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Syntheses, displacement behavior, hetero-atom carbene, and crystal structures of platinum complexes containing the *N*,*N*-dimethylthiocarbamoyl, $Me_2NC{=}S$, ligand: Structures of $[Pt(PPh_3)(Cl)]_2(\mu,\eta^2\text{-}SCNMe_2)_2$, $[Pt(PPh_3)(\eta^2\text{-dppa})\text{-}\{\eta^1\text{-}C(S)NMe_2\}][Cl]$, and $[Pt(PPh_3)_2\{\eta^1\text{-}C(SEt)(NMe_2)\}(\eta^2\text{-}S_2CO)]$

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Abstract

In solution state, the complex $[Pt(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$ (**1**) shows intermolecular displacement of two triphenylphosphine ligands to form the bridging η^2-thiocarbamoyl diplatinum complex $[Pt(PPh_3)Cl]_2(\mu,\eta^2\text{-}SCNMe_2)_2$ (**2**). Intramolecular displacement of the chloride product η^2-thiocarbamoyl complex $[Pt(PPh_3)_2(\eta^2\text{-}SCNMe_2)][Cl]$ (**3**) was not been detected from the $^{31}P\{^1H\}$ NMR experiments. However, the chelating η^2-thiocarbamoyl complex $[Pt(PPh_3)_2(\eta^2\text{-}SCNMe_2)][PF_6]$ (**4**) can be produced by the reaction of **1** with NH_4PF_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 $[Pt(PPh_3)(\eta^2\text{-dppa})\{\eta^1\text{-}C(S)NMe_2\}][Cl]$ (**5**). Treatment of **4** with $EtOCS_2K$ or $MeOCS_2K$ yields Fischer-type carbene-complex $[Pt(PPh_3)\{\eta^1\text{-}C(SEt)(NMe_2)\}(\eta^2\text{-}S_2CO)]$ (**7**) or $[Pt(PPh_3)\{\eta^1\text{-}C(SMe)(NMe_2)\}(\eta^2\text{-}S_2CO)]$ (**8**). The carbene-complexes **7** and **8** are formed via alkyl migration of the alkyldithiocarbonate ligand to the thiocarbamoyl ligand. Complex **1** reacts with $EtOCS_2K$, resulting in the formation of the η^2-dithiocarbonate complex $[Pt(PPh_3)(\eta^1\text{-}SCNMe_2)(\eta^2\text{-}S_2COEt)]$ (**6**) and the carbene-complex $[Pt(PPh_3)\{\eta^1\text{-}C(SEt)(NMe_2)\}(\eta^2\text{-}S_2CO)]$ (**7**) with a ratio of 3:2 according to the integration of the $^{31}P\{^1H\}$ NMR spectra. By continuously stirring mixtures **6** and **7** in the CH_2Cl_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.

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 (VIIIB) [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, $Me_2NC({=}S)Cl$, 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 η^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 [Pt(PPh$_3$)$_2$(η^1-SCNMe$_2$)(Cl)] (**1**) with neutral phosphorus ligand. Three X-ray crystal structure analyses have been carried out to provide structural parameters.

2. Results and discussion

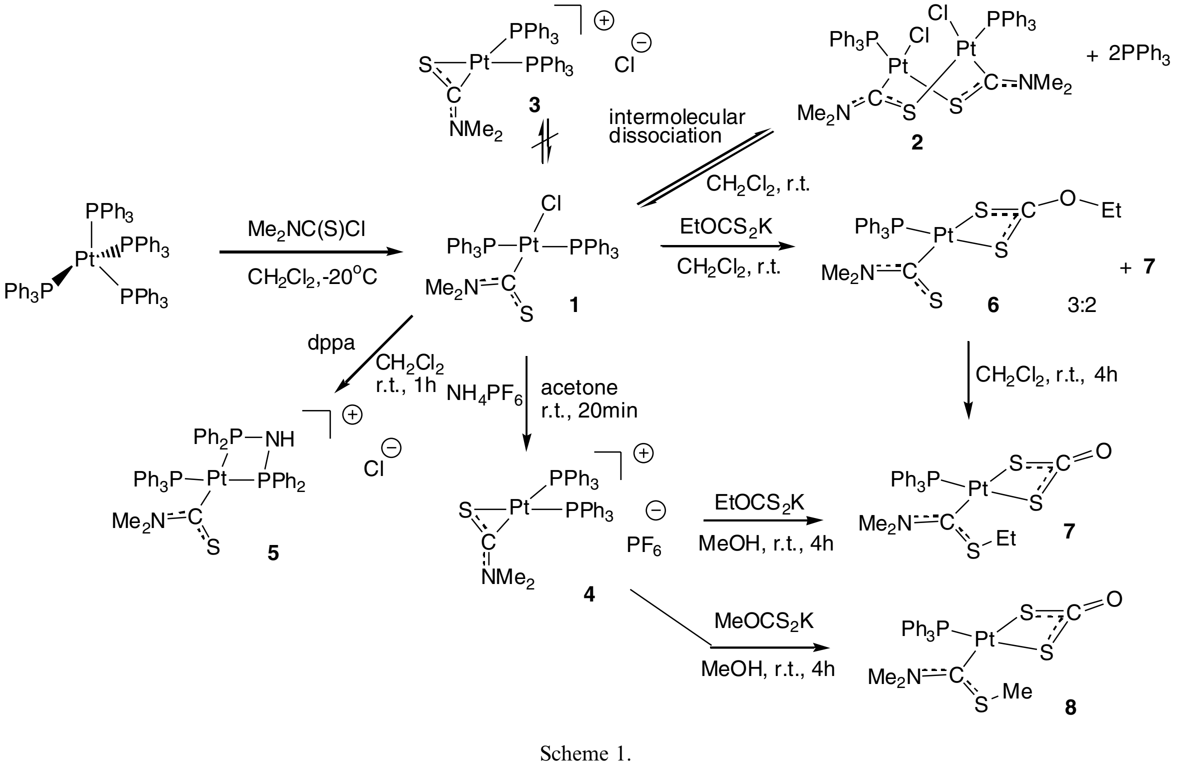
2.1. Syntheses

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

The dichloromethane solution of **1** undergoes intermolecular displacement of the triphenylphosphine ligand of **1** to form the bridging η^2-thiocarbamoyl diplatinum complex [Pt(PPh$_3$)Cl]$_2$(μ,η^2-SCNMe$_2$)$_2$ (**2**) but the intramolecular displacement of the chloride ligand of **1** to form the chelating η^2-thiocarbamoyl complex [Pt(PPh$_3$)$_2$(η^2-SCNMe$_2$)][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 [Pt(PPh$_3$)$_2$(η^2-SCNMe$_2$)][PF$_6$] (**4**) can be synthesized from the reaction of **1** and ammonium hexafluorophosphate, NH$_4$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 [Pd(PPh$_3$)$_2$(η^1-SCNMe$_2$)(Cl)], showing the inter- and intramolecular displacement behavior, was shown to form complexes [Pd(PPh$_3$)Cl]$_2$(μ,η^2-SCNMe$_2$)$_2$ and [Pd(PPh$_3$)$_2$(η^2-SCNMe$_2$)][Cl] [12] and the displacement of either the phosphine or the chloride ligand occurred in CH$_2$Cl$_2$ solution of complex [Pd(PPh$_3$)$_2$(η^1-CH$_2$SCH$_3$)Cl] [15] to form monomer complexes [Pd(PPh$_3$)(η^2-CH$_2$SCH$_3$)Cl] and [Pd(PPh$_3$)$_2$(η^2-CH$_2$SCH$_3$)][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 [Pt(PPh$_3$)(η^2-dppa){η^1-C(S)NMe$_2$}][Cl] (**5**) with 88% isolated yield.

Nucleophilic displacement of the chloride in **1** with anionic dithiocarbonate ligand, EtOCS$_2^-$, in dichloromethane at room temperature produces complex [Pt(PPh$_3$)-(η^1-SCNMe$_2$)(η^2-S$_2$COEt)] (**6**) and carbene-complex [Pt(PPh$_3$)- {η^1-C(SEt)(NMe$_2$)}(η^2-S$_2$CO)] (**7**) in good yields and ^{31}P{^{1}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 [Pt(PPh$_3$){η^1-C(SMe)-(NMe$_2$)}(η^2-S$_2$CO)] (**8**) with 85% isolated yield. The conversion of complex **6** to carbene complex **7** is proposed to



Scheme 1.