

# Syntheses, displacement behavior, hetero-atom carbene, and crystal structures of platinum complexes containing the *N,N*-dimethylthiocarbamoyl, $\text{Me}_2\text{NC}=\text{S}$ , ligand: Structures of $[\text{Pt}(\text{PPh}_3)(\text{Cl})]_2(\mu, \eta^2\text{-SCNMe}_2)_2$ , $[\text{Pt}(\text{PPh}_3)(\eta^2\text{-dppa})\{\eta^1\text{-C}(\text{S})\text{NMe}_2\}][\text{Cl}]$ , and $[\text{Pt}(\text{PPh}_3)_2\{\eta^1\text{-C}(\text{SEt})(\text{NMe}_2)\}(\eta^2\text{-S}_2\text{CO})]$

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## Abstract

In solution state, the complex  $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$  (**1**) shows intermolecular displacement of two triphenylphosphine ligands to form the bridging  $\eta^2$ -thiocarbamoyl diplatinum complex  $[\text{Pt}(\text{PPh}_3)\text{Cl}]_2(\mu, \eta^2\text{-SCNMe}_2)_2$  (**2**). Intramolecular displacement of the chloride product  $\eta^2$ -thiocarbamoyl complex  $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-SCNMe}_2)][\text{Cl}]$  (**3**) was not been detected from the  $^{31}\text{P}\{^1\text{H}\}$  NMR experiments. However, the chelating  $\eta^2$ -thiocarbamoyl complex  $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-SCNMe}_2)][\text{PF}_6]$  (**4**) can be produced by the reaction of **1** with  $\text{NH}_4\text{PF}_6$  in acetone at ambient temperature. Treatment of **1** with *dppa* {bis(diphenylphosphino)amine} in dichloromethane at room temperature results in the formation of the complex  $[\text{Pt}(\text{PPh}_3)(\eta^2\text{-dppa})\{\eta^1\text{-C}(\text{S})\text{NMe}_2\}][\text{Cl}]$  (**5**). Treatment of **4** with  $\text{EtOCS}_2\text{K}$  or  $\text{MeOCS}_2\text{K}$  yields Fischer-type carbene-complex  $[\text{Pt}(\text{PPh}_3)\{\eta^1\text{-C}(\text{SEt})(\text{NMe}_2)\}(\eta^2\text{-S}_2\text{CO})]$  (**7**) or  $[\text{Pt}(\text{PPh}_3)\{\eta^1\text{-C}(\text{SMe})(\text{NMe}_2)\}(\eta^2\text{-S}_2\text{CO})]$  (**8**). The carbene-complexes **7** and **8** are formed via alkyl migration of the alkylthiocarbonate ligand to the thiocarbamoyl ligand. Complex **1** reacts with  $\text{EtOCS}_2\text{K}$ , resulting in the formation of the  $\eta^2$ -dithiocarbonate complex  $[\text{Pt}(\text{PPh}_3)(\eta^1\text{-SCNMe}_2)(\eta^2\text{-S}_2\text{COEt})]$  (**6**) and the carbene-complex  $[\text{Pt}(\text{PPh}_3)\{\eta^1\text{-C}(\text{SEt})(\text{NMe}_2)\}(\eta^2\text{-S}_2\text{CO})]$  (**7**) with a ratio of 3:2 according to the integration of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra. By continuously stirring mixtures **6** and **7** in the  $\text{CH}_2\text{Cl}_2$  solution for 4 h, complex **7** was formed as the final product. All of the complexes were identified by spectroscopic methods and complexes **2**, **5**, and **7** were determined by single-crystal X-ray diffraction. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Platinum; *N,N*-D imethylthiocarbamoyl ligand; Carbene; Ethyldithiocarbonate ligand; Crystal structures

## 1. Introduction

Although thiocarbamoyl metal complexes are known in Nb, Ta (VB) [1], Mo, W (VIB) [2,3], Ru, Rh, and Ir (VIII B) [4,5], the Pt thiocarbamoyl complex has received little attention. These complexes have been prepared from the

reaction of metal carbonylates with *N,N*-dimethylthiocarbamoyl chloride,  $\text{Me}_2\text{NC}(\text{=S})\text{Cl}$ , via nucleophilic displacement of chloride [6], nucleophilic attack by an amine on an electrophilic thiocarbonyl complex [7], electrophilic attack at a coordinated isothiocyanate [8], reaction of hydrosulfide with haloaminocarbene [9] or isonitrile [10] ligands, cleavage of a dithiocarbamate ligand [2], or C–H activation of thioformamides [11]. Oxidative addition [4] of both chloride and *N,N*-dimethylthiocarbamoyl ligand to the metal complex is most generally used and is relevant to the work described herein.

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Our previous report showed that the sulfur atom of the thiocarbamoyl ligand assists the displacement of either the chloride or the triphenylphosphine ligand to form the  $\eta^2$ -thiocarbamoyl palladium complexes [12]. We report here the formation of two hetero-atom carbene complexes of the platinum via alkyl migration of the alkyldithiocarbonate to thiocarbamoyl ligand, as well as the displacement behavior and reactions of  $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$  (**1**) with neutral phosphorus ligand. Three X-ray crystal structure analyses have been carried out to provide structural parameters.

## 2. Results and discussion

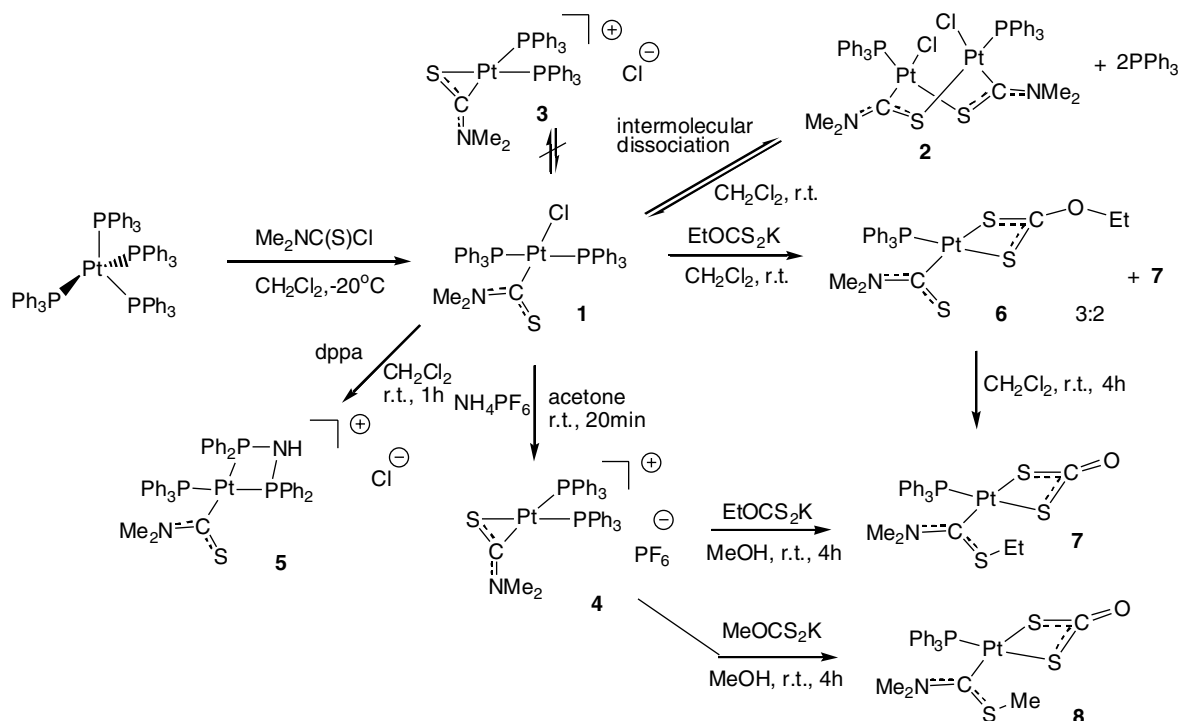
### 2.1. Syntheses

We have previously reported the reaction of  $\text{Pt}(\text{PPh}_3)_4$  with *N,N*-dimethylthiocarbamoyl chloride,  $\text{Me}_2\text{NC}(=\text{S})\text{Cl}$ , in dichloromethane at  $-20^\circ\text{C}$ , yielding the air-stable yellow complex  $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$  (**1**) [13].

The dichloromethane solution of **1** undergoes intermolecular displacement of the triphenylphosphine ligand of **1** to form the bridging  $\eta^2$ -thiocarbamoyl diplatinum complex  $[\text{Pt}(\text{PPh}_3)_2(\mu, \eta^2\text{-SCNMe}_2)_2]$  (**2**) but the intramolecular displacement of the chloride ligand of **1** to form the chelating  $\eta^2$ -thiocarbamoyl complex  $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-SCNMe}_2)]\text{Cl}$  (**3**) has not been found (Scheme 1). Continuous refluxing of the chloroform solution of these mixtures for 8 h produces complex **2** as the final product with 93% isolated yield (Fig. 1). Complex  $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-SCNMe}_2)]\text{PF}_6$  (**4**) can be synthesized from the reaction of **1** and ammonium hexafluorophosphate,  $\text{NH}_4\text{PF}_6$ , in acetone with 92% isolated yield at ambient temperature [14]. The yellow-orange complex **4** is more stable and is less soluble than that of **1**. In the Pd analog, complex  $[\text{Pd}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$ , showing the inter- and intramolecular displacement behavior, was shown to form complexes  $[\text{Pd}(\text{PPh}_3)_2(\mu, \eta^2\text{-SCNMe}_2)_2]$  and  $[\text{Pd}(\text{PPh}_3)_2(\eta^2\text{-SCNMe}_2)]\text{Cl}$  [12] and the displacement of either the phosphine or the chloride ligand occurred in  $\text{CH}_2\text{Cl}_2$  solution of complex  $[\text{Pd}(\text{PPh}_3)_2(\eta^1\text{-CH}_2\text{SCH}_3)\text{Cl}]$  [15] to form monomer complexes  $[\text{Pd}(\text{PPh}_3)(\eta^2\text{-CH}_2\text{SCH}_3)\text{Cl}]$  and  $[\text{Pd}(\text{PPh}_3)_2(\eta^2\text{-CH}_2\text{SCH}_3)]\text{Cl}$ . It is plausible that the sulfur atom of the thiocarbamoyl ligand assists triphenylphosphine displacement of **1** to form **2**.

In the reaction of **1** with *dppa* {bis(diphenylphosphino)amine} in dichloromethane at room temperature, a chloride and triphenylphosphine were displaced, forming complex  $[\text{Pt}(\text{PPh}_3)(\eta^2\text{-dppa})\{\eta^1\text{-C}(\text{S})\text{NMe}_2\}]\text{Cl}$  (**5**) with 88% isolated yield.

Nucleophilic displacement of the chloride in **1** with anionic dithiocarbonate ligand,  $\text{EtOCS}_2^-$ , in dichloromethane at room temperature produces complex  $[\text{Pt}(\text{PPh}_3)(\eta^1\text{-SCNMe}_2)(\eta^2\text{-S}_2\text{COEt})]$  (**6**) and carbene-complex  $[\text{Pt}(\text{PPh}_3)\{\eta^1\text{-C}(\text{SEt})(\text{NMe}_2)\}(\eta^2\text{-S}_2\text{CO})]$  (**7**) in good yields and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum indicates the 3:2 ratio of **6** and **7**. The dichloromethane solution of the mixtures **6** and **7** slowly undergo the ethyl-thiocarbamoyl coupling reaction of **6** to give **7** as the final product with 78% isolate yield over 4 h at room temperature. The same procedure was used to prepare the other carbene-complex  $[\text{Pt}(\text{PPh}_3)\{\eta^1\text{-C}(\text{SMe})(\text{NMe}_2)\}(\eta^2\text{-S}_2\text{CO})]$  (**8**) with 85% isolated yield. The conversion of complex **6** to carbene complex **7** is proposed to



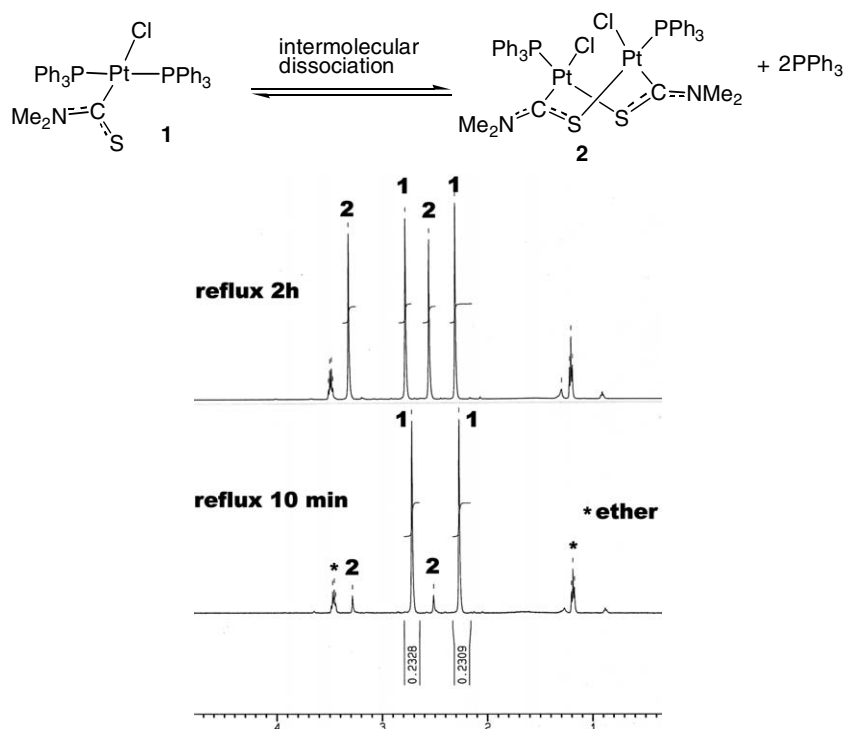
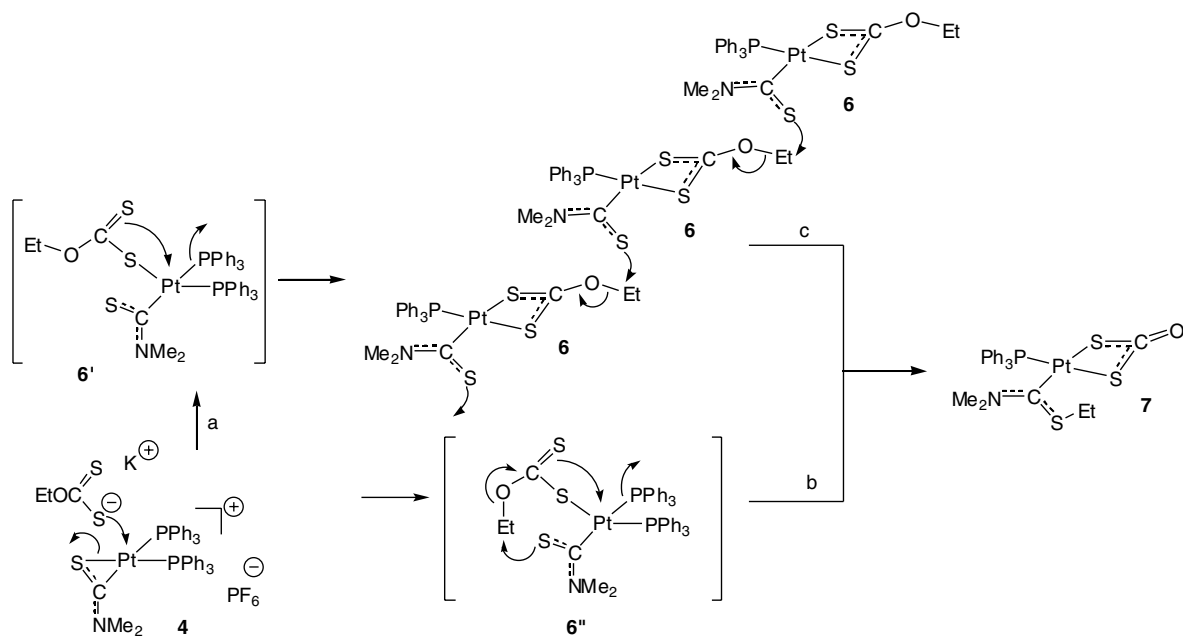


Fig. 1. Refluxing-temperature  $^1\text{H}$  NMR spectra of the mixtures **1** and **2** in  $\text{CDCl}_3$  (\* is the diethyl ether).

proceed via (path c) sulfur atom of the thiocarbamoyl ligand of **6** to attack the ethyl group of the ethyldithiocarbonate ligand of another complex **6** to form **7** (Scheme 2). The formation of **7** from the reaction of **4** with potassium ethyldithiocarbonate is proposed to proceed via (path a) the anionic ethyldithiocarbonate ligand to attack cationic Pt complex **4** to form the intermediate **6'**, followed by the formation of chelating ethyldithiocarbonate ligand with releasing one  $\text{PPh}_3$  ligand to form **6** and then underwent path c to

form **7** or via (path b) the intermediate complex **6''** processing intramolecular ethyl abstraction inducing the chelating dithiocarbonate ligand with releasing one  $\text{PPh}_3$  ligand to form the carbene complex **7**.

The air-stable yellow-orange compounds **7** and **8** are soluble in polar solvent, and insoluble in diethyl ether and *n*-hexane. Complexes **7** and **8** both include a dithiocarbonate group,  $\text{S}_2\text{CO}_2^-$ . Dithiocarbonate metal complexes have previously been prepared by a variety of synthetic routes



Scheme 2.

including reactions of metal carbonyl sulfide complexes with COS [16], reactions of metal carbon disulfide complexes with dioxygen [17], and dealkylation [18], iodide abstraction [19], and hydrolysis [20] of alkoxydithiocarbamate metal complexes. Syntheses of carbene complexes by the reaction of Pt thiocarbamoyl and thio ester complexes with electrophiles have been reported [21]. To our knowledge, our discussion here of the formation of dithiocarbonate carbene-complex from the alkyl-thiocarbamoyl coupling reaction is the first example in the literature.

The isolated compounds **2**, **4–8** were already of good purity, but analytically pure samples could be obtained by slow *n*-hexane diffusion into a dichloromethane solution at +4 °C. All characterization data are consistent with the proposed constitution.

## 2.2. IR and MS spectroscopy

In the infrared spectra of **5** and **6**, the C–N stretches for the SCNMe<sub>2</sub> group are in the region of 1429–1437 cm<sup>-1</sup>, typical for a η<sup>1</sup>-bound SCNMe<sub>2</sub> group [22] with partially multiple C–N bond of the thiocarbamoyl ligand. The peaks at 1520 and 1526 cm<sup>-1</sup> in the IR spectra of **7** and **8** indicate a delocalized C(SR)NMe<sub>2</sub> group. The IR spectra of **7** and **8** show the C=O stretching band of the coordinated carbonate ligand at 1680, 1612 and at 1683, 1618 cm<sup>-1</sup>, respectively, which are indicative of a chelate dithiocarbonate ligand [16–20]. The FAB mass spectra of **6–8** show parent peaks with the typical Pt isotope distribution corresponding to [M<sup>+</sup>] molecular masses, respectively. In the FAB mass spectra, base peaks with the typical Pt isotope distribution are respectively in agreement with the [M<sup>+</sup> – Cl] molecular masses of **2** and **5**.

## 2.3. NMR spectroscopy

After refluxing **1** in CDCl<sub>3</sub> for 2 h, the <sup>1</sup>H NMR spectra of **1** clearly showed four methyl resonances for the mixtures of **1** and the diplatinum complex [Pt(PPh<sub>3</sub>)Cl]<sub>2</sub>(μ,η<sup>2</sup>-SCNMe<sub>2</sub>)<sub>2</sub> (**2**) (Fig. 1). Two methyl resonances of the SCNMe<sub>2</sub> ligand are observed in the <sup>1</sup>H NMR spectra of complexes **2**, **4–8**, consistent with hindered rotation about the partially multiple C–N bond. The <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the methyl signals of complexes **2**, **4–8** are in the region from δ 39.8 to δ 54.0. The low-field sections of the <sup>13</sup>C{<sup>1</sup>H} NMR spectra consist of one resonance attributable on intensity grounds to the thiocarbamoyl carbon atom in the region from δ 213.6 to δ 233.8. In the <sup>1</sup>H NMR spectra of **8** and **7**, one resonance at δ 2.82 and two resonances at δ 1.26 and δ 4.07, together with their corresponding <sup>13</sup>C{<sup>1</sup>H} NMR signals at δ 21.8 and at δ 13.7, δ 39.8, are attributed to the S–CH<sub>3</sub> [23a] and the S–CH<sub>2</sub>CH<sub>3</sub> [23b] groups, respectively. The <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **7** and **8** reveal two doublets (9.2, 9.5 Hz) at the lowest field, which are assigned to the carbon atoms of the carbene (δ 226.5 and δ 229.8) and dithiocarbonate (δ 194.4 and δ 195.5) carbon nuclei, respectively.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **4** shows two doublet resonances at δ 16.3 and δ 22.7 with satellites (*J*<sub>Pt–P</sub> = 1525, *J*<sub>Pt–P</sub> = 2097 Hz) due to the <sup>195</sup>Pt nuclei, and so the relative downfield resonance compared to those of **1** (δ 15.9), **2** (δ 9.51), **7** (δ 15.5), and **8** (δ 15.4) shows the cationic character of **4**. From this description, it is clear that the compound **4** is side-on bound through the C–S moiety of the SCNMe<sub>2</sub> ligand. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **5** shows two broad multiplet resonances at δ 13.3 and δ 16.1 with satellites (*J*<sub>Pt–P</sub> = 1417, *J*<sub>Pt–P</sub> = 729 Hz) with 2:1 ratios.

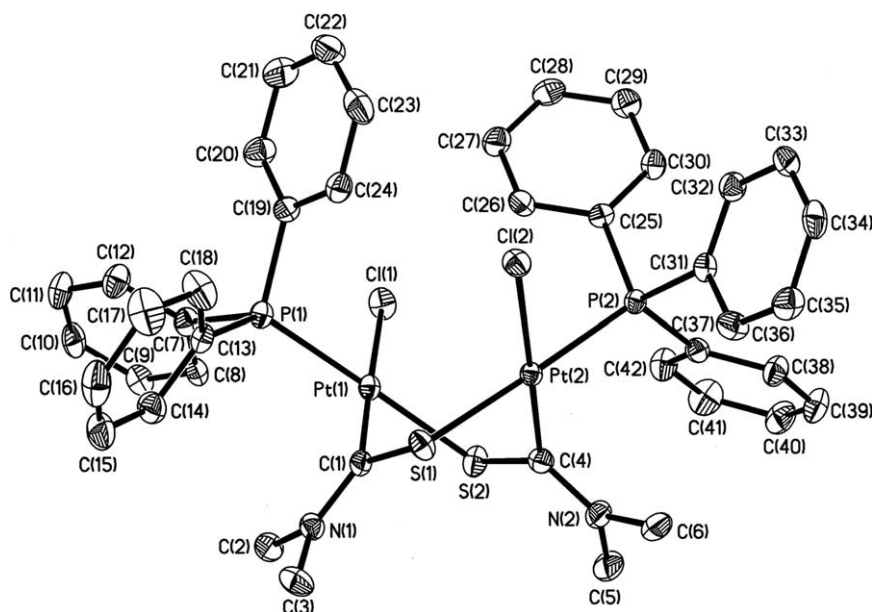


Fig. 2. An ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the complex [Pt(PPh<sub>3</sub>)Cl]<sub>2</sub>(μ,η<sup>2</sup>-SCNMe<sub>2</sub>)<sub>2</sub> (**2**).

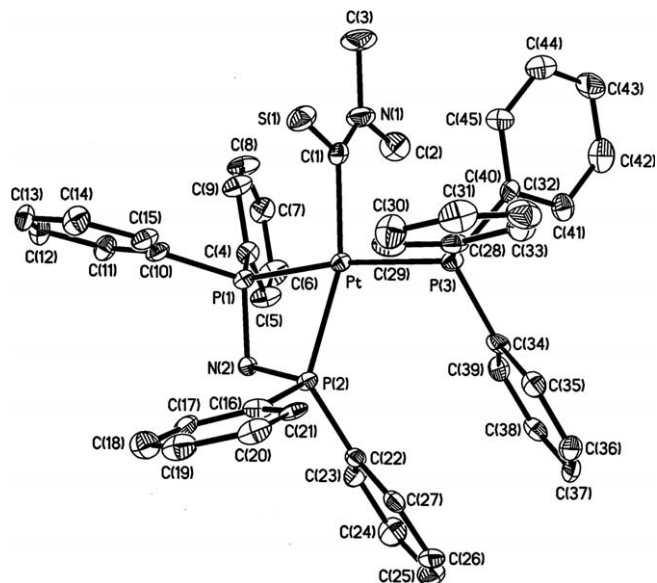


Fig. 3. An ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the cationic complex  $[\text{Pt}(\text{PPh}_3)(\eta^2\text{-dppa})(\eta^1\text{-C}(\text{S})\text{NMe}_2)]\text{[Cl]}$  (**5**).

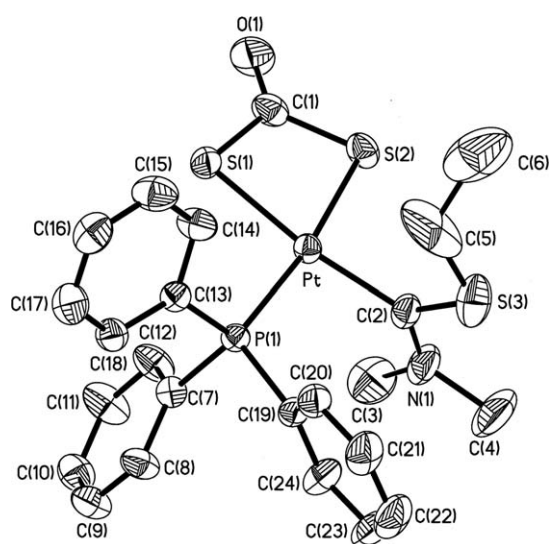


Fig. 4. An ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for the complex  $[\text{Pt}(\text{PPh}_3)(\eta^1\text{-C}(\text{SEt})(\text{NMe}_2))(\eta^2\text{-S}_2\text{CO})]$  (**7**).

#### 2.4. X-ray single-crystal structures of **2**, **5**, and **7**

To confirm the thiocarbamoyl platinum and the ethyl-thiocarbamoyl coupling carbene-complex, the aforementioned compounds **2**, **5**, and **7** were examined by single-crystal X-ray diffraction studies. Single crystals of the three complexes were grown by slow *n*-hexane diffusion into a dichloromethane solution at +4 °C. ORTEP plots

with atom labels of **2**, **5**, and **7** are shown in Figs. 2–4. Crystal data and refinement details and selected interatomic distances (Å) and angles (°) of complexes **2**, **5**, and **7** are listed in Tables 1 and 2, respectively.

Complex **2** is a dimer with each  $\text{SCNMe}_2$  unit bridging through carbon atoms of the thiocarbamoyl group to one platinum metal center and sulfur atom to the other platinum, forming a six-membered ring with boat-form geometry. These geometries are consistent with the significant

Table 1

Crystal data and refinement details for complexes **2** ·  $2\text{CH}_2\text{Cl}_2$ , **5** ·  $2\text{CH}_2\text{Cl}_2$ , and **7** ·  $\text{H}_2\text{O}$

	<b>2</b> · $2\text{CH}_2\text{Cl}_2$	<b>5</b> · $2\text{CH}_2\text{Cl}_2$	<b>7</b> · $\text{H}_2\text{O}$
Chemical formula	$\text{C}_{43}\text{H}_{44}\text{Cl}_4\text{N}_2\text{P}_2\text{S}_2\text{Pt}_2$	$\text{C}_{47}\text{H}_{46}\text{Cl}_5\text{N}_2\text{P}_3\text{Spt}$	$\text{C}_{24}\text{H}_{28}\text{NO}_2\text{PS}_3\text{Pt}$
Formula weight	1246.84	1136.17	684.71
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$Cc$	$P2_1/n$
<i>a</i> (Å)	9.8523(3)	14.7638(7)	12.4263(6)
<i>b</i> (Å)	11.4246(4)	37.9156(18)	17.3026(9)
<i>c</i> (Å)	20.7734(7)	9.7706(4)	12.5437(6)
$\alpha$ (°)	104.499(1)	90	90
$\beta$ (°)	94.639(1)	120.477(1)	92.564(1)
$\gamma$ (°)	105.226(1)	90	90
<i>V</i> (Å <sup>3</sup> )	2157.22(12)	4715.1(4)	2694.3(2)
<i>Z</i>	2	4	4
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.920	1.601	1.688
$\mu(\text{Mo K}\alpha)$ (mm <sup>-1</sup> )	6.931	3.441	5.520
$\lambda$ (Å)	0.71073	0.71073	0.71073
<i>T</i> (K)	150(1)	150(1)	295(2)
$\theta$ Range (°)	1.03–27.50	1.07–27.50	2.01–27.50
Independent reflections	9862	10246	6191
Number of variables	496	532	289
<i>R</i> <sup>a</sup>	0.026	0.043	0.037
<i>R</i> <sub>w</sub> <sup>b</sup>	0.058	0.085	0.100
<i>S</i> <sup>c</sup>	1.031	0.986	1.075

<sup>a</sup>  $R = \sum||F_o| - |F_c|| / \sum|F_o|$ .

<sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2}$ ;  $w = 1/s^2(|F_o|)$ .

<sup>c</sup> Quality-of-fit =  $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observed}} - N_{\text{parameters}})]^{1/2}$ .

Table 2  
Selected interatomic distances (Å) and angles (°) for **2**, **5**, and **7**

	<b>2</b>	<b>5</b>	<b>7</b>
Pt–P	2.2716(10) 2.2691(10)	2.2973(18) 2.3211(19) 2.3320(18)	2.2698(13)
Pt–CS	1.965(4), 1.975(4)	2.059(7)	2.012(6)
Pt–S	2.3481(10) 2.3647(9)	–	2.3325(16) 2.3336(15)
C=S	1.739(4), 1.726(4)	1.679(7)	1.762(6), 1.726(7) 1.707(7)
C–N	1.318(5), 1.324(5)	1.307(9)	1.347(9)
N–Me	1.471(5), 1.463(5) 1.463(5), 1.464(5)	1.445(10), 1.477(9)	1.523(12), 1.485(10)
C–Pt–X (Cl,P,S)	178.29(11), 178.44(12)	162.89(19)	169.97(19)
Pt–C–S	117.3(2), 118.4(2)	109.9(4)	124.5(4)

partial double bond character in the C–S and SC–N bonds of the SCNMe<sub>2</sub> ligands. Thus, the C–S bond distances (1.739(4) and 1.726(4) Å) are comparable to the C–S double bond in ethylenethiourea, although they are longer than those in free CS<sub>2</sub> (1.554 Å). The SC–N bond distances (1.318(5) and 1.324(5) Å) are typical for a C–N bond having partial double bond character, and are certainly much shorter than the normal C–N (1.47 Å) single bond.

In complex **5**, the SCNMe<sub>2</sub> ligand is  $\sigma$  bound to the Pt atom through the carbon atom of the thiocarbamoyl group. The S–Pt bond distance of 3.096 Å in **5** indicates that there is no bonding interaction between the sulfur atom and platinum metal atom. The platinum atom has a distorted square planar geometry. One of the phosphorus atom of the dppa ligand is *trans* to the triphenylphosphine ligand: P(3)–Pt–P(1), 168.35(7)°, while the other is *trans* to the carbon atom of the thiocarbamoyl ligand: P(2)–Pt–C(1), 162.89(19)°.

In complex **7**, the platinum atom has a distorted square planar geometry and the carbene carbon, Pt, S, and N all are coplanar to within 0.0093 Å. Three bond angles of C(2) (120.9°, 124.5°, and 114.6°) clearly show the sp<sup>2</sup> character of the carbon. One of the sulfur atoms of dithiocarbonate ligand is *trans* to the triphenylphosphine: S(2)–Pt–P(1), 171.27(5)°, while the other is *trans* to the carbene ligand: S(1)–Pt–C(2), 169.97(19)°. The Pt–C(2) bond distance, 2.012(6) Å, is longer than the other Pt<sup>II</sup>–carbon–(carbonyl) distances, and similar to those of Pt–C(carbene) distances [24]. Within the carbene C(SMe)(NMe<sub>2</sub>), the geometry is consistent with significant partial double bond character in the S(3)–C(2) (1.707(7) Å) and C(2)–N(1) (1.347(9) Å) bonds. This implies P <sub>$\pi$</sub> –P <sub>$\pi$</sub>  overlap, involving

the empty P orbital of C(2) atom. The Pt–S(1) (2.3325(16) Å) and Pt–S(2) (2.3336(15) Å) bond distances are within the normal Pt–S length range (2.23–2.32 Å) [25]. The bond distances within the dithiocarbonate ligand, S–C(av), 1.762(7) Å, and C(1)–O(1), 1.212(7) Å, fall in the range of values found for other dithiocarbonate complexes; and they are indicative of an overall electronic delocalization within the S<sub>2</sub>CO group [16].

## 2.5. Conclusion

In this article we report the syntheses, dissociation behavior and X-ray crystal structures of thiocarbamoyl Pt complexes. These observations confirm that the sulfur atom of the thiocarbamoyl ligand assists in the displacement of the triphenylphosphine ligand to form a diplatinum complex **2**. The bridging thiocarbamoyl dinuclear complex [Pt(PPh<sub>3</sub>)Cl]<sub>2</sub>( $\mu$ , $\eta^2$ -SCNMe<sub>2</sub>)<sub>2</sub> (**2**), including a six-membered ring, is an organometallic dinuclear compound. A novel alkyl-thiocarbamoyl coupling reaction produces the N,S-hetero-atom carbene-complexes **7** and **8** from the reaction of **1** with alkyldithiocarbonate ligands. Two important factors in forming the carbene-complexes are (1) the  $\pi$  interaction between the carbene-carbon and SR or NMe<sub>2</sub> and (2) the greater chelation ability of the dithiocarbonate ligand than the alkyldithiocarbonate ligand. Three bonding modes of the thiocarbamoyl ligand are observed: (1) monodentate coordination through carbon atom (complexes **5** and **6**), (2) bidentate through carbon and sulfur atoms by chelation (complex **4**) and (3) bridging between two metal centers (complex **2**).

### 3. Experimental

#### 3.1. Materials

All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. NMR spectra were recorded on a Bruker AM-500 WB FT-NMR spectrometer and are reported in units of  $\delta$  (ppm) with residual protons in the solvent as an internal standard ( $\text{CDCl}_3$ ,  $\delta$  7.24). IR spectra were measured on a Nicolet Avator-320 instrument and were referenced to a polystyrene standard, using cells equipped with calcium fluoride windows. Mass spectra were recorded on a JEOL SX-102A spectrometer. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. *n*-Hexane, diethyl ether, THF and benzene were distilled from sodium-benzophenone. Acetonitrile and dichloromethane were distilled from calcium hydride. Methanol was distilled from magnesium. All other solvents and reagents were of reagent grade and were used as received. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrumentation located at the National Taiwan University.  $\text{PtCl}_2 \cdot x\text{H}_2\text{O}$  was purchased from Strem Chemical,  $\text{EtOCS}_2\text{K}$ , dppa, and  $\text{NH}_4\text{PF}_6$  were purchased from Merck.

#### 3.2. Bis-[(chlorotriphenylphosphine)][ $\mu$ -bis- $\{\eta^2$ -*N,N*-dimethylthiocarbamoyl}] platinum(II) (2)

$\text{CHCl}_3$  (20 ml) was added to a flask (100 ml) containing  $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$  (**1**) [**13b**] (0.843 g, 1.0 mmol). The solution was refluxed for 8 h then diethyl ether (30 ml) was added to the solution and a yellow precipitate was formed. The precipitate was collected by filtration (G4) washed with *n*-hexane ( $2 \times 10$  ml) and then dried in vacuo yielding 0.54 g (93%) of **2**. Spectroscopy for **2**: IR (KBr,  $\text{cm}^{-1}$ )  $\nu(\text{CN})$  1481(m), 1435(m).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  9.51 (s,  $\text{PPh}_3$ ,  $J_{\text{Pt-P}} = 1826$  Hz), 2.48, 3.27 (s, 6H,  $\text{NCH}_3$ ), 7.28–7.80 (m, 30H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  39.8, 48.7 (s,  $\text{NCH}_3$ ), 127.8–135.3 (m, C of Ph), 213.6 (s, CS). MS (FAB, NBA,  $m/z$ ): 1125 [ $\text{M}^+ - \text{Cl}$ ]. Anal. Calc. for  $\text{C}_{42}\text{H}_{42}\text{Cl}_2\text{N}_2\text{P}_2\text{S}_2\text{Pt}_2$ : C, 43.41; H, 3.64; N, 2.41. Found: C, 43.28; H, 3.58; N, 2.20%.

#### 3.3. [(Bis(triphenylphosphine) ( $\eta^2$ -*N,N*-dimethylthiocarbamoyl) platinum(II)) [hexafluorophosphate] (4)

Acetone (20 ml) was added to a flask (100 ml) containing  $\text{NH}_4\text{PF}_6$  (0.163 g, 1.0 mmol) and  $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$  (**1**) (0.843 g, 1.0 mmol). The solution was stirred for 20 min at room temperature. The solvent was then removed under vacuum. The remaining solid was dissolved in 10 ml of  $\text{CH}_2\text{Cl}_2$  and the solution was filtered to remove excess  $\text{NH}_4\text{Cl}$ . The solution is concentrated under

vacuum and *n*-hexane (10 ml) was added to initiate precipitation. The yellow-orange solids **4** were formed which were isolated by filtration (G4), washed with *n*-hexane ( $2 \times 10$  ml) and subsequently dried under vacuum yielding  $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-SCNMe}_2)][\text{PF}_6]$ , **4** (0.88 g, 92%). Further purification was accomplished by recrystallization from 1/10  $\text{CH}_2\text{Cl}_2$ /*n*-hexane. Spectroscopic data of **4** are as follows. IR (KBr,  $\text{cm}^{-1}$ )  $\nu(\text{CN})$  1476(m), 1432(m);  $\nu(\text{PF}_6)$  837(vs).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  2.35, 3.57 (s, 6H,  $\text{NCH}_3$ ), 7.24–7.46 (m, 35H, Ph).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  16.3, 22.7 (d,  $\text{PPh}_3$ ,  $^2J_{\text{P-P}} = 11$ ,  $J_{\text{Pt-P}} = 1525$ ,  $J_{\text{P-P}} = 2097$ ),  $-143.9$  (sep,  $\text{PF}_6$ ,  $J_{\text{P-F}} = 713$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  46.3, 54.0 (d,  $\text{NCH}_3$ ,  $^4J_{\text{P-C}} = 6.19$ ), 129.3–134.8 (m, C of Ph), 216.2 (d, CS,  $^2J_{\text{P-C}} = 6.2$ ). MS (FAB, NBA,  $m/z$ ): 807.3 [ $\text{M}^+ - \text{PF}_6$ ], 719.3 [ $\text{M}^+ - \text{PF}_6 - \text{CSNMe}_2$ ], 545.1 [ $\text{M}^+ - \text{PF}_6 - \text{PPh}_3$ ]. Anal. Calc. for  $\text{C}_{39}\text{H}_{36}\text{F}_6\text{NP}_3\text{Spt}$ : C, 49.16; H, 3.81; N, 1.47. Found: C, 49.28; H, 4.06; N, 1.51%.

#### 3.4. [ $\{\eta^2$ -Bis(triphenylphosphino)amine $\}(\eta^1$ -*N,N*-dimethylthiocarbamoyl)(triphenylphosphine) platinum(II)] [chloride] (5)

$\text{CH}_2\text{Cl}_2$  (40 mL) was added to a flask (100 mL) containing  $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$  (**1**) (0.843 g, 1.0 mmol) and dppa (0.384 g, 1.0 mmol) and the solution was stirred at room temperature. After stirring 1 h, MeOH (10 mL) was added to the solution and the brown solids were formed which were isolated by filtration (G4), washed with *n*-hexane ( $2 \times 10$  ml) and subsequently dried under vacuum yielding 0.85 g (88%) of  $[\text{Pt}(\eta^1\text{-SCNMe}_2)(\eta^2\text{-dppa})(\text{PPh}_3)][\text{Cl}]$  (**5**). IR (KBr,  $\text{cm}^{-1}$ )  $\nu(\text{CN})$  1470(m), 1429(m).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  2.58, 2.81 (s, 6H,  $\text{NCH}_3$ ), 7.14–7.76 (m, 30H, Ph).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  13.3 (m, dppa,  $J_{\text{Pt-P}} = 1417$ ), 16.1 (m,  $\text{PPh}_3$ ,  $J_{\text{Pt-P}} = 729$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  40.3, 45.7 (d,  $\text{NCH}_3$ ,  $^4J_{\text{P-C}} = 4.53$ ), 128.2–137.2 (m, C of Ph), 225.5 (s, CS). MS (FAB, NBA,  $m/z$ ): 930.4 [ $\text{M}^+ - \text{Cl}$ ], 842.4 [ $\text{M}^+ - \text{Cl} - \text{SCNMe}_2$ ]. Anal. Calc. for  $\text{C}_{45}\text{H}_{42}\text{ClN}_2\text{P}_3\text{Spt}$ : C, 55.93; H, 4.38; N, 2.90. Found: C, 56.04; H, 4.46; N, 3.08%.

#### 3.5. [ $(\eta^2$ -Ethylthiocarbonate)( $\eta^1$ -*N,N*-dimethylthiocarbamoyl)(triphenylphosphine) platinum(II)] (6)

IR (KBr,  $\text{cm}^{-1}$ )  $\nu(\text{CN})$  1475(m), 1437(m).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  1.35 (t, 3H,  $\text{OCH}_2\text{CH}_3$ ,  $J_{\text{H-H}} = 4.7$ ), 2.95, 3.22 (s, 6H,  $2\text{NCH}_3$ ), 4.07 (q, 2H,  $\text{OCH}_2$ ,  $J_{\text{H-H}} = 4.7$ ), 7.17–7.75 (m, 15H, Ph).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  11.2 (s,  $\text{PPh}_3$ ,  $J_{\text{Pt-P}} = 2128$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  31.5 (s,  $\text{OCH}_2\text{CH}_3$ ), 39.8, 48.9 (s,  $\text{NCH}_3$ ,  $J_{\text{Pt-C}} = 17.4$ , 47.1), 68.7 (s,  $\text{OCH}_2$ ), 128.2–134.4 (m, C of Ph), 194.4 (s,  $\text{S}_2\text{CO}$ ), 233.8 (s,  $\text{NCSEt}$ ). MS (FAB, NBA,  $m/z$ ): 667 [ $\text{M}^+$ ].

### 3.6. $[(\eta^2\text{-Dithiocarbonate})(\eta^1\text{-}N,N\text{-dimethylthioethyl-carbene})(\text{triphenylphosphine})\text{ platinum(II)}]$ (**7**)

MeOH (10 mL) was added to a flask (100 mL) containing  $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-SCNMe}_2)][\text{PF}_6]$  (**4**) (0.952 g, 1.0 mmol) and EtOCS<sub>2</sub>K (0.160 g, 1.0 mmol) at room temperature. After stirring for 4 h, the yellow-orange precipitate was formed. The precipitate was collected by filtration (G4), washed with *n*-hexane (2 × 10 mL) and then dried in vacuo to yield 0.52 g (78%) of complex  $[\text{Pt}(\text{PPh}_3)\{\eta^1\text{-C}(\text{SEt})(\text{NMe}_2)\}(\eta^2\text{-S}_2\text{CO})]$  (**7**). IR (KBr, cm<sup>-1</sup>)  $\nu(\text{CO})$  1680(vs), 1612(vs). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub> 298 K):  $\delta$  1.26 (t, 3H, SCH<sub>2</sub>CH<sub>3</sub>,  $J_{\text{H-H}} = 7.1$ ), 2.82, 3.48 (s, 6H, 2NCH<sub>3</sub>), 4.07 (q, 2H, SCH<sub>2</sub>,  $J_{\text{H-H}} = 7.1$ ), 7.37–7.86 (m, 15H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub> 298 K):  $\delta$  15.5 (s, PPh<sub>3</sub>,  $J_{\text{Pt-P}} = 1625$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub> 298 K):  $\delta$  13.7 (s, SCH<sub>2</sub>CH<sub>3</sub>,  $J_{\text{Pt-C}} = 47.1$ ), 39.8 (s, SCH<sub>2</sub>,  $J_{\text{Pt-C}} = 17.4$ ), 43.8, 51.8 (s, NCH<sub>3</sub>,  $J_{\text{Pt-C}} = 17.4$ , 32.4), 128.2–134.4 (m, C of Ph), 194.4 (s, S<sub>2</sub>CO), 226.5 (d, NCSEt,  $J_{\text{P-C}} = 9.2$ ). MS (FAB, NBA,  $m/z$ ): 667 [ $\text{M}^+$ ]. Anal. Calc. for C<sub>24</sub>H<sub>26</sub>NOPS<sub>3</sub>Pt: C, 43.23; H, 3.93; N, 2.10. Found: C, 43.35; H, 4.08; N, 2.02%.

### 3.7. $[(\eta^2\text{-Dithiocarbonate})(\eta^1\text{-}N,N\text{-dimethylthiomethyl-carbene})(\text{triphenylphosphine})\text{ platinum(II)}]$ (**8**)

The synthesis and work-up were similar to those used in the preparation of complex **7**. The complex  $[\text{Pt}(\text{PPh}_3)\{\eta^1\text{-C}(\text{SMe})(\text{NMe}_2)\}(\eta^2\text{-S}_2\text{CO})]$  (**8**) was isolated in 85% yield as a yellow-orange microcrystalline solid. IR (KBr, cm<sup>-1</sup>)  $\nu(\text{CO})$  1683(vs), 1618(vs). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub> 298 K):  $\delta$  2.82 (s, 3H, SCH<sub>3</sub>), 2.93, 3.49 (s, 6H, 2NCH<sub>3</sub>), 7.28–7.76 (m, 15H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub> 298 K):  $\delta$  15.4 (s, PPh<sub>3</sub>,  $J_{\text{Pt-P}} = 1662$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub> 298 K):  $\delta$  21.8 (s, SCH<sub>3</sub>,  $J_{\text{Pt-C}} = 34.5$ ), 43.2, 51.2 (s, NCH<sub>3</sub>,  $J_{\text{Pt-C}} = 17.5$ , 30.8), 128.1–137.2 (m, C of Ph), 195.5 (s, S<sub>2</sub>CO), 229.8 (d, NCSMe,  $J_{\text{P-C}} = 9.5$ ). MS (FAB, NBA,  $m/z$ ): 653 [ $\text{M}^+$ ]. Anal. Calc. for C<sub>23</sub>H<sub>24</sub>NOPS<sub>3</sub>Pt: C, 42.32; H, 3.71; N, 2.15. Found: C, 42.48; H, 3.80; N, 2.01%.

### 3.8. X-ray crystallography

#### 3.8.1. Single-crystal X-ray diffraction analyses of **2**, **5**, and **7**

Single crystals of **2**, **5**, and **7** suitable for X-ray diffraction analyses were grown by recrystallization from 20/1 *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>. The diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. The raw intensity data were converted to structure factor amplitudes and their esd's after corrections for scan speed, background, Lorentz, and polarization effects. An empirical absorption correction, based on the azimuthal scan data, was applied to the data. Crystallographic computations were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package [26].

A suitable single crystal of **2** was mounted on the top of a glass fiber with glue. Initial lattice parameters were determined from 24 accurately centered reflections with  $\theta$  values in the range from 1.03° to 27.50°. Cell constants and other pertinent data were collected and are recorded in Table 1. Reflection data were collected using the  $\theta/2\theta$  scan method. Three check reflections were measured every 30 min throughout the data collection and showed no apparent decay. The merging of equivalent and duplicate reflections gave a total of 28 150 unique measured data, of which 9862 reflections with  $I > 2\sigma(I)$  were considered observed. The first step of the structure solution used the heavy-atom method (Patterson synthesis), which revealed the positions of metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The quantity minimized by the least-squares program was  $w(|F_o| - |F_c|)^2$ , where  $w$  is the weight of a given operation. The analytical forms of the scattering factor tables for the neutral atoms were used [27]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. All hydrogens were assigned isotropic thermal parameters 1–2 Å<sup>2</sup> larger than the equivalent  $B_{\text{iso}}$  value of the atom to which they were bonded. The final residuals of this refinement were  $R = 0.026$  and  $R_w = 0.058$ .

The procedures for **5** and **7** were similar to those for **2**. The final residuals of this refinement were  $R = 0.043$  and  $R_w = 0.085$  for **5**, and  $R = 0.037$  and  $R_w = 0.100$  for **7**. Selected bond distances and angles are listed in Table 2. X-ray crystallographic files, in CIF format, for the structures of complexes **2**, **5**, and **7** are given in supplementary material.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.001.

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