Pt{C₆H₄–CH=N–CH(CO₂Me)–CH₂–CH₂–SMe}Cl(PPh₃)₂] (7a): This complex was prepared on an NMR spectroscopic scale. A 10 mg ($2.05 \cdot 10^{-5}$ mol) amount of **3a** was dissolved in 0.7 mL of CDCl₃, then PPh₃ (11 mg, $4.16 \cdot 10^{-5}$ mol) was added. The mixture was stirred vigorously for 5 min. at ca. 20 °C and the pale solution was characterized by NMR spectroscopies. – ¹H NMR spectroscopic data (in CDCl₃):^[33] δ = 2.59 (s, 3 H, –SMe), 2.54 and 2.72 (m, 2 H, –SCH₂–), 2.61 and 2.75 (m, 2 H, –CH₂–), 3.75 (s, 3 H, –OMe), 5.72 [br., 1 H, >CH–], 6.45 [d, 1 H, H³], 6.90 [t, 1 H, H⁴], 6.58 (t, 1 H, H⁵), 8.68 (s, 1 H, –CH=N–) and 7.10–7.80 (m, 31 H, H⁶ and protons of PPh₃). – ¹³C{¹H} NMR spectroscopic data (in CDCl₃):^[33–35] δ = 16.6 (–SMe), 29.9 (–SCH₂–), 30.0 (–CH₂–), 57.7 (–OMe), 68.3 (>CH–), 171.4 (–CO₂), 168.6 (–CH=N–), 131.8 (C³), 123.4 (C⁴), 132.6 (C⁵), 138.1 (C⁶). – ¹⁹⁵Pt NMR (in CDCl₃): δ = –4439, ¹J(¹⁹⁵Pt–³¹P) = 3637. – ³¹P NMR spectroscopic data (in CDCl₃): δ = 13.69, ¹J(³¹P–¹⁹⁵Pt) = 3635.

Preparation of (S_C) -[Pd{C₆H₄–CH=N–CH(CO₂Me)–CH₂–CH₂–SMe}Cl(PPh₃)₂] (9a): This complex was prepared according to the procedure described for **7a** but using **6a** (40 mg, $5.1 \cdot 10^{-5}$ mol) and PPh₃ (54 mg, $2.06 \cdot 10^{-5}$ mol). – ¹H NMR spectroscopic data (in CDCl₃):^[33] δ = 2.09 (s, 3 H, –SMe), 2.38 and 2.48 (m, 2 H, –SCH₂–), 2.60 and 2.65 (m, 2 H, –CH₂–), 3.74 (s, 3 H, –OMe), 5.46 (m, 1 H, >CH–), 6.39 (d, 1 H, H³), 6.90 (t, 1 H, H⁴), 6.56 (t, 1 H, H⁵), 8.42 (s, 1 H, –CH=N–), 7.30–8.60 (m, 31 H, H⁶ and protons of PPh₃). – ¹³C{¹H} NMR spectroscopic data (in CDCl₃):^[33–34] δ = 15.3 (–SMe), 30.5 (–SCH₂–), 31.8 (–CH₂–), 52.4 (–OMe), 65.0 (>CH–), 171.7 (–CO₂), 177.3 (–CH=N–), 158.8 (C¹), 147.90 (C²), 130.8 (C³), 124.0 (C⁴), 128.9 (C⁵), 138.1 (C⁶). – ³¹P NMR spectroscopic data (in CDCl₃): δ = 28.86.

Crystallography: A prismatic crystal of **3a** was selected and mounted on an Enraf CAD4 four-circle diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections in the range 12° < Θ < 21° and refined by least-squares method. Intensities were collected with graphite monochromated Mo-K α radiation, using $\omega/2\Theta$ scan technique. Three reflections were measured every 2 h as orientation and intensity control, and no significant intensity decay was observed. Lorentz-polarization and absorption corrections were made. The structure was solved by Direct methods using the SHELXS97 computer program^[36] and refined by full-matrix least-squares method with the SHELXL97 computer program^[37] using 2526 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w[F_o - F_c]^2$, where $w = [\sigma^2(I) + (0.0795 P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. f , f' , and f'' were obtained from the literature.^[38] The chirality of the structure was defined from the Flack coefficient.^[39] All the hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. The final R (on F) factor was 0.048 and wR (on F) = 0.112. Further details concerning the resolution and refinement of the crystal structure of **3a** are presented in Table 1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152831. Copies of the data can be ob-

Table 1. Crystal data and details of the refinement of the crystal structure of **3a**

Empirical formula	C ₁₃ H ₁₆ ClNO ₂ PtS
<i>Mr</i>	480.88
Crystal size [mm × mm × mm]	0.1 × 0.1 × 0.2
<i>a</i> [Å]	8.797(4)
<i>b</i> [Å]	9.605(9)
<i>c</i> [Å]	18.205(6)
α , β , γ [deg.]	90.0
<i>V</i> [Å ³]	1538.2(17)
Crystal System	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>Z</i>	4
λ [Å]	0.71069
<i>T</i> [K]	293(2)
<i>D</i> _{calcd.} [Mg·m ^{–3}]	2.081
Absorption coefficient [mm ^{–1}]	9.891
<i>F</i> (000)	912
Θ range for data collection [deg.]	from 2.57 to 29.94
Refinement method	Full-matrix least-squares on <i>F</i> ²
Number of collected reflections	2571
Number of independent reflections	2552 [<i>R</i> (int) = 0.0107]
Number of data	2526
Number of parameters	173
Goodness of fit on <i>F</i> ²	0.994
Final <i>R</i> indices [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0484, <i>wR</i> ₂ = 0.1124
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0709, <i>wR</i> ₂ = 0.1205
Absolute structure parameter	0.00(2)
Largest difference peak and hole [eÅ ^{–3}]	0.835 and –0.894

tained free of charge on applications to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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