Activation of σ(C−H) Bonds in $C_6H_5CH{=}NCH_2CH_2SEt$ Induced by Platinum(II). X-ray Crystal Structure of $[Pt\{C_6H_4CH{=}NCH_2CH_2SEt\}Cl]$

Xavier Riera,[†] Amparo Caubet,*[,†] Concepción López,*[,†] Virtudes Moreno,[†] Xavier Solans,[‡] and Mercè Font-Bardía[‡]

Departament de Química Inorgànica, Facultat de Química, Martí Franquès 1-11, Universitat de Barcelona, 08028-Barcelona, Spain, and Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Martí Franquès s/n, Universitat de Barcelona, 08028-Barcelona, Spain

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The study of the reactivity of $C_6H_5CH{=}NCH_2CH_2SEt$ with platinum(II) salts is reported. These studies have established the relative importance of the factors governing the formation of $[Pt\{C_6H_4CH{=}NCH_2CH_2SEt\}Cl]$, in which the ligand acts as a $[C,N,S]^-$ terdentate group.

The study of cyclometalated complexes has attracted great interest in the past decade mainly due to their applications in several areas.[1] Among the wide variety of cyclometalated complexes reported so far, those containing platinum have attracted additional attention since some of them have shown outstanding photochemical, photophysical, and electrochemical properties.[2] In addition, several examples of platinacycles showing antitumor activity have also been reported.[3,4]

A wide variety of cycloplatinated complexes containing $[C,N]^-$ bidentate[4−6] and $[C,N,N']^-$ or $[N,C,N']^-$ terdentate groups[7] have been described. However, few articles focus on platinacycles with terdentate $[C,N,S]^-$ groups. To our knowledge, only three examples of platinacycles containing $[C,N,S]^-$ chelating ligands have been reported.[8−10] Two of them arise from the activation of $\sigma(C_{sp^2}-H)$ bonds of benzylthio- or benzosulfinyl-substituted azobenzenes (Figure 1, **1** and **2** respectively),[8,9] and the other involves an N-donor substrate in which the sulfur atom belongs to a thiophene ring (Figure 1, **3**).[10] On this basis we decided to prepare and characterize the ligand $C_6H_5CH{=}NCH_2CH_2SEt$ (**4**) (Figure 1) and to study its reactivity versus platinum(II).

Ligand **4** may produce different sorts of platinum(II) compounds depending on the mode of coordination of the ligand. In addition, recent studies on the cycloplatination of 2-methyl-1-phenylbutan-1-one oxime, using *cis*-$[PtCl_2(dmso)_2]$ as metalating agent, report the isolation and structural characterization of the platinum(IV) derivative $[PtCl_3(SMe_2)\{C_6H_4[C(Et)]{=}NOH\}]$.[11] Consequently, the formation of the platinum(IV) derivatives cannot be ruled out.

The ligand was prepared by condensation of equimolar amounts of benzaldehyde and (2-ethylthio)ethylamine and characterized by infrared and NMR spectroscopy (see Experimental Section). According to NMR data, only one isomer (*E*-form) of **4** was present in solution. When **4** was treated with *cis*-$[PtCl_2(dmso)_2]$

[†] Departament de Química Inorgànica
[‡] Departament de Cristal.lografia.

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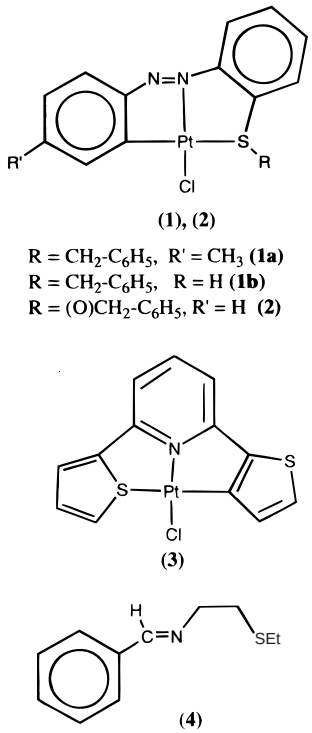


Figure 1. Schematic view of the platinum(II) compounds containing terdentate $[C,N,S]^-$ ligands described so far, **1**−**3**, and of ligand **4**.

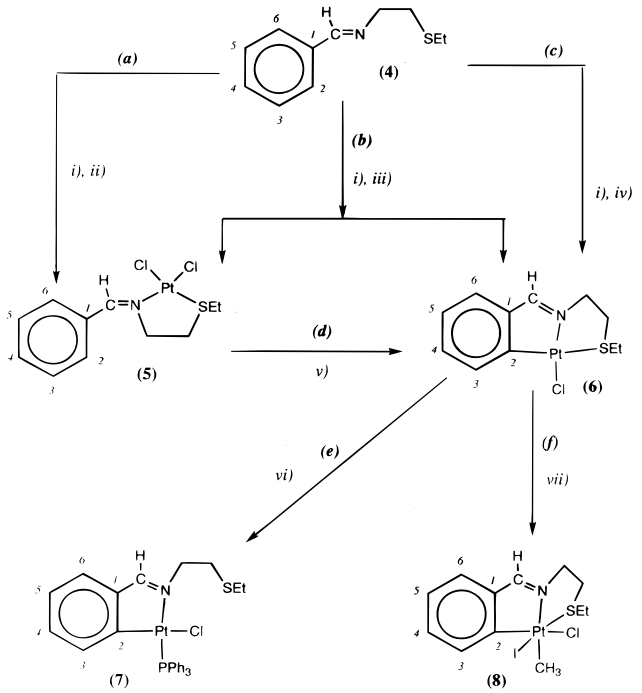
{Scheme 1, step (*a*)} for 1 h in refluxing methanol complex, *cis*-[Pt{C_6H_5CH═NCH_2CH_2SEt}Cl_2] (**5**) formed. In **5**, the ligand behaves as a neutral [N,S] bidentate group, and NMR data indicated that the ligand adopts the *Z*-form.

However, when the reaction time was progressively increased, the yield of **5** decreased {80% (1 h) and 58% (3 h)}, and an orange crystalline solid was isolated, by slow evaporation of the filtrate, in a low yield (ca. 13%) {Scheme 1, step (*b*)}. This material was identified (vide infra) as the cycloplatinated complex [Pt{C_6H_4CH═NCH_2CH_2SEt}Cl] (**6**), in which the ligand acts as a $[C,N,S]^-$ terdentate group. Compound **6** arises from the activation of the ortho σ(C−H) bond of the aryl ring, and its X-ray crystal (see below) revealed an *E*-form of the ligand. The ratio of **6** to **5** increased with time, which suggested that **5** might be an intermediate compound between the starting material **4** and **6**. This finding is consistent with the results obtained by Ryabov et al.[11] on the cyclopalladation of aryl and ferrocenyloximes and agrees with the mechanism proposed for the cycloplatination of N-donor ligands.[12]

The transformation of **5** to **6** requires the isomerization of the ligand {from the *Z*-form (in **5**) to the *E*-form (in **6**)} and the formation of a σ(Pt−C) bond, in which the HCl is abstracted. On this basis, we decided to study if the presence of a base would favor the formation of **6**. When the reaction was performed in the presence of $NaCH_3COO$ {Scheme 1 step (*c*)}, **6** was isolated in a higher yield. In addition, when **5** was treated with $NaCH_3COO$ {Scheme 1 step (*d*)}, a 72% conversion of **5** into **6** was achieved after 2 h, thus confirming that the presence of the acetate favors the formation of **6**.

To fulfill the study of the reactivity of **4** versus platinum(II) salts, the method reported by Chakravorty et al.[8,9] for the cycloplatination of benzylthio- and benzosulfinyl-substituted azobenzenes (Figure 1, **1** and **2**) was also used. When **4** was used as starting material, a solid formed. Its ^1H NMR spectrum revealed the presence of **5**, *cis*-[Pt{$H_2NCH_2CH_2SEt$}Cl_2] (**5′**), previously reported,[13] and benzaldehyde, but no evidence for the formation of any platinacycle was detected. The formation of **5′** and the aldehyde may be related to higher proclivity of **4** to hydrolysis.

Scheme 1[a]



[a] (*i*) *cis*-[$PtCl_2(dmso)_2$] in refluxing methanol. (*ii*) 1 h. (*iii*) See text. (*iv*) In the presence of a stoichiometric amount of $NaCH_3COO$ under reflux (12 h). (*v*) $NaCH_3COO$ in refluxing methanol (2 h). (*vi*) PPh_3 in $CDCl_3$ at room temperature. (*vii*) CH_3I in acetone at room temperature (4 h).

All the reactions summarized in this section reveal the advantages of using *cis*-[$PtCl_2(dmso)_2$] or even **5** as starting materials to activate the σ($C_{sp^2,aryl}$−H) bond in **4**. On the other hand, since **4** has a prochiral S-donor atom, and there is no other source of chiral induction, **6** is expected to consist of an equimolar mixture of the two enantiomers.

Potentially terdentate chelating ligands $[N,C,X]^-$ {where X = N, P, or O} or [C,N,N′] may adopt different bonding modes and hapticities, which is relevant to catalytic processes. Furthermore, some platinum(II) metallacycles containing bi- {$[C,N]^-$} or terdentate {$[C,N,N']^-$ or $[N,C,N']^-$} ligands undergo oxidative addition in the presence of alkyl halides or Cl_2 in mild conditions to produce platinum(IV) compounds.[14] On these bases, and in order to explore the bonding abilities and the proclivity of the platinum(II) to oxidize in **6**, we proceeded to study its reactivity versus PPh_3 and CH_3I.

The addition of a stoichiometric amount of PPh_3 to a solution of **6** in $CDCl_3$ at room temperature produced

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[Pt($C_6H_4CH{=}NCH_2CH_2SEt$}Cl(PPh_3)] (**7**) {Scheme 1 step (*e*)}, which results from the cleavage of the Pt−S bond and the incorporation of a PPh_3 in the coordination sphere of the platinum(II), thus suggesting that in **6** the Pt−S bond is more labile than the Pt−N bond. This result is similar to that reported for the related platinacycles with $[C,N,N']^-$ terdentate ligands, such as [PtMe{($C_6R_xH_{(4-x)}$)$CH{=}NCH_2CH_2NMe_2$}] {R = Cl or F}.[7c,d] When **7** was treated with an excess of PPh_3 {molar ratio **7**:PPh_3 = 1:5} in $CDCl_3$, no significant changes were detected in the NMR spectra in any case, thus suggesting that the cleavage of the Pt−N bond did not occur. This finding is consistent with previous studies on platinacycles containing $[C,N]^-$ chelating groups which have shown that, depending on the nature of the metallacycle and the basicity of the nitrogen, the Pt−N bond can be cleaved.[15]

As a first approach to study proclivity of the platinum(II) in **6** to oxidize, its reactivity with CH_3I was studied by NMR. Addition of a large excess of CH_3I to an acetone solution of **6** produced [PtMeICl{$C_6H_4CH{=}NCH_2CH_2SEt$}] (**8**), which arises from the oxidative addition of CH_3I to the platinum(II) {Scheme 1, step (*f*)}. This result is similar to that obtained in the reaction of [PtMe{(3-ClC_6H_3)$CH{=}NCH_2CH_2NMe_2$}] (which contains a $[C,N,N']^-$ terdentate ligand) with CH_3I to produce the platinum(IV) complex [$PtMe_2I${(3-ClC_6H_3)$CH{=}NCH_2CH_2NMe_2$}] under mild conditions.[7c]

All these compounds were characterized by elemental analyses and infrared and NMR spectroscopy. In all cases the elemental analyses were consistent with the proposed formulas (see Experimental Section). The infrared spectra of **5**−**8** showed a sharp, intense band in the range 1500−1650 cm^{-1}, which is ascribed to the stretching of the >C=N− group. This band appears at lower frequencies than for **4**, indicating the binding of the nitrogen to the platinum. Similar trends have also been reported for cyclopalladated[16] and cycloplatinated complexes derived from aldimines and ketimines.[6c,17,18]

Proton-NMR spectroscopic data for the compounds under study are summarized in the Experimental Section. In some cases the spectra were recorded in different solvents to facilitate the interpretation of the variations observed in the positions of the signals. Previous NMR studies of palladium(II) and platinum(II) compounds containing imines have shown that the chemical shift of the methinic proton is indicative of the conformation of the ligand.[6c,17−19] For instance, if the ligand is in the *Z*-form, the signal of the imine proton in the complexes is shifted downfield relative to the corresponding free ligand; this variation is due to the paramagnetic anisotropy of the metal,[20] which is close to the imine proton. In contrast, for complexes containing the imine in the *E*-form, the signal due to the proton of the −CH=N− group is shifted upfield. So, comparison of the ^1H NMR spectra of the platinum(II) compounds and that of **4** reveals not only the mode of binding of the ligand but also its conformation (*E*- or *Z*-form). The shift of the signal due to the imine proton in **4** {δ = 8.36 ppm, in dmso-d_6} and in **5** {δ = 9.49 ppm, in dmso-d_6} suggested a *Z*-form of the imine in **5**. This finding agrees with the results reported for *trans*-[Pt{(η^5-C_5H_5)-Fe[(η^5-C_5H_3)C(H)=NR]}Cl_2(dmso)] {with R = CH_2CH_2-NMe_2, CH_2CH_2SEt, or CH(COOMe)CH_2CH_2SMe}.[17] In contrast, the signal of the imine proton in **6** {δ = 7.84 ppm in $CDCl_3$} appeared at higher fields than in **4** {δ = 8.29 ppm in $CDCl_3$}, thus suggesting that the imine is in the *E*-form. The formation of the platinacycle requires the appropiate orientation of the σ(C−H) bond to be activated versus the metal. This is possible only if the aryl ring and the group bound to the nitrogen are in trans-arrangement (*E*-form).

The imine proton is strongly coupled with ^{195}Pt in **6** and **7** {^3J(Pt−H) = 134 Hz for **6** and 92 Hz for **7**}, and this coupling is stronger than that observed for the [PtMe{$C_6H_xR_{(4-x)}CH{=}NCH_2CH_2NMe_2$}] with R = Cl or F {$^3J$(Pt−$H_{imine}$) falls in the range 50−70 Hz}.[7c,d] In addition, the formation of the platinacycle produces a strong high-field shift of the signal due to the proton in the adjacent position to the metalated carbon, H^3. This trend is in good agreement with the results reported for platinacycles containing σ(Pt−$C_{sp^2,aryl}$) bonds.[7c,d,8,9,11,21] Furthermore, the H^3 proton is strongly coupled with the platinum. The values of ^3J(Pt−H) are {42 Hz in **6** and 49 Hz in **7**} similar to those of [Pt{C_6H_4−C(R)=NOH}-Cl(dmso)] with R = CH_3 (51 Hz) or NH_2 (52 Hz).[11]

The signals due to the protons of the ">N−CH_2−CH_2−S−" fragment appeared as multiplets in the platinum compounds due to their diastereotopicity. For **8**, the resonance of the methyl group {δ = 1.27 ppm} and the value of the coupling constant {^2J(Pt−H) = 98 Hz} are consistent with a trans-arrangement of the CH_3 group and the nitrogen {δ(CH_3) (in acetone-d_6) in the range 1.20−1.50 ppm and ^2J(Pt−H) varying from 59 to 80 Hz}.[6c,7c,d] Since oxidative additions of methylhalides to platinum(II) complexes occur with trans-stereochemistry, this finding suggests that a rearrangement of ligands similar to those reported for [$PtMe_2I${$C_6H_4CH{=}NCH_2CH_2NMe_2$}I] takes place after the oxidative addition.[7a]

Carbon-13 NMR and 2D {^1H−^{13}C} heteronuclear NMR experiments showed a downfield shift of the resonances due to the imine carbon {ca. 10−18 ppm} and to the metalated C^2 atom upon coordination and confirmed the mode of binding of the ligand in **5**−**7**.

The ^{195}Pt NMR spectra not only provided convincing evidence for the coordination sphere and structure of the platinum(II) derivatives but also explained the variations produced by the different mode of binding of **4** in the platinum(II) complexes. The spectrum of **5** showed one signal at −2927 ppm, the position of which is consistent with the values reported for related complexes containing an [N,S,Cl_2] environment around the platinum(II).[22] The differences detected in the

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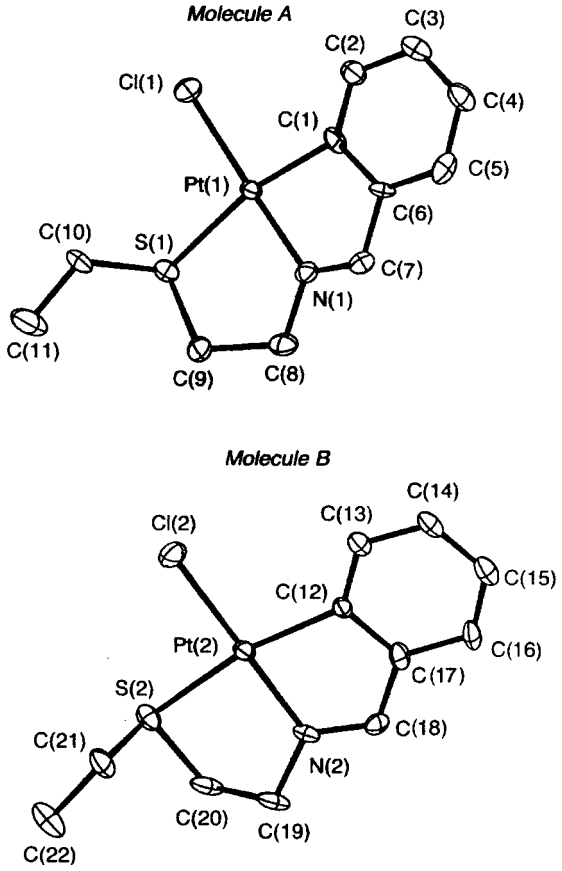

Figure 2. View of the two independent molecules (**A** and **B**) found in the crystal structure of **6** together with the atom-numbering scheme.

chemical shift of ^{195}Pt of **5** [−2927 ppm] and **5′**, in which the (2-ethylthio)ethylamine acts as an [N,S] bidentate group [δ = −2972 ppm],[13] can be interpreted on the basis of the different basicity of the N-donor group {N_{amine} in **5′** and N_{imine} in **5**}.

The chemical shift of ^{195}Pt in **6** [δ = −3716 ppm] was consistent with the range expected for complexes containing a [C,N,S,Cl] environment around the platinum(II).[6b] The comparison of the positions of the signals in **5** [δ = −2927 ppm] and **6** [δ = −3716 ppm] reveals that the formation of the metallacycle is reflected in an upfield shift, which is typical of a strong donor interaction with platinum(II). This finding has also been reported for platinum(II) compounds containing neutral N-donor ferrocenylamines and their cycloplatinated derivatives.[6a,b]

The ^{195}Pt NMR spectra of **7** showed a doublet {^1J(P−Pt) = 3806 Hz} centered at −4485 ppm. The position and multiplicity of the signal are consistent with a [C,N,P,Cl] environment around the platinum(II)[6a,b] such as [Pt{(η^5-C_5H_5)Fe[(η^5-C_5H_3)CH_2NMe_2}Cl(PPh_3)] (**7′**) [δ = −4173 ppm].[6a] According to the literature, an upfield shift in ^{195}Pt NMR is related to a strong donor interaction, and since **7** and **7′** differ only in the nature of their chelating [C,N]$^-$ ligand, the variations observed in their ^{195}Pt NMR spectra can be ascribed to the different donor abilities of the metalated group.

The ^{31}P chemical shift of **7** [δ = 19.15 ppm, ^1J(Pt−P) = 3801 Hz] suggested a trans-arrangement of the PPh_3 and the imine nitrogen. Similar values have been reported for **7′** [δ = 17.21 ppm, ^1J(Pt−P) = 4291 Hz][6a]

Table 1. Selected Bond Lengths (in Å) and Angles (in deg) for the Two Molecules (A and B) of [Pt{C_6H_4CH=NCH_2CH_2SEt}Cl] (6)[a]

(a) Bond Lengths

molecule **A**		molecule **B**	
Pt(1)−C(1)	1.994(8)	Pt(2)−C(12)	2.030(7)
Pt(1)−Cl(1)	2.280(3)	Pt(2)−Cl(2)	2.296(3)
Pt(1)−S(1)	2.327(3)	Pt(2)−S(2)	2.341(3)
Pt(1)−N(1)	1.948(6)	Pt(2)−N(2)	1.963(7)

(b) Bond Angles

molecule **A**		molecule **B**	
N(1)−Pt(1)−C(1)	80.8(3)	N(2)−Pt(2)−C(12)	82.1(3)
C(1)−Pt(1)−Cl(1)	96.2(3)	C(12)−Pt(2)−Cl(2)	97.0(2)
N(1)−Pt(1)−S(1)	86.4(2)	N(2)−Pt(2)−S(2)	85.4(2)
Cl(1)−Pt(1)−S(1)	96.57(10)	Cl(2)−Pt(2)−S(2)	95.56(11)
N(1)−Pt(1)−C(1)	176.4(2)	N(2)−Pt(2)−Cl(2)	178.3(2)

[a] Standard deviation parameters are given in parentheses.

and related mono- and bis(cycloplatinated) complexes with a [C,N,Cl,P] environment around the platinum(II) and a similar distribution of the N- and P-donor groups.[6]

The molecular structure of **6** together with the atom-labeling scheme is depicted in Figure 2, and a selection of bond lengths and angles is presented in Table 1. The structure consists of two different and discrete molecules of [Pt(C_6H_4CH=NCH_2CH_2SEt}Cl] (hereinafter referred to as **A** and **B**), separated by van der Waals contacts. In these two molecules, the platinum {Pt(1) or Pt(2)} is bound to a chloride {Cl(1) or Cl(2)}, a sulfur {S(1) or S(2)}, the imine nitrogen {N(1) or N(2)}, and the ortho carbon of the phenyl ring {C(1) or C(12)} in a slightly distorted square-planar environment.[23] Each molecule contains a [5,5,6] tricyclic system derived from the fusion of the five-membered chelate ring formed by the coordination of the sulfur and nitrogen to the platinum(II), a five-membered platinacycle, and the phenyl ring. This confirms the conclusions reached from NMR studies, which suggested that the ligand behaves as a monoanionic [C,N,S]$^-$ terdentate ligand in this case.

The Pt−S bond lengths [2.327(3) Å in **A** and 2.341(3) Å in **B**] are clearly greater than the value usually reported for platinum(II)−S(thioether) derivatives [ca. 2.25 Å].[24] This variation can be explained in terms of the strong trans-influence of the metalated carbon.[25] The remaining Pt−ligand bond distances are similar to those found in five-membered platinacycles containing a σ(Pt−$C_{sp^2,aryl}$) bond derived from arylimines.[26]

The metallacycles that are formed by the atoms Pt(1), C(1), C(6), C(7), and N(1) in **A** and Pt(2), C(12), C(17),

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(23) The least-squares equation of the planes defined by the sets of atoms Pt(1), Cl(1), N(1), S(1), and C(1) (in **A**) and Pt(2), Cl(2), N(2), S(2), and C(12) (in **B**) are (0.1639)XO + (0.9322)YO + (−0.3226)ZO = −0.3687 and (−0.1740)XO + (0.9760)YO + (0.1312)ZO = 6.1251, respectively. The deviations from the main planes are in **A** Pt(1), −0.013; S(1), −0.015; N(1), +0.027; Cl(1), +0.019; and C(1), −0.019 Å, and in **B** Pt(2), −0.062; Cl(2), −0.025; S(2), +0.059; N(2), −0.041; and C(12), +0.069 Å.

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C(18) and N(2) in **B** are practically planar[27] and contain the >C=N− functional group (*endocyclic*). The >C=N− bond lengths [1.249(10) Å (in **A**) and 1.304(10) Å (in **B**)] lie in the range described in the literature for related five-membered platinacycles derived from imines.[26] The ligand has an anti-conformation {*E*-form}, as reflected in the torsion angles C(6)−C(7)−N(1)−C(8) = 168.17(7)° (in **A**) and C(17), C(18), N(2), and C(19) = 168.17(7)° (in **B**). The phenyl rings are planar, and they form an angle of 4.7° or 3.8° (**A** and **B**, respectively) with the plane of the corresponding platinacycle.

The five-membered chelate rings formed by the platinum and the "{=N−CH_2−CH_2−S−}" moiety exhibit an envelope-like conformation. In **A** the atoms Pt(1), S(1), N(1), and C(8) are nearly coplanar,[28] and the C(9) deviates by 0.5855 Å toward the C(10) atom; in **B** the C(20) is {−0.8278 Å} out of the plane[29] defined by the remaining atoms, in the opposite direction of C(21).

To elucidate whether the different nature of the terdentate group $[C,N,S]^-$ could affect the structures of the platinacycles, a comparison of bond lengths and angles involving the platinum(II) in **6** (Table 1) and in **1a**[9] was carried out. In the two independent molecules of **6**, the Pt−C, Pt−N, and Pt−Cl bond distances are similar to those of **1a** {Pt−C 1.999(8) Å, Pt−N 1.946(8) Å, and Pt−Cl 2.293(3) Å}, while the Pt−S bond is slightly shorter [Pt−S in **1a** 2.359(3) Å] (if significant, since the differences hardly exceed 3σ). The main structural differences are found in N−Pt−C and Cl−Pt−S bond angles. In **1a**, the N−Pt−C bond angle [79.1(3)°] is smaller than in **6**, while the opposite trend is found for the Cl−Pt−S bond angle [in **1a** 92.2(1)° and in **6** 96.57(10)° (in **A**) and 95.56(11)° (in **B**)]. The normalized (S,N) bite, $b_{(S,N)}$ {1.36}, for **1a** and **6** does not differ significantly from that reported for the 2-(ethylthio)ethylamine {$b_{(S,N)}$ = 1.38(1)}.[13,26]

The high values obtained for the intermolecular Pt(1)···Pt(2) (5.5803(2) Å) and S(1)···S(2) (5.3329(4) Å) distances preclude any direct interaction between the two pairs of atoms. The crystal structure also confirms that **6** consists of a 1:1 mixture of the two enantiomers {*R* and *S* isomers}, which is consistent with the lack of chiral induction during the cycloplatination process.

Conclusions. Although several authors have reported the syntheses of cycloplatinated(II) complexes, in most of the cases the isolation of these complexes proceeds in low yield. The results presented here provide (a) a useful method to prepare platinum(II) compounds in which **4** can act not only as a neutral [S,N] donor (in **5**) and as monoanionic bidentate $[C,N]^-$ ligand (in **7**) but also as a $[C,N,S]^-$ terdentate group (in **6** and **8**), in good yields and (b) conclusive evidence for the importance of the presence of $NaCH_3COO$ in the cycloplatination process.

On the other hand, it has been recently reported that platinum(II) complexes of general formula *cis*-$[PtCl_2\{[4\text{-}RC_6H_4]CH_2CH{=}NNHC(S)NH_2\}]$ {with R = H or CHMe}[30] (formally analogous to **5**) show higher cytotoxic activity versus cisplatin-resistant tumor cells than that of other antitumor drugs (i.e., etoposide and andriamycin) and have a greater capacity to form DNA interstrand cross-links than cisplatin. Furthermore, the antitumor properties of cyclometalated platinum(II) and even platinum(IV) complexes containing bi- and terdentate ligands have also been reported.[3,4,31] Thus, the compounds reported here (especially **5** and **6**) appear to be excellent candidates to study their interaction with DNA as well as their cytotoxic activity. Further work on this area is currently under way.

Experimental Section

General Comments. The benzaldehyde was obtained from standard sources and purified by distillation before use. The 2-(ethylthio)ethylamine hydrochloride was obtained from Aldrich and transformed to the free amine before use. *cis*-$[PtCl_2(dmso)_2]$ was prepared as described before.[32] All the solvents used in this study were HPLC grade. Elemental analyses (C, H, N, and S) were carried out at the Serveis Científico-Tècnics(Universitat de Barcelona). Infrared spectra were obtained with a NICOLET-Impact 400 instrument. ^{1}H NMR and the 2D-heteronuclear {^{1}H−^{13}C} NMR experiments were run at 500 MHz either in a Varian VXR-500 or in a Bruker Avance 500DMX-500 instrument. The solvents and references used are specified in the characterization section of each compound. ^{13}C NMR spectra and ^{195}Pt NMR spectra of **5**−**7** were recorded with a Bruker-250 DRX instrument. The ^{195}Pt chemical shifts given are referred to a $Na_2[PtCl_6]$ solution in D_2O as the external reference. ^{31}P NMR spectrum of **7** was obtained with a Bruker-250-DRX instrument using $CDCl_3$ as solvent and $P(OMe)_3$ as reference [$\delta^{31}P\{P(OMe)_3\}$ = 140.17 ppm]. In all cases the chemical shifts (δ) are given in ppm and the coupling constants (J) in Hz. The conductivity of the 10^{-3} M solutions of **5**−**8** were determined with a CRISON microCM 2200 conductimeter.

Preparation of 4. Benzaldehyde (390 mg, 3.68×10^{-3} mol) was added to a solution formed by the amine $H_2NCH_2CH_2$-SEt (284 mg, 3.66×10^{-3} mol) and 15 cm^3 of ethanol. The mixture was refluxed for 3 h. After this period the resulting solution was concentrated to dryness on a rotary evaporator to give a pale yellow oil (yield: 0.674 g, 95.4%). *Characterization data*: IR (NaCl disks): ν(>C=N−): 1644 cm^{-1}. ^{1}H NMR (in $CDCl_3$):[33] 1.25 [t, 3H, $-CH_3$, ^3J(H−H) = 7], 2.57 [q, 2H, −S-CH_2−CH_3, ^3J(H−H) = 7], 2.86 [t, 2H, $-CH_2-$, ^3J(H−H) = 7], 3.81 [t, 2H, N−CH_2-, ^3J(H−H) = 7], 7.42 [m, 3H, H^3, H^4, and H^5], 7.72 [d, 2H, H^2 and H^6, ^3J(H−H) = 8], 8.29 [s, 1H, −CH=N−]. In dmso-d_6:[33] 1.18 [t, 3H, $-CH_3$, ^3J(H−H) = 7], 2.57 [q, 2H, −S-CH_2−CH_3, ^3J(H−H) = 7], 2.80 [t, 2H, $-CH_2-$, ^3J(H−H) = 7], 3.75 [t, 2H, N−CH_2-, ^3J(H−H) = 7], 7.46 [m, 3H, H^3, H^4, and H^5], 7.76 [d, 2H, $H^2$and H^6, ^3J(H−H) = 8], 8.36 [s, 1H, −CH=N−]. ^{13}C NMR (in $CDCl_3$):[33] 15.46 [$-CH_3$], 25.87 [−S−CH_2−CH_3], 32.40 [$-CH_2-$], 61.24 [N−CH_2-], 135.56 [C^1], 129.20 [C^2 and C^6], 128.46 [C^3 and C^5], 131.23 [C^4]

(27) The least-squares equation of the planes defined by the sets of atoms Pt(1), N(1), C(1), C(6), and C(7) in **A** and Pt(2), N(2), C(12), C(17), and C(18) in **B** are (0.1927)XO + (0.9068)YO + (−0.3750)ZO = −0.6516 and (−0.2085)XO + (0.9711)YO + (0.1161)ZO = 6.1197. The deviations from the main plane are Pt(1), 0.352; N(1), −0.042; C(1), −0.034; C(6), 0.021; and C(7), 0.023 Å (in **A**) and Pt(2), 0.032; N(2), −0.031; C(12), 0.041; C(17), −0.033; and C(18), −0.006 Å in **B**.

(28) The least-squares equation of the plane defined by the atoms Pt(1), S(1), N(1), and C(8) is (0.0991)XO + (0.9425)YO + (−0.3192)ZO. The deviations from the main plane are Pt(1), −0.057; S(1), 0.037; N(1), 0.086; and C(8), −0.066 Å.

(29) The least-squares equation of the plane defined by the atoms Pt(2), S(2), N(2), and C(19) is (−0.1352)XO + (0.9763)YO + (0.1688)ZO = 6.0908. The deviations from the main plane are Pt(2), 0.0005; S(2), −0.0003; N(2), −0.0008; and C(19), 0.0006 Å.

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(33) Numbering of the atoms corresponds to that shown in Scheme 1.

and 162.19 [−*C*H═N−]. In dmso-d_6:[33] 14.93 [−CH_3], 26.38 [−S−CH_2−CH_3], 32.44 [−CH_2−], 61.65 [N−CH_2−], 135.86 [C^1], 128.83 [C^2 and C^6], 128.10 [C^3 and C^4], 130.68 [C^4] and 162.03 [−*C*H═N−].

Preparation of 5. *cis*-[$PtCl_2$(dmso)$_2$][32] (219 mg, 5.2×10^{-4} mol) was suspended in 40 cm^3 of methanol and refluxed until complete dissolution. Then **4** (100 mg, 5.2×10^{-4} mol) was added, and the mixture was refluxed for 1 h. The yellow solid formed was collected by filtration, washed in small amounts of methanol, air-dried, and finally dried on a silica desiccator (yield: 195 mg, 80%). *Characterization data*: Anal. (%) Calcd for $C_{11}H_{15}NCl_2PtS$ (found): C, 28.77 (28.85); H, 3.29 (3.25); N, 3.05 (2.9); and S, 6.98 (6.70). IR (KBr pellets): ν(>C═N−): 1625 cm^{-1}. ^{1}H NMR (in dmso-d_6):[33] 1.40 [t, 3H, −CH_3, ^3J(H−H) = 7], 2.70−3.00 [m, 2H, −S−CH_2−CH_3], 3.00−3.20 [m, 2H, −CH_2−], 4.00−4.30 [m, 2H, N−CH_2−], 7.00−7.40 [m, 5H, H^2, H^3, H^4 H^5, and H^6], 9.49 [s, 1H, −C*H*═N−, ^3J(Pt−H) = 52]. ^{13}C NMR (in dmso-d_6):[33] 12.98 [−CH_3], 31.80 [−S−CH_2−CH_3], 36.26 [−CH_2−], 60.64 [N−CH_2−], 130.57 [C^1], 129.57 [C^2 and C^6], 129.44 [C^3 and C^4], 132.26 [C^5], and 170.41 [−*C*H═N−]. ^{195}Pt NMR (in dmso-d_6): $\delta = -2927$.

Preparation of 6. A stoichiometric amount of **4** (45 mg, 2.33×10^{-4} mol) and $NaCH_3COO$ (20 mg, 2.4×10^{-4} mol) were added to a hot solution formed by *cis*-[$PtCl_2$(dmso)$_2$] (100 mg, 2.36×10^{-4} mol) and 20 cm^3 of methanol. The resulting suspension was refluxed for 12 h and filtered out to remove the unreacted **5**. The orange filtrate was then concentrated to ca. 10 cm^3 on a rotary evaporator. The slow evaporation of the solvent at ca. 20 °C produced bright orange crystals, which were collected by filtration and air-dried (yield: 82 mg, 82%). *Characterization data*: Anal. (%) Calcd for $C_{11}H_{14}NClPtS$ (found): C, 31.25 (31.3); H, 3.34 (3.3); N, 3.31 (3.1); S, 7.58 (7.7). IR (KBr pellets): ν(>C═N−): 1596 cm^{-1}. ^{1}H NMR (in $CDCl_3$):[33] 1.42 [t, 3H, −CH_3, ^2J(H−H) = 15, ^4J(Pt−H) = 26], 3.10 [br m, 4H, −S−CH_2−CH_3 and −CH_2−], 3.90 [m, 2H, N−CH_2−], 7.02 [t, 1H, H^5, ^3J(H−H) = 8, ^4J(Pt−H) = 26], 7.12 [d, 1H, H^3, ^3J(H−H) = 8, ^3J(Pt−H) = 42], 7.29 [t, 1H, H^4, ^3J(H−H) = 7, ^4J(Pt−H) = 46], 7.76 [d, 1H, H^6, ^3J(H−H) = 8, ^4J(Pt−H) = 35], 7.84 [t, 1H, −C*H*═N−, ^3J(H−H) = 2, ^3J(Pt−H) = 134]. In acetone-d_6:[33] 1.42 [t, 3H, −CH_3, ^3J(H−H) = 7], ^4J(Pt−H) = 21], 3.10 [br m, 2H, −S−CH_2−CH_3], 3.15 [t, 2H, −CH_2−, ^3J(H−H) = 7, ^3J(Pt−H) = 54], 4.20 [br m, 2H, N−CH_2−], 7.02 [d, 1H, H^5, ^3J(H−H) = 7, ^4J(Pt−H) = 30], 7.26 [d, 1H, H^3, ^3J(H−H) = 7, ^4J(Pt−H) = 40], 7.28 [t, 1H, H^4, ^3J(H−H) = 6, ^4J(Pt−H) = 55], 7.65 [d, 1H, H^6, ^3J(H−H) = 7, ^4J(Pt−H) = 43], 8.61 [s, 1H, −C*H*═N−, ^4J(H−H) = 2, ^3J(Pt−H) = 133]. ^{13}C NMR (in $CDCl_3$):[33] 13.37 [−CH_3, ^3J(Pt−C) = 41], 30.59 [−S−CH_2−CH_3, ^2J(Pt−C) = 49], 37.87 [−CH_2−, ^3J(Pt−C) = 45], 57.60 [N−CH_2−, ^2J(Pt−C) = 69], 152.24 [C^2], 127.75 [C^3, ^3J(Pt−C) = 33], 123.97 [C^4, ^3J(Pt−C) = 29], 131.84 [C^5], 131.71 [C^6, ^3J(Pt−C) = 41], and 174.02 [−*C*H═N−, ^2J(Pt−C) = 102]. ^{195}Pt NMR (in $CDCl_3$): $\delta = -3716$. Λ_M (10^{-3}M in $CHCl_3$): 32 Ω^{-1} cm^2 mol^{-1}.

Preparation of 7. PPh_3 (17.6 mg, 6.7×10^{-5} mol) was added to a solution formed by 28.6 mg (6.7×10^{-5} mol) of **6** and 0.5 cm^3 of $CDCl_3$. During the addition of the PPh_3, the color of the mixture changed from orange to bright yellow. The resulting solution was shaken vigorously for 5 min, and the solvent was then allowed to evaporate at ca. 20 °C. The pale yellow residue was treated with 5 cm^3 of *n*-hexane, and the solid was collected by filtration, washed in *n*-hexane, and air-dried (yield: 34 mg, 74%). *Characterization data:* Anal. (%) Calcd for $C_{29}H_{29}NClPPtS$ (found): C, 50.84 (50.5); H, 4.27 (4.4); N, 2.04 (2.05); S, 4.68 (4.2). IR (KBr pellets): ν(>C═N−): 1615 cm^{-1}. ^{1}H NMR (in $CDCl_3$):[33] 0.92 [t, 3H, −CH_3, ^3J(H−H) = 7], 2.30 [br m, 2H, −S−CH_2−CH_3], 3.30 [br m, 2H, −CH_2−], 4.65 [br m, 2H, N−CH_2−], 6.94 [t, 1H, H^5, ^3J(H−H) = 7], 6.66 [t, 1H, H^4, ^3J(H−H) = 7, ^4J(Pt−H) = 30], 6.36 [d, 1H, H^3, ^3J(H−H) = 7, ^3J(Pt−H) = 48], 7.41−7.61 [m, 16H, H^6 and PPh_3], 9.01 [d, 1H, −C*H*═N−, ^3J(Pt−H) = 92, ^4J(P−H) = 10]. ^{13}C NMR (in $CDCl_3$):[33] 14.11 [−CH_3, ^3J(Pt−C) = 18], 29.31 [−S−CH_2−CH_3], 36.96 [−CH_2−], 58.06 [N−CH_2−, ^2J(Pt−C) = 44], 141.76 [C^1], 150.74 [C^2, ^1J(C−Pt) = 85], 128.50 [C^3], 125.24 [C^4], 129.46 [C^5], 136.70 [C^6] and 179.65 [−*C*H═N−, ^2J(C−Pt) = 73] and four additional doublets centered at 134.49, 131.95, 131.22, and 128.91 due to the carbons of the PPh_3 ligand. ^{31}P NMR (in $CDCl_3$): $\delta = 19.15$ [^1J(Pt−P) = 3801]. ^{195}Pt NMR (in $CDCl_3$): $\delta = -4485$ [d, ^1J(P−Pt) = 3806]. Λ_M (10^{-3}M in acetone): 50 Ω^{-1} cm^2 mol^{-1}.

Preparation of 8. This complex was prepared at NMR scale as follows: **6** (6 mg, 1.4×10^{-6} mol) was dissolved in 2 cm^3 of acetone, and CH_3I (0.5 cm^3, 1.5×10^{-3} mol) was then added. The mixture was stirred at ca. 20 °C for 4 h. The solution was then filtered out, and the yellow filtrate was concentrated to dryness in a vacuum. *Characterization data*: IR (KBr pellets): ν(>C═N−): 1607 cm^{-1}. ^{1}H NMR (in acetone-d_6):[33] 1.27 [t, 3H, Pt−CH_3, ^2J(Pt−H) = 98], 1.42 [t, 3H, −CH_3, ^3J(H−H) = 7], 2.98 [m, 2H, −S−CH_2−CH_3], 3.35 [m, 2H, −CH_2−], 3.50 [br, m, 2H, N−CH_2−], 7.18 [d, 1H, H^3,^3J(H−H) = 7], 7.66 [t, 1H, H^4, ^3J(H−H) = 7], 7.38 [br, 1H, H^5], 7.76 [d, 1H, H^6, ^3J(H−H) = 7], 8.76 [s, 1H, −C*H*═N−, ^3J(H−Pt) = 112].

Crystallography. A bright orange prismatic crystal of **6** was selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit cell parameters (Table 2) were calculated from accurate settings of 25 automatically centered reflections in the range $12° \le \theta \le 21°$ and refined by the least-squares method. Intensities were collected with graphite-monochromated Mo Kα radiation using the $\omega-2\theta$ scan technique. The numbers of collected reflections were in the range $2.08° \le \theta \le 29.96°$, and those assumed as observed [$I > 2\sigma(I)$] are presented in Table 2. Three reflections were measured every 2 h as orientation and intensity control, and no significant intensity decay was observed. Lorentz−polarization corrections but not for absorption were made. The structure was solved by direct methods using the SHELXS computer program[34] and refined by full-matrix least-squares method with the SHELX93 computer program[35] using 5318 reflections (very

Table 2. Crystallographic Data for [Pt{C_6H_4CH═NCH_2CH_2SEt}Cl] (6)

formula	$C_{11}H_{14}ClNPtS$
M	422.844
T (K)	293(2)
cryst dimens (mm)	0.1 × 0.1 × 0.1
cryst syst	monoclinic
space group	$P2_1/n$
a (Å)	8.270(7)
b (Å)	14.917(6)
c (Å)	19.610(14)
α (deg)	90.0
β (deg)	92.04(7)
γ (deg)	90.0
V (Å^3)	2418(3)
Z	8
ρ_{calcd} (g cm^{-3})	2.329
μ (mm^{-1})	11.967
F(000)	1592
θ range for data collection (deg)	2.08−29.96
h, *k*, *l* ranges	$-11 \le h \le 11$; $0 \le k \le 20$; $0 \le l \le 27$
no. of collected reflns	5551
no. of ind reflns	5368 [*R*(int) = 0.0337]
no. of data/restrains/params	5318/0/272
goodness of fit on F^2	0.904
$R1$ [$F_o > 2\sigma(F_o^2)$][a]	0.0382
wR2[b]	0.0862
largest diff peak and hole (e Å^{-3})	0.858 and −0.754

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2 = \sum w(|F_o|^2 - |F_c|^2)/\sum w(|F_o|^2)$.

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negative intensities were not assumed). The function minimized was $\sum w||F_o|^2 - |F_c|^2|$, where $w = [\sigma^2(I) + (0.0536P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f', and f'' were obtained from the literature.[36] All hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. Further details concerning the resolution and refinement of the structure are presented in Table 2.

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Supporting Information Available: Tables containing final atomic coordinates for non-hydrogen atoms and equivalent isotropic temperature displacement parameters, a complete list of bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and hydrogen bond lengths and angles for **6** have been deposited as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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