

# A new Pd(II) complex of a sulfur ylide; Synthesis, X-ray characterization, theoretical study and catalytic activity toward the Suzuki–Miyaura reaction



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## ABSTRACT

The new sulfonium salt  $[\text{SMe}_2\text{CH}_2\text{C}(\text{O})\text{C}_6\text{H}_4\text{-}m\text{-OCH}_3]\text{Br}$  (**1**) was synthesized from the reaction of dimethyl sulfide and 2-bromo-3'-methoxyacetophenone. Further treatment with NaOH 10% gave the  $\alpha$ -keto stabilized sulfur ylide  $\text{SMe}_2\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{-}m\text{-OCH}_3$  (**2**). This ligand was reacted with the dichloro(1,5-cyclooctadiene)palladium(II) complex,  $[\text{PdCl}_2(\text{cod})]$ , in a 2:1 ratio to give the new  $\text{C}\alpha$ -coordinated complexes *cis*- and *trans*- $[\text{PdCl}_2(\text{SMe}_2\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{-}m\text{-OCH}_3)_2]$  (**3a** and **3b**). Characterization of the obtained compounds was performed by elemental analysis, IR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and mass spectroscopies. Since complexes **3a** and **3b** were insoluble in most organic solvents, we chose DMSO as a suitable solvent for the NMR spectroscopies. Crystallization of above solution led to the formation of single crystals. The X-ray analysis results revealed that complex **3a** has undergone a ligand replacement reaction and the complex  $[\text{PdCl}_2(\text{SMe}_2\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{-}m\text{-OCH}_3)\cdot\text{DMSO}]$  (**4**) was formed. This complex has two Cl atoms in *cis* positions, one sulfur ylide and one S-coordinated DMSO as ligands. The air/moisture stable complexes **3a** and **3b** were employed as efficient catalysts for the Suzuki–Miyaura cross-coupling reaction of several aryl halides. The coupled products of these reactions were obtained in good to excellent yields and purity, with short reaction times and low catalyst loading. Also a theoretical study on the structure and nature of the Pd–C bond in complex **4** is reported here at the BP86/def2-SVP level of theory.

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## 1. Introduction

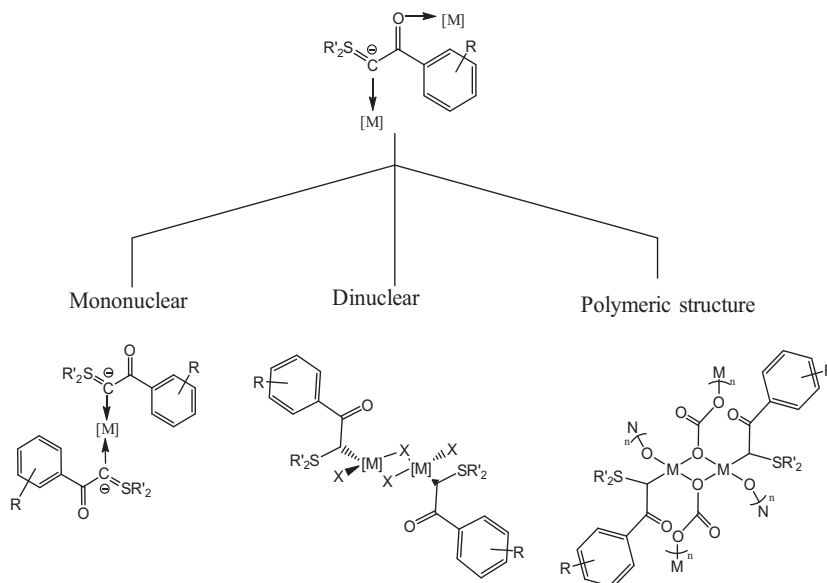
Sulfur ylides,  $\text{R}_2\text{S}=\text{C}(\text{R}')(\text{R}'')$ , are an important class of compounds that have attracted considerable interest because of their value for a variety of industrial, biological and chemical synthetic uses [1–4]. The high stability and ambidentate character of these ylides makes them an appropriate choice for organometallic synthesis [5–7]. The coordination behaviour of these compounds towards several metal ions has been well studied and it was found that they can coordinate through the carbanion or the enolate oxygen atom [8–10]. The  $\text{C}\alpha$  coordinated complexes exhibit three canonical bonding modes, as depicted in Scheme 1: mononuclear, binuclear and polymeric structures. Metal ions such as Pd(II) can interact with the methinic carbon atom of the ylidic group and form a mononuclear structure [11]. If metal ions containing bridging ligands, such as  $\text{HgX}_2$  (X = Cl, Br, I), react with sulfur ylides, a

binuclear structure can form with two halide bridging atoms [12]. Finally, polymeric structure complexes are observed when the metal ions have polymerizing ligands. For example,  $\text{AgNO}_3$  interacts with the  $\text{C}\alpha$  atom of these ylides and makes a structure with a metallic skeleton based on the polymeric nitrate group [13]. Although, O-coordination modes of these compounds are possible, only a few examples of these complexes are known [14].

Over the past 30 years, palladium-catalyzed cross-coupling reactions have gained popularity, especially as a suitable technique for the formation of carbon–carbon bonds [15,16]. Specifically, the Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids has emerged as the most important reaction and a reliable method for the construction of asymmetric biaryls [17,18]. Recently, the application of some phosphorus and sulfur ylides in such cross-coupling reactions by our group was reported [19–21]. Although palladium complexes of phosphorus ylides show high efficiency and moisture/air stability, most of them are expensive and have environmental considerations. The application of complexes containing sulfur or nitrogen as phosphine free

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**Scheme 1.** The canonical bonding modes of  $R_2SCHC(O)C_6H_4R$  to metal ions.

catalytic systems were developed recently to eliminate or reduce costs, operational hazards and environmental pollution [22,23]. For example, Sindhuja et al. reported the synthesis and application of palladium catalysts containing modified sulfur ligands which can accelerate the coupling reactions of aryl bromides with phenylboronic acid [24]. It was found that the release of Pd(0) species in such cross-coupling reactions depends on the nature of the ligands around the palladium centre [20]. Organochalcogen ligands, such as sulfur ylides, show rivalry with their respective phosphorus ylide analogues for releasing of Pd(0) species in the Suzuki–Miyaura reaction [25]. The low catalyst loading and more environmentally safe reagent than the other organometallic reagents make these ligands and their Pd(II) complexes ideal catalysts for the Suzuki–Miyaura reaction [26,27].

The complexation of sulfur ylides to various transition metals has been extensively studied [9,11–13], however the synthesis, X-ray characterization, theoretical study and also application of a palladium complex of a sulfur ylide as a precursor in the Suzuki–Miyaura coupling reaction are the key advantages of this study.

This paper includes the synthesis, spectroscopic and X-ray crystallographic characterization, theoretical study and application of new palladium(II) complex of an  $\alpha$ -keto stabilized sulfur ylide in the Suzuki–Miyaura cross-coupling reaction.

## 2. Experimental

### 2.1. Physical measurements and materials

All of the reactions were carried out under air. All the solvents and starting materials were purchased from commercial sources and used without further purification. The starting material, the dichloro(1,5-cyclooctadiene)palladium(II) complex [PdCl<sub>2</sub>(cod)], was prepared according to the published procedures [28]. Melting points were measured on a SMP3 apparatus. IR spectra were recorded in the range 4000–400 cm<sup>-1</sup> on a Shimadzu 435-U-04 spectrophotometer from KBr pellets. NMR spectra (<sup>1</sup>H and <sup>13</sup>C) were recorded on 500 MHz and 250 MHz Bruker and 90 MHz Jeol spectrometers in DMSO-*d*<sub>6</sub> or CDCl<sub>3</sub> as the solvent at 25 °C. Coupling constants are given in Hz. Elemental analyses for carbon, nitrogen and hydrogen atoms were determined by using a Perkin Elmer 2400 series analyzer.

### 2.2. Synthesis of the compounds

#### 2.2.1. Synthesis of the sulfonium salt [Me<sub>2</sub>SCH<sub>2</sub>C(O)C<sub>6</sub>H<sub>4</sub>-*m*-OMe]Br (1)

Dimethyl sulfide (0.06 g, 1 mmol) was added to an acetic solution (5 ml) of the ketone [BrCH<sub>2</sub>C(O)C<sub>6</sub>H<sub>4</sub>-*m*-OMe] (0.22 g, 1 mmol). The mixture was stirred for 12 h. The resulting precipitate was filtered off and the obtained salt **1** was washed with acetone and dried.

#### 2.2.2. Data for [Me<sub>2</sub>SCH<sub>2</sub>C(O)C<sub>6</sub>H<sub>4</sub>-*m*-OMe]Br

Yield: 0.26 g, 0.93 mmol, 93%. Anal. Calc. for C<sub>11</sub>H<sub>15</sub>O<sub>2</sub>SBr: C, 45.36; H, 5.15; S, 11.01. Found: C, 45.44; H, 5.01; S, 11.13%. Melting point: 132–134 °C. IR (KBr disk)  $\nu$ (cm<sup>-1</sup>): 1676 (CO); 787 (C<sup>-</sup>S<sup>+</sup>). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm)  $\delta$ : 2.97 (s, 6H, S(CH<sub>3</sub>)<sub>2</sub>); 3.84 (s, 3H, OCH<sub>3</sub>); 5.49 (s, 2H, CH<sub>2</sub>); 7.50 (br, 4H, Ph). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, ppm)  $\delta$ : 24.44 (s, S(CH<sub>3</sub>)<sub>2</sub>); 52.68 (s, CH<sub>2</sub>); 55.67 (s, OCH<sub>3</sub>); 113.18 (s, Ph); 119.19 (s, Ph); 121.06 (s, Ph); 130.28 (s, Ph); 135.31 (s, Ph); 159.58 (s, Ph); 191.33 (s, CO).

#### 2.2.3. Synthesis of the sulfur ylide [Me<sub>2</sub>SCHC(O)C<sub>6</sub>H<sub>4</sub>-*m*-OMe] (2)

Treatment of compound **1** (0.29 g, 1 mmol) with H<sub>2</sub>O (0.5 ml) and aqueous NaOH 10% solution (2 ml) led to elimination of HBr, giving the sulfur ylide **2**. The mixture was stirred for 30 min. Ligand **2** was obtained by extraction of the resulting solution with chloroform, followed by precipitation with petroleum benzene and dried.

#### 2.2.4. Data for [Me<sub>2</sub>SCHC(O)C<sub>6</sub>H<sub>4</sub>-*m*-OMe]

Yield: 0.18 g, 0.86 mmol, 86%. Anal. Calc. for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>S: C, 62.84; H, 6.66; S, 15.26. Found: C, 62.94; H, 6.7; S, 15.27%. IR (KBr disk)  $\nu$ (cm<sup>-1</sup>): 1596 (CO); 847 (C<sup>-</sup>S<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm)  $\delta$ : 2.90 (s, 6H, S(CH<sub>3</sub>)<sub>2</sub>); 3.79 (s, 3H, OCH<sub>3</sub>); 4.99 (s, 1H, CH); 6.89–7.23 (mm, 4H, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm)  $\delta$ : 28.53 (s, S(CH<sub>3</sub>)<sub>2</sub>); 52.79 (s, CH<sub>2</sub>); 55.24 (s, OCH<sub>3</sub>); 110.88 (s, Ph); 116.04 (s, Ph); 118.97 (s, Ph); 120.00 (s, Ph); 142.25 (s, Ph); 159.38 (s, Ph); 182.69 (s, CO).

#### 2.2.5. Synthesis of the Pd(II) complexes *cis*- and *trans*-[PdCl<sub>2</sub>(Me<sub>2</sub>SCHC(O)C<sub>6</sub>H<sub>4</sub>-*m*-OMe)<sub>2</sub>] (3a and 3b)

A dichloromethane solution of ylide **2** (0.21 g, 1 mmol, 5 ml) was added to a dichloromethane solution of [PdCl<sub>2</sub>(cod)] (0.14 g,

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