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Graphical abstract: pictogram

Pd(II) and Pt(II) complexes of α -keto stabilized sulfur ylide: Synthesis, structural, theoretical and catalytic activity studies

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ABSTRACT: Reaction of dimethyl sulfide with 2, 3'-dibromoacetophenone led to formation of sulfonium salt [Me₂SCH₂C(O)C₆H₄-*m*-Br]Br (**1**). The resulted sulfonium salt was treated with NaOH and gave the α -keto stabilized sulfur ylide Me₂SC(H)C(O)C₆H₄-*m*-Br (**2**). This ligand was reacted with [MCl₂(cod)] (M = Pd, Pt; cod = 1,5-cyclooctadiene) to form the new *cis*- and *trans*-[MCl₂(ylide)₂] (M = Pd (*cis*- and *trans*-**3**), Pt (*cis*- and *trans*-**4**)) complexes. Characterization of the obtained compounds was performed by elemental analysis, IR, ¹H and ¹³C NMR. Recrystallization of dichlorobis(ylide) palladium(II) and platinum(II) complexes from DMSO solution yielded the crystalline products, which X-ray diffraction data revealed that the both compounds were crystallized as *cis*-[MCl₂(ylide)(DMSO)] (M = Pd (**5**), Pt (**6**)) complexes. Also, a theoretical study on structure and nature of the M–C bonding between the Y ligand (ylide) and [MCl₂.DMSO] fragments in [YMCl₂.DMSO] (M=Pd, Pt) complexes has been reported via NBO and energy-decomposition analysis (EDA). Furthermore, the palladium catalyzed Suzuki-Miyaura reaction of various aryl chlorides with arylboronic acids was performed. The results

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showed that the Pd(II) complexes *cis*- and *trans*-**3** catalyzed efficiently coupling reactions at low catalyst loading and short reaction time.

Keywords: Synthesis; Pd(II) and Pt(II) complexes; Sulfur ylide; X-ray characterization; Theoretical study; Suzuki-Miyaura reaction.

1. Introduction

Sulfur ylides are a group of reactive compounds which have attracted considerable interest in recent years [1-3]. This is not least because of their significant role in organic synthesis, including Johnson-Corey-Chaykovsky reaction [4], which is due to the high stability and ambidentate character as ligand can engage as an appropriate ligand for organometallic synthesis [5-7]. The coordination chemistry of these compounds has been investigated extensively and it was found that they can bond to a metal center through the carbanion or the enolate oxygen (Scheme 1) [8-10]. From consideration of the Hard-Soft-Acid-Base principle (HSAB) [11], it can be hypothesized that the title ligands tend to coordinate to soft metal ions *via* the soft ylidic carbon as opposed to the hard carbonyl oxygen atom. The more observed C α -coordination mode corresponds to the transition metal complexes of Hg(II) [9], Cd(II) [10], Ag(I) [3] and Pd(II) [12], while the O-coordination mode of these compounds is limited to a small number of complexes with hard oxophilic metals such as tungsten [13].

Scheme 1 here

The palladium catalyzed Suzuki-Miyaura reaction is one of the most reliable methods for the construction of C_{sp2} - C_{sp2} bond [14-16]. Although this reaction originally catalyzed by palladium complexes containing bulky phosphine ligands [17,18], but most of them are moisture/air

sensitive and have environmental considerations. Application of more stable and cheaper complexes containing sulfur or nitrogen ligands was developed to eliminate or reduce costs, operational hazards and environmental pollution [19-21]. Very recently, our group reported the synthesis of sulfur-containing palladium complexes and successful application as catalyst precursors for the Mizoroki-Heck reaction [22]. Furthermore, attempts to use more economical aryl chlorides which are less reactive than aryl bromides and iodides in C-C coupling reactions showing a noteworthy growth [23-25]. Mostly electron-poor aryl chlorides, which are easier to activate, have been used successfully in these reactions and non-activated aryl chlorides or even deactivated aryl chlorides such as chloroanisoles were coupled by applying palladium complexes in combination with phosphonium salts [26].

Notwithstanding this background, we choose the Pd(II) and Pt(II) complexes of sulfur ylides as attractive candidates for the synthesis, X-ray characterization and theoretical studies. Although, the complexation of sulfur ylides to various transition metals has been extensively studied, however, application of the Pd(II) complexes of sulfur ylides in the Suzuki-Miyaura reaction of less reactive aryl chlorides is the key advantage of this study.

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 $[PdCl_2(cod)]$ and $[PtCl_2(cod)]$ were prepared according to the published procedures [27]. Melting points were measured on a SMP3 apparatus. IR spectra were recorded in the range of 4000–400

cm⁻¹ and on a Shimadzu 435-U-04 spectrophotometer from KBr pellets. NMR spectra (¹H and 13 C) were recorded on 500 MHz, 400 MHz and 250 MHz Bruker and 90 MHz Jeol spectrometers in DMSO-d₆ or CDCl₃ as the solvent at 25 °C. Elemental analyses for Carbon, nitrogen, hydrogen and sulfur atoms were determined by using a PerkinElmer 2400 series analyzer.

2.2. Synthesis of compounds

2.2.1. Synthesis of [Me₂SCH₂C(O)C₆H₄-*m*-Br]Br (1)

Dimethyl sulfide (0.28 mL, 3 mmol) was added to an acetone solution (5 mL) of ketone BrCH₂C(O)C₆H₄-*m*-Br (0.28 g, 1 mmol). The mixture was stirred for 15 h. The resulting solution was filtered off, and the obtained precipitate **1** washed with acetone and dried. Yield 0.31 g, 95%. Anal. Calcd. for C₁₀H₁₂Br₂OS (%): C, 35.32; H, 3.56; S, 9.43. Found: C, 35.44; H, 3.61; S, 9.32. Melting point: 197–199 °C. IR (KBr disk): v(cm⁻¹) 1682 (CO); 802 (C⁻-S⁺). ¹H NMR (89.60 MHz, DMSO-d₆) $\delta_{\rm H}$ (ppm): 3.04 (s, 6H, S(CH₃)₂); 5.65 (s, H, CH); 7.38 (s, H, Ph); 7.58 (s, H, Ph); 7.67 (s, H, Ph); 7.94 (s, 1H, Ph); 8.17 (s, H, Ph). ¹³C NMR (62.90 MHz, DMSO-d₆) $\delta_{\rm C}$ (ppm): 25.10 (s, S(CH₃)₂); 53.10 (s, CH₂); 122.79 (s, Ph); 127.94 (s, Ph); 131.65 (s, Ph); 136.36 (s, Ph); 137.88 (s, Ph); 190.87 (s, CO).

2.2.2. Synthesis of $Me_2SCHC(O)C_6H_4$ -*m*-Br (2)

Treatment of compound **1** (0.31 g, 0.9 mmol) with H₂O (0.5 mL) and aqueous NaOH 10% solution (2 mL) led to elimination of HBr, affording the sulfur ylide **2**. The mixture was stirred for 30 min. Ligand **2** as orange oil was obtained by extraction of resulting solution with chloroform, followed by washing with petroleum benzine. Yield 0.21 g, 84%. Anal. Calcd. for $C_{10}H_{11}BrOS$ (%):C, 46.35; H, 4.28; S, 12.37. Found: C, 46.40; H, 4.39; S, 12.17. IR (Nojul):

v(cm⁻¹) 1577 (CO); 853 (C⁻-S⁺). ¹H NMR (89.60 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 2.98 (s, 6H, S(CH₃)₂); 4.65 (s, H, CH); 7.27 (s, H, Ph); 7.45 (s, H, Ph); 7.64 (s, H, Ph); 7.93 (s, 1H, Ph). ¹³C NMR (22.53 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 28.08 (s, S(CH₃)₂); 54.97 (s, CH); 121.30 (s, Ph); 124.24 (s, Ph); 128.74 (s, Ph); 131.29 (s, Ph); 142.44 (s, Ph); 179.17 (s, CO).

2.2.3. Synthesis of cis- and trans-[PdCl₂(Me₂SCHC(O)C₆H₄-m-Br)₂] (cis- and trans-3)

Dichloromethane solution of ylide **2** (0.21 g, 0.8 mmol, 5 mL) was added to a solution of [PdCl₂(cod)] (0.12 g, 0.4 mmol, 5 mL, CH₂Cl₂). The mixture was stirred for 2 h at room temperature. The separated yellow solid was filtered and washed with diethyl ether and dried. Yield 0.24 g, 85%. Anal. Calcd. for C₂₀H₂₀Br₂Cl₂O₂PdS₂ (%):C, 34.63; H, 2.91; S, 9.24. Found: C, 34.71; H, 2.99; S, 9.11. Decomposition at: 181-193 °C. IR (KBr disk): v(cm⁻¹) 1624 (CO); 798 (C⁻-S⁺). Far-IR v(cm⁻¹): 256 (Pd-Cl) (*cis* isomer); 333 (Pd-Cl) (*trans* isomer). ¹H NMR (250.13 MHz, DMSO-d₆) $\delta_{\rm H}$ (ppm): 2.59-2.81 (m, 6H, S(CH₃)₂) (*trans* isomer); 2.72-3.13 (m, 6H, S(CH₃)₂) (*cis* isomer); 5.67-5.72 (m, 1H, CH) (*cis* isomer); 7.28-8.43 (m, 8H, Ph). ¹³C NMR (62.90 MHz, DMSO-d₆) $\delta_{\rm C}$ (ppm): 26.46-27.43 (m, S(CH₃)₂) (*trans* isomer), 26.76-27.65 (m, S(CH₃)₂) (*cis* isomer); 49.13 (s, SCH) (*trans* isomer), 49.78 (s, SCH) (*cis* isomer).

2.2.4. Synthesis of *cis*- and *trans*-[PtCl₂(Me₂SCHC(O)C₆H₄-*m*-Br)₂] (*cis*- and *trans*-4)

Dichloromethane solution of ylide **2** (0.21 g, 0.8 mmol, 5 mL) was added to a solution of $[PtCl_2(cod)]$ (0.15 g, 0.4 mmol, 5 mL, CH_2Cl_2). The mixture was stirred for 4 h at room temperature. The separated pale yellow solid was filtered and washed with diethyl ether and dried. Yield 0.23 g, 72%. Anal. Calcd. for $C_{20}H_{20}Br_2Cl_2O_2PtS_2$ (%):C, 30.63; H, 2.83; S, 8.18.

Found: C, 30.71; H, 2.90; S, 8.12. Decomposition at: 190-198 °C. IR (KBr disk): v(cm⁻¹) 1634 (CO); 796 (C⁻-S⁺). ¹H NMR (250.13 MHz, DMSO-d₆) $\delta_{\rm H}$ (ppm): 2.60-2.78 (m, 6H, S(CH₃)₂) (*trans* isomer); 3.01-3.18 (m, 6H, S(CH₃)₂) (*cis* isomer); 5.70 (m, 1H, CH) (*trans* isomer); 5.90 (s, 1H, CH, ²J_{Pt-H} = 377.68 Hz) (*cis* isomer); 7.28-8.48 (m, 8H, Ph). ¹³C NMR (62.90 MHz, DMSO-d₆) $\delta_{\rm C}$ (ppm): 25.68-26.68 (m, S(CH₃)₂) (*trans* isomer), 27.14-27.47 (m, S(CH₃)₂) (*cis* isomer); 49.13 (s, SCH) (*trans* isomer), 47.12 (s, SCH) (*cis* isomer), 121.54-145.95 (m, Ph); 193.45-193.54 (m, CO) (*trans* isomer); 193.75- 193.87 (m, CO) (*cis* isomer).

2.2.5. Synthesis of cis-[PdCl₂(Me₂SCHC(O)C₆H₄-m-Br)(DMSO)] (5)

0.03 g (0.05 mmol) of complexes *cis*- and *trans*-**3** was dissolved in DMSO (1 mL). The yellow crystals were formed by the slow diffusion of methanol into the DMSO solution over two weeks. The separated crystals were filtered and washed with diethyl ether and dried. Decomposition at: 181-193 °C. IR (KBr disk): v(cm⁻¹) 1623 (CO); 1163 (SO). ¹H NMR (250.13 MHz, DMSO-d₆) $\delta_{\rm H}$ (ppm): 2.59-2.81 (m, 6H, S(CH₃)₂) (*trans* isomer); 2.72-3.13 (m, 6H, S(CH₃)₂) (*cis* isomer); 4.99 (s, 1H, CH) (*trans*, major diastereoisomer); 5.07 (s, 1H, CH) (*trans*, minor diastereoisomer); 5.67-5.72 (m, 1H, CH) (*cis* isomer); 7.28-8.43 (m, 8H, Ph). ¹³C NMR (62.90 MHz, DMSO-d₆) $\delta_{\rm C}$ (ppm): 26.46-27.43 (m, S(CH₃)₂) (*trans* isomer), 26.76-27.65 (m, S(CH₃)₂) (*cis* isomer); 49.13 (s, SCH) (*trans* isomer), 49.78 (s, SCH) (*cis* isomer), 121.97-139.71 (m, Ph); 192.71-192.85 (m, CO) (*trans* isomer); 193.86 (m, CO) (*cis* isomer).

2.2.6. Synthesis of *cis*-[PtCl₂(Me₂SCHC(O)C₆H₄-*m*-Br)(DMSO)] (6)

0.04 g (0.05 mmol) of complexes *cis*- and *trans*-4 was dissolved in DMSO (1 mL). The pale yellow crystals were formed by the slow diffusion of methanol into the DMSO solution over two weeks. The separated crystals were filtered and washed with diethyl ether and dried. Decomposition at: 190-198 °C. IR (KBr disk): $v(cm^{-1})$ 1633 (CO); 1130 (SO). ¹H NMR (250.13

MHz, DMSO-d₆) $\delta_{\rm H}$ (ppm): 2.60-2.78 (m, 6H, S(CH₃)₂) (*trans* isomer); 3.01-3.18 (m, 6H, S(CH₃)₂) (*cis* isomer); 5.70 (m, 1H, CH) (*trans* isomer); 5.90 (s, 1H, CH, ²J_{Pt-H} = 377.68 Hz) (*cis* isomer); 7.28-8.48 (m, 8H, Ph). ¹³C NMR (62.90 MHz, DMSO-d₆) $\delta_{\rm C}$ (ppm): 25.68-26.68 (m, S(CH₃)₂) (*trans* isomer), 27.14-27.47 (m, S(CH₃)₂) (*cis* isomer); 49.13 (s, SCH) (*trans* isomer), 47.12 (s, SCH) (*cis* isomer), 121.54-145.95 (m, Ph); 193.45-193.54 (m, CO) (*trans* isomer); 193.75-193.87 (m, CO) (*cis* isomer).

2.3. X-ray crystallography:

Suitable crystals of complexes **5** and **6** were selected and mounted on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 130.00(10) K during data collection. Using Olex2 [28], the structure was solved with the ShelXT [29] structure solution program using Direct Methods and refined with the ShelXL [30] refinement package using Least Squares minimisation. All non-Hydrogen atoms were refined with anisotropic displacement parameters; all H-atoms were constrained at geometrical estimates, with isotropic displacement parameters of either 1.5 times (Me) or 1.2 times (other) the displacement parameters of the parent carbon atom.

2.4. Computational studies

All of these studies have been down at DFT level of theory using the exchange functional of Becke and the correlation functional of Perdew (BP86) [<u>31,32</u>]. The geometries of [YPdCl₂DMSO] and [YPtCl₂DMSO] complexes were optimized at BP86/def2-SVP [<u>33</u>] with C1 symmetry. All calculations were performed using the Gaussian 09 set of programs [<u>34</u>]. NBO [<u>35</u>] analysis was performed using internal model GAUSSIAN 09, and it gives good information about the nature of bonding. For bonding analyses in the terms of energy-decomposition analysis, were carried out at BP86/TZ2P(ZORA)//BP86/def2-TZVPP with C1 symmetry. The

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basis sets for all elements have triple- ζ quality augmented by one set of polarization functions (ADF basis set TZP(ZORA)) with the program package ADF2009.01.

2.5. General procedure for Suzuki-Miyaura reaction

A one-pot mixture of aryl chloride (0.5 mmol), arylboronic acid (0.75 mmol), catalyst (1 mol%), Cs_2CO_3 (1 mmol) and DMF/H₂O (2 mL, 1:1) was heated to 100 °C for 2 h. The reaction progress was monitored by thin layer chromatography (TLC). After completion of the reaction, the tube was cooled and the mixture was diluted with *n*-hexane (15 mL) and water (15 mL). The resulting organic layer was washed with brine (15 mL) and dried over CaCl₂. Purification was done either by flash chromatography (*n*-hexane:EtOAc, 8:2) or by recrystallization and the final product was then characterized by ¹H and ¹³C NMR spectroscopies.

2.6. Characterization of the Suzuki-Miyaura coupling products

2.6.1. 4-Nitro-biphenyl (7a)

Melting point: 67-69 °C. ¹H NMR (89.6 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 6.74-8.15 (m, 9H, biphenyl). ¹³C NMR (100.62 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 124.08-147.59 (m, biphenyl).

2.6.2. 4-Acetyl-biphenyl (**7b**)

Melting point: 105–108 °C. ¹H NMR (89.6 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 3.40 (s, 3H, CH₃), 7.46-8.21 (m, 9H, biphenyl). ¹³C NMR (100.62 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 26.75 (s, CH₃), 127.11-145.63 (m, biphenyl), 197.53 (s, CO).

2.6.3. Biphenyl (7c)

Melting point: 67-69 °C. ¹H NMR (400.61 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 7.40-7.64 (m, 10H, phenyl). ¹³C NMR (100.62 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 127.21-141.29 (m, biphenyl).

2.6.4. 4-Methyl-biphenyl (7d)

8

Melting point: 48-50 °C. ¹H NMR (89.6 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 2.46 (s, 3H, CH₃), 7.26-7.61 (m, 9H, phenyl). ¹³C NMR (100 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 21.08 (s, CH₃), 126.94-141.11 (m, biphenyl).

2.6.5. 4-Methoxy-biphenyl (7e)

Melting point: 90-92 °C. ¹H NMR (400.61 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 3.78 (s, 3H, OCH₃), 6.90-7.49 (m, 9H, phenyl). ¹³C NMR (100.62 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 55.36 (s, OCH₃), 114.20-159.15 (m, biphenyl).

2.6.6. 4-Nitro-4'-ethyl biphenyl (7f)

Melting point: 82-83 °C. ¹H NMR (400 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 1.32 (t, 3H, CH₃), 2.75 (q, 2H, CH₂), 7.28-8.32 (m, 8H, biphenyl). ¹³C NMR (100 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 15.50 (s, CH₃), 28.60 (s, CH₂), 124.11-147.61 (m, biphenyl).

2.6.7. 4-Acetyl-4'-ethyl biphenyl (7g)

Melting point: 105–108 °C. ¹H NMR (400.61 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 1.29 (t, 3H, CH₃), 2.71 (s, 3H, CH₃), 2.74 (q, 2H, CH₂), 7.26-8.03 (m, 8H, biphenyl). ¹³C NMR (100.62 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 15.52 (s, CH₃), 26.64 (s, CH₃), 28.55 (s, CH₂), 126.90-154.74 (m, biphenyl), 197.76 (s, CO).

2.6.8. 4-Ethyl- biphenyl (**7h**)

Melting point: 82-83 °C. ¹H NMR (89.6 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 1.39 (t, 3H, CH₃), 2.78 (q, 2H, CH₂), 7.32-7.67 (m, 9H, biphenyl). ¹³C NMR (100 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 15.59 (s, CH₃), 28.48 (s, CH₂), 126.89-143.33 (m, biphenyl).

2.6.9. 4-Ethyl- 4'-methyl biphenyl (7i)

Melting point: 90-91 °C. ¹H NMR (400 MHz, CDCl₃) δ_{H} (ppm): 1.32 (t, 3H, CH₃), 2.44 (s, 3H,

CH₃), 2.74 (q, 2H, CH₂), 7.27-7.57 (m, 8H, biphenyl). ¹³C NMR (100 MHz, CDCl₃) δ_{C} (ppm): 15.64 (s, CH₃), 21.12 (s, CH₃), 28.54 (s, CH₂), 126.88-143.01 (m, biphenyl).

2.6.10. 4-Methoxy- 4'-ethyl biphenyl (7j)

Melting point: 73-75 °C. ¹H NMR (89.6 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 1.29 (t, 3H, CH₃), 2.67 (q, 2H, CH₂), 3.86 (s, 3H, OCH₃), 6.93–7.46 (m, 8H, biphenyl). ¹³C NMR (250 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 15.56 (s, CH₃), 31.15 (s, CH₂), 55.23 (s, OCH₃), 114.03-158.66 (m, biphenyl).

3. Results and discussion

3.1. Synthesis

As shown in <u>Scheme 2</u>, dimethyl sulfide reacts with the 2, 3'-dibromoacetophenone in equimolar ratios, forming the sulfonium salt **1** in 95% yields. The resulted salt was treated with NaOH 10% to obtain the sulfur ylides **2** in 85% yields. Reaction of this ylide with $[MCl_2(cod)]$ (M = Pd and Pt) in 2:1 ratio gives the new square-planar complexes *cis*- and *trans*- $[MCl_2(Me_2SCHC(O)C_6H_4-m-Br)_2]$ (M = Pd, *cis*- and *trans*-**3**; M = Pt, *cis*- and *trans*-**4**). Recrystallization of these complexes from DMSO solution leads to ligand replacement reaction, affording the DMSO coordinated *cis*- $[MCl_2(ylide)(DMSO)]$ (M = Pd (**5**), Pt (**6**)) complexes. Because of the very low solubility of these complexes in most of common solvents such as chloroform, acetone and ethanol, we chose DMSO as a suitable solvent for the NMR spectroscopies and crystallization.

Scheme 2 here

3.2. Spectroscopy

The structures were characterized successfully by elemental analysis, IR, ¹H and ¹³C NMR spectroscopies. The CHNS elemental analysis of complexes **3** and **4** confirmed the complexation

of sulfur ylide with MCl_2 (M = Pd, Pt) in a 2:1 stoichiometry. <u>Table 1</u> shows the brief summary of the spectroscopic data.

Table 1 here

The v(CO) in the IR spectrum of sulfur ylide **2** was observed as a sharp band around 1577 cm⁻¹ which shows lower frequency shift than the related sulfonium salt **1** (1682 cm⁻¹). This absorption band is sensitive to the coordination mode of ylide; that is coordination through the carbanion shifts the v(CO) to higher frequencies in complexes **3** and **4**, while, if the complexation occurred through oxygen atom, we expect decrease of v(CO) [15]. Mid-IR spectroscopy could not differentiate between geometric isomers (*cis* and *trans*) of these complexes. However, the far IR spectrum of complexes *cis*- and *trans*-**3** exhibit two Pd-Cl stretching band around the 333 and 256 cm⁻¹, indicating presence of both *cis*- and *trans*-dichlorobis(sulfur ylide) structure in the solid state [<u>36</u>].

¹H NMR spectrum of the sulfur ylide **2** exhibits the SCH signals at lower frequencies compared to that of the sulfonium salt **1**. This upfield shift is due to the presence of formal negative charge on the methinic carbon, which increases the electron density in C-H bond. The SCH signals in the ¹H NMR spectra of complexes **3** and **4** are the best spectroscopic probe for determining the coordination mode of ylide to metal center. These signals are appeared at higher frequencies compared to the ylide **2**, indicating that the C α -coordination of ylide has occurred. ¹H NMR spectroscopic studies was also confirmed the presence of both the *cis* and *trans* isomers of complexes **3** and **4**. ¹H NMR spectra of these complexes show two sets of doublet peaks for SMe₂ and methine groups. The higher field pair of SMe₂ and the methinic proton signals may be assigned to the *trans* isomer [<u>36</u>]. Because these complexes have chiral centres at methinic carbons, two diastereoisomers (RR/SS or RS/SR) are expected for each of them [<u>3,13</u>]. Also, it

was concluded from the integrated intensities of the SMe₂ signals in the ¹H NMR spectrum of complexes *cis*- and *trans*-**3** that the ratio of the *cis* to *trans* isomer was about 2:1. The fact that *trans*-PdCl₂(ylide)₂ is a major portion of isomers mixture would be mainly attributed to a smaller steric repulsion between ylide ligands [<u>36</u>]. However, the signals of methine proton in the ¹H NMR spectrum of complexes *cis*- and *trans*-PtCl₂(ylide)₂ show similar intensities and implies that both isomers have same proportion in the *cis*- and *trans*-**4** complexes.

In the ¹³C NMR spectrum of sulfur ylide **2**, the signals of methinic carbon was shifted to higher frequencies than those of sulfonium salt **1**. Contrariwise, coordination of the sulfur ylide through C α , causes to an upfield shift of the signals due to the ylidic carbon atoms in complexes **3** and **4** [3]. This is the most important aspect of the ¹³C NMR spectra of these complexes and attributed to the change in hybridization of the ylidic carbon atom upon coordination to metal ions [37]. The ¹³C chemical shifts of the CO group for complexes **3** and **4** were found to be around 190 ppm, compared with 180 ppm for the same carbon in the parent free ylide, indicating a much lower shielding of the CO group in these complexes [3]. Also, the ¹³C NMR spectra of two geometric isomers. Such geometrical and optical isomerism led to observation of four CH₃ signals due to the two SMe₂ groups and two SCH signals due to the two methinic group in the ¹³C NMR spectra [36].

3.3. Crystallography

Yellow single crystals of complexes **5** and **6** were grown by vapour diffusion of methanol into DMSO. The molecular structures of these complexes were shown in <u>Fig. 1</u>. Relevant parameters concerning data collection, refinement and bond angles were given in <u>Table 2</u>. Selected bond distances for the unit cells of **5** and **6** are displayed in <u>Table 3</u>.

Fig. 1 here

Table 2 here

Table 3 here

The Pd and Pt atoms in complexes **5** and **6** are in a square planar environment, coordinated by one ylide, two chlorides and a DMSO molecule. The bromo substituted aromatic ring is oriented such that the bromine atom is *trans* to the ketone oxygen. There are number of weak inter- & intra- molecular C-H...Cl, C-H...Br, C-H...O and C-H...S interactions. There is also a π ... π interaction between the aromatic rings of two adjacent molecules. These interactions link the molecules into 3D network.

3.4. DMSO as ligand

Although DMSO is known as one of the best solvents for dissolving such compounds, but it can behave as an ambidentate ligand and bind to a metal center either through the sulfur atom or through the oxygen atom. Estimation of the coordination mode of DMSO is highly depends on both electronic and steric factors [38]. Especially in the case of S-bonding, steric demands of coordination have more contribution than the moderate π -acceptor properties [39]. For example, our group reported the synthesis of Hg(II) complexes of type [HgCl₂.(P-ylide).DMSO], in which P-ylide was a bulky phosphine ligand (Ph₃PCHC(O)C₆H₄Cl) [39, 40]. Despite the fact that Hg(II) is a soft metal ion and S-bonding mode is preferred, but the steric hindrance of such bulky ligands induce the O-bonding mode.

Based on the above mentioned rationale, such ligand-replacement reaction is expected for the DMSO solution of complexes *cis-* and *trans-3* and 4. Non-bulky sulfur ylide ligands and relatively soft metal ions such as Pd(II) and Pt(II) lead to preferring of S-bonding coordination mode of DMSO in complexes 5 and 6. Even though the attempts to achieve suitable single

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crystal of complexes *cis*- and *trans*-**3** and **4** for X-ray characterization were unsuccessful, the obtained new DMSO coordinated complexes **5** and **6** are good evidence for complex formation between the Pd(II) or Pt(II) metal ions and the sulfur ylide **2**.

3.5. Computational studies

A theoretical study on structures and nature of bond in [Y.PdCl₂.DMSO] and [Y.PtCl₂.DMSO] (Y= ylide **2**) complexes at the BP86/def2-SVP level of theory has been reported. It has been shown that BP86 is suitable level for calculation of bonding situation between the M←L in such as these complexes [40-55]. X-Ray crystal structures confirm that both of [YPdCl₂.DMSO] and [YPtCl₂.DMSO] have square planar structures with two chlorine atom in cis position (see Fig. 2). Thus, further studies including geometry optimization, NBO and EDA analysis were performed on the Cis-like structure. The optimized structures of [YPdCl₂.DMSO] and[YPtCl₂.DMSO] using BP86/def2-SVP level are shown in Fig 2 and also selected experimental and calculated bond lengths, and bond angles for latter complexes are illustrated in Table 4. The calculated bond lengths and bond angles of these complexes are in good agreement with the experimental values.

Fig. 2 here

Table 4 here

In continuation the NBO analyses used for estimate the delocalization of electron density between occupied Lewis-type orbitals and formally unoccupied non-Lewis NBOs (antibonding or Rydberg), which corresponds to stabilizing donor-acceptor interaction [56].

The values of partial charges and WBI for Pd, Pt, C and Cl atoms involved in the bonding interactions between [PdCl₂DMSO] and [PtCl₂DMSO] with Y fragment in [YMCl₂DMSO] (M= Pd, Pt) complexes as well as, the total charge of [MCl₂.DMSO] (M= Pd, Pt) fragments were also

evaluated through natural population analysis and are given in <u>Table 5</u>. The result showed that the calculated partial charges on the C and M atoms in [YMCl₂.DMSO] (M=Pd, Pt) complexes are negative and positive. Thus, it can conclude that there is σ donation between the lone pair of C atom for Y fragment and also empty orbital of M atoms from [MCl₂DMSO] (M=Pd, Pt) in M–C bond (see <u>Table 5</u>).

Table 5 here

Also the negative value of total charge of [MCl₂.DMSO] (M=Pd, Pt) fragments show that there are charge transfers about 0.4 from Y ligand to [MCl₂.DMSO] (M=Pd, Pt) fragments in [YMCl₂.DMSO] complexes. These data could confirm the existence of a strong interaction between the Y ligand and [MCl₂.DMSO] (M=Pd, Pt) fragments in [YMCl₂.DMSO] complexes. In continuation, a second-order perturbation theory analysis of the Fock matrix was carried out to evaluate the donor–acceptor interactions on the base of NBO analysis. The values of donoracceptor interactions for latter complexes are given in <u>Table 6</u>. The calculated data showed that the important donor–acceptor interactions in the case of Pd–C bonds in [YPdCl₂DMSO] complex were concern to σ (Pd–C), σ (Pd–Cl) and LP of Cl atoms as donors and σ^* (Pd–C), σ^* (C–O), as acceptors. Also in the case of Pt–C bonds in [YPtCl₂DMSO] complex they concern to σ (Pt– C), and LP of S atoms as donors and σ^* (Pd–C), σ^* (C–O), and LP* of Pt as acceptors (see <u>Table 6</u>).

Table 6 here

To better understand the nature of the M–C bonding between the Y ligand and [MCl₂.DMSO] fragments in [YMCl₂.DMSO] (M=Pd, Pt) complexes, we carried out quantum chemical calculations in the terms of energy-decomposition analysis at the

BP86-D3/TZ2P(ZORA)//BP86/def2-SVP with C_1 symmetry with the program package ADF2009.01.

The ΔE_{int} between two investigated fragments in [YPdCl₂DMSO] complex is about 73 kcal mol⁻¹ (see <u>Table 7</u>) and that for [YPtCl₂DMSO] complex is about 85 kcal mol⁻¹. The result shows that the binding of Y fragment to [PdCl₂DMSO] in [YPdCl₂DMSO] complex is stronger than that in [YPtCl₂.DMSO] complex. The breakdown of the ΔE_{int} values into the Pauli repulsion ΔE_{Pauli} and the two attractive components shows that roughly 62-60% comes from the electrostatic attraction ΔE_{elstat} while ~33% comes from the orbital term ΔE_{orb} and the remaining concern to $\Delta E_{dispersion}$ for [YMCl₂DMSO] (M=Pd, Pt) respectively. Also, the values of ΔE_{elstat} showed that the percent of electrostatic nature of Pd–C bonding in [Y.PdCl₂.DMSO] is slightly more than [Y.PtCl₂.DMSO]. The covalent bonding between the [MCl₂.DMSO] fragment and Y ligand in [Y.MCl₂.DMSO] (M=Pd, Pt) complexes becomes visible by the calculated deformation densities $\Delta \rho$.

Table 7 here

Fig. 3 and Fig. 4 show the important deformation densities $\Delta \rho$ and the associated energy values which provide about 90 % of the overall orbital interactions for the complex. Visual inspection of Fig. (3a, c and 4a, c) indicates the $\Delta \rho 1$ and $\Delta \rho 3$, which show the main contribution to ΔE_{orb} and comes from the [DMSOCl₂M \leftarrow Y] σ donation. Also Fig. (3b, d, e and 4b, d, e) display the deformation density $\Delta \rho 2$, $\Delta \rho 4$, and $\Delta \rho 5$, which come from the [MCl₂DMSO] (M=Pd, Pt) to Y fragment π -back donation.

Fig. 3 here

Fig. 4 here

3.6. Catalytic activity

Suzuki-Miyaura coupling reaction of varous aryl chlorides with arylboronic acids was then examined by using the palladium complexes *cis*- and *trans*-**3**. As noted in literature, release of Pd(0) as catalytic active species in C-C coupling reactions is highly depends on the nature of ligands around the palladium center [57]. Although a wide variety of palladium(II) complexes containing phosphorus ylide efficiently promote such coupling reactions, their sulfur ylide analogues show rivalry for releasing of Pd(0) species in these reactions [58]. In order to investigate the catalytic activity of the Pd(II) complexes *cis*- and *trans*-**3**, we carried out a model reaction to optimize the reaction conditions including solvent, base, temperature and catalyst loading (Table 8). As these catalysts are not sensitive to oxygen, the reactions were carried out in the air atmosphere. Reaction of phenylboronoic acid with chlorobenzene in EtOH (2 mL) at 75°C in the presence of K_3PO_4 (1 mmol) and 1 mol% of complexes *cis*- and *trans*-**3** was chosen as model reaction. The reaction led to formation of coupled product in 38% yield (Table 8, entry 1). Then, a series of experiments was performed to find the optimum reaction conditions.

Table 8 here

At the first stage of optimization, we study the effect of base and solvent on the reaction. Since the solubility and basicity of the base strongly depend on the solvent used, these two parameters are closely connected. This optimization was done with several commonly used bases and solvents, inclouding organic and inorganic bases and polar protic solvents to non-polar aprotic solvents. The use of strong base Cs_2CO_3 led to increase in conversion (Table 8, entry 7); However, the organic base NEt₃ was ineffective and gave the coupled product in lower yield (Table 8, entry 13). The higher solubility of catalyst in a dipolar aprotic solvent (DMF) rather than a dipolar protic solvent (EtOH) resulted in higher yield of coupled product (Table 8, entries 2, 8 and 14). Addition of water to DMF in 1:1 (v/v) ratio leads to complete dissolution of the

both of catalyst and base. Interestingly, the coupling reactions carried out in aqueous DMF gave the the desired coupled product in highest yields (<u>Table 8</u>, entries 5, 11 and 17). Althogh the reactions in EtOH/H₂O gives more conversion in compared to the reactions in EtOH, but the complexes *cis*- and *trans*-**3** remains almost insoluble and causes low efficiencies (<u>Table 8</u>, entries 4, 10 and 16). Also, very poor catalytic activity for complex *cis*- and *trans*-**3** was observed in the toluene and water, due to low solubility of complexes *cis*- and *trans*-**3** in these solvents (<u>Table 8</u>, entries 3, 9, 15 and 6, 12, 18, respectively). These results indicates that solubility of both the catalyst and base plays an important role in such catalytic systems.

Next, we investigate the effect of catalyst loading on the reaction. As expected, varying the catalyst loading has a significant effect on the performance of catalyst. We choose the reaction condition including DMF/H₂O as solvent and Cs₂CO₃ as base (<u>Table 8</u>, entry 11) for more investigation. When the loading of complexes *cis*- and *trans*-**3** decreased to 0.2 mol%, the coupling reaction will proceed slowly and even slower when the catalyst loading was 0.1 mol% (<u>Table 8</u>, entries 20 and 21). Also, excessive amount of catalyst did not increase the yield significantly (<u>Table 8</u>, entry 19). Therefore, with respect to the economic aspect, low catalyst loading of 1 mol% was chosen as the best loading of catalyst.

Finally, the reactions were carried out at different temperature. Decreasing the temperature of the reactions has led to fall-off of the yields and increase of the reaction time to completion of the reactions (Table 8, entry 23). Also, the reaction at 100 °C yielded the corresponding coupled product in almost quantitative yield (Table 8, entry 22). Thus, the optimum condition obtained for Suzuki-Miyaura coupling reaction consisting the DMF/H₂O as solvent, Cs_2CO_3 as base, 1 mol% of complexes *cis*- and *trans*-**3** as catalyst and reaction at reflux temperature (100 °C) for 2 h.

Using the optimized reaction conditions, palladium complexes *cis*- and *trans*-3 were applied to a range of aryl chlorides bearing electron-donating and electron-withdrawing substituents in Suzuki-Miyaura reaction. Various functionalized aryl chlorides reacted with phenylboronic acid and were converted into the corresponding coupled products in high to excellent yields (Table 9). Conversely, increasing electron density on the aryl chlorides lowered the catalyst activity. That is, excellent yields were achieved when phenylboronic acid reacted with aryl chlorides with electron-withdrawing substituent such as -NO₂ and -COCH₃ (Table 9, entries 1 and 2). Deactivated aryl chlorides 4-chlorotoluene and 4-chloroanisol gave lower yields indicating that the reaction was sensitive to the electron density on the aryl chlorides (Table 9, entries 4 and 5). The reaction of electronically neutral chlorobenzene with phenylboronic acid was also produced good amounts of the product (Table 9, entry 3). It is noteworthy that the reactions of arylboronic acid containing electron-donating substituent with aryl chlorides furnishes good amounts of desired biaryls, albeit with reduced yields (Table 9, entries 6-10).

Table 9 here

Several studies on chemistry of palladium catalyzed coupling reactions indicate that the palladium complexes may behave as a mere resource for producing Pd(0) nanoparticles. To evaluate the homogeneous or heterogeneous nature of the active species, we carried out the mercury drop test [59]. Addition of a drop of mercury to the reaction mixture at t=0 did not affect the conversion of reaction, which suggests that amalgamation had not occurred and the catalysis was homogeneous in nature.

As can be seen in <u>Table 9</u>, by using Pd(II) complexes of sulfur ylide ligand good amounts of functionalized biaryl derivatives are yielded. The higher C–Cl bond dissociation energy compared with C–Br and C–I bonds disfavors oxidative addition step in catalytic coupling

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reactions of less reactive aryl chlorides which makes this step becoming rate-determining step [60]. However, more electron-rich and less bulky ligands facilitate the oxidative addition step and counter wise, more bulky and less electron-rich ligands facilitate the reductive elimination step [61, 62]. Therefore, sulfur ylides with low steric hindrance and suitable electron donating properties can act as an ideal ligand for such coupling reactions, as well as their phosphorous analogous or N-heterocyclic carbene (NHCs) ligands. <u>Table 10</u> shows a comparison between the efficiency of this catalytic system in Suzuki-Miyaura coupling reaction of aryl chlorides and other catalytic systems. On the whole, the results of this comparison showed that the catalytic activity of these Pd(II) complexes with sulfur ylide ligands are similar to or slightly better than those of mono-and bidentate Pd(II) complexes of phosphine and NHCs ligands. From an industrial view point, simple synthetic procedure, low catalyst loading and short reaction time make these Pd(II) complexes one of the best choices for the Suzuki-Miyaura coupling reaction.

Table 10 here

4. Conclusion

In summary, the present study describes the synthesis and characterization of sulfonium salt 1, sulfur ylide 2, and its new Pd(II) and Pt(II) complexes *cis*- and *trans*-3 and 4. On the basis of physico-chemical and spectroscopic data, we propose C-coordination of ylide 2 to the metal ions, which is further confirmed by the X-ray crystal structures. Density functional theory study has been done on structures and nature of M-C bonding in [YMCl₂DMSO] (M=Pd, Pt) complexes via NBO and EDA analysis. The result of NBO analyses showed that there are charge transfers about 0.4 from Y ligand to [MCl₂DMSO] (M=Pd, Pt) fragments in [YMCl₂DMSO] complexes. The EDA analyses confirm that the contribution of the electrostatic interactions (ΔE_{elstat}) and ΔE_{orb} in C-M bond of the present complexes are about 60% and 33% respectively. Also the

EDA-NOCV showed that the main contribution to ΔE_{orb} comes from the [DMSOCl₂M \leftarrow Y] σ donation and [MCl₂DMSO] (M=Pd, Pt) to Y fragment π -back donation. The catalytic activity of complexes *cis*- and *trans*-3 toward Suzuki-Miyaura reaction between various aryl chlorides and arylboronic acids in DMF/H₂O at reflux temperature was investigated. Results showed that these complexes act as efficient catalysts in Suzuki-Miyaura reaction for preparation of functionalized biaryls.

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Appendix A. Supplementary material

Materials, physical measurements and selected ¹³C and ¹H NMR spectra of all compounds can be found in the online version. Also, details of the refinement procedures for the crystal structures are supplied. The deposition number of the studied complexes **5** and **6** are CCDC 1438730 and. This data can be obtained free-of-charge via <u>www.ccdc.cam.ac.uk/data_request/cif</u>, by emailing data <u>request@ccdc.cam.ac.uk</u>, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

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Scheme 1. Two coordination modes of Me₂SCHC(O)C₆H₄R.





Fig. 1. ORTEP view of X-ray crystal structures of (a) 5 and (b) 6.

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Fig. 2. Optimized structures of the [YPdCl₂.DMSO] (a) and [YPtCl₂.DMSO] (b)

complexes at BP86/SVP level of theory.



Fig. 3. Deformation densities $\Delta \rho$ associated with the most important orbital interactions in [YPdCl₂DMSO].



Fig. 4. Deformation densities $\Delta \rho$ associated with the most important orbital interactions in [YPtCl₂DMSO]. Note that the colour in this Figure, denotes the charge flow, which is from the red to the blue region.

Compound	IR; $v(CO)$ cm ⁻¹	¹ H NMR; δ(SCH) ppm	¹³ C NMR; δ (CO) ppm
1	1682	5.65 ^a	190.87
2	1577	4.65	179.17
3	1624	5.03 (trans)	192.78 (trans)
		5.70 (<i>cis</i>)	193.86 (<i>cis</i>)
4	1634	5.70 (<i>trans</i>)	193.49 (trans)
		5.90 (<i>cis</i>)	193.81 (<i>cis</i>)
^a δ(SCH ₂)			S. Y.

Table 1.	Selected s	pectroscop	oic data	for com	pounds 1-4.
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	Compound 5	Compound 6
Empirical formula	$C_{12}H_{17}BrCl_2O_2PdS_2$	$C_{12}H_{17}BrCl_2O_2PtS_2$
Formula weight	514.58	603.27
<i>T</i> [K]	130.00(10)	130.00(10)
Crystal system	orthorhombic	orthorhombic
Space group	Pbca	Pbca
a [Å]	15.9615(3)	15.8900(5)
<i>b</i> [Å]	9.26239(16)	9.2781(2)
<i>c</i> [Å]	22.8926(5)	23.0926(7)
α [°]	90	90
<i>B</i> [°]	90	90
γ [°]	90	90
V [Å ³]	3384.49(11)	3404.53(16)
Ζ	8	8
$D_c [{\rm Mg \ m^{-3}}]$	2.020	2.354
$\mu [\mathrm{mm}^{-1}]$	4.017	23.338
F(000)	2016.0	2272.0
Crystal size[mm ³]	$0.3981 \times 0.196 \times 0.156$	$0.1449 \times 0.03 \times 0.02$
Radiation	MoK_{α} ($\lambda = 0.71073$)	CuKa ($\lambda = 1.54184$)
2θ range [°]	6.208 to 64.678	7.656 to 153.982
Index ranges	$-20 \le h \le 23, -13 \le k \le 13,$	$-19 \le h \le 19, -11 \le k \le$
	$-32 \le 1 \le 32$	7, $-29 \le 1 \le 26$
Refl. collected	48725	12655
Independent reflections	5757 [$\mathbf{R}_{int} = 0.0381$,	$3554 [R_{int} = 0.0308,$
	$R_{sigma} = 0.0228$]	$R_{sigma} = 0.0276$]
Data/restr./param.	5757/0/185	3554/0/185
Goodness-of-fit on F^2	1.075	1.112
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0281, wR_2 = 0.0622$	$R_1 = 0.0322, wR_2 =$
		0.0847
Final R indexes [all data]	$R_1 = 0.0355, wR_2 = 0.0652$	$R_1 = 0.0361, wR_2 =$
		0.0881
Largest diff. peak/hole[e Å ⁻³]	2.64/-0.93	2.38/-2.06

 Table 2. Crystal data and structure refinements for 5 and 6.

	M = Pd, Compound 5	M = Pt, Compound 6
Bond lengths		
M1-Cl1	2.3203(6)	2.3258(12)
M1-Cl2	2.3722(5)	2.3704(12)
M1-S2	2.2424(6)	2.1986(12)
M1-C1	2.065(2)	2.068(5)
S1-C1	1.793(2)	1.809(5)
S2-O2	1.4892(17)	1.485(4)
Bond angles		
Cl1-M1-Cl2	92.97(2)	91.17(4)
S2-M1-Cl1	175.03(2)	175.81(5)
S2-M1-Cl2	88.15(2)	89.13(4)
C1-M1-Cl1	89.37(6)	89.04(15)
C1-M1-Cl2	174.46(6)	174.73(14)
C1-M1-S2	89.95(6)	91.04(15)
O2-S2-M1	118.29(7)	118.30(17)
C2-C1-M1	109.68(14)	111.1(3)

 Table 3. Selected bond lengths [Å] and bond angles [°] for 5 and 6.

	[YPdCl ₂ .DMSO]	[YPtCl ₂ .DMSO]
Bond Lengths		
M(1)-S(27)	$2.28(2.24)^{a}$	2.25(2.20)
M(1)-C(4)	2.08(2.06)	2.08(2.07)
M(1)-Cl(2)	2.33(2.32)	2.34(2.33)
M(1)-Cl(3)	2.39(2.37)	2.40(2.37)
Bond angles		
Cl(2)-Pd(1)-C(4)	79.43(89.37)	87.939(89.04)
Cl(2)-Pd(1)-Cl(3)	93.39(92.97)	92.098(91.17)
Cl(3)-Pd(1)-S(27)	85.58(88.15)	87.556(89.13)
C(4)-Pd(1)-S(27)	102.60(89.95)	92.423(91.04)

Table 4. Selected bond lengths (A°) and bond angles (°) of [YM Cl₂DMSO] (M=Pd, Pt) complexes at the BP86/def2-SVP level of theory.

[YPdCl ₂ DMSO]			[YPtCl ₂ DMSO]		
	Pd-C	0.52	Pt-C	0.57	
WBIs	Pd-Cl(2)	0.67	Pd-Cl(2)	0.75	
	Pd-Cl(3)	0.59	Pd-Cl(3)	0.66	
	Pd	0.14	Pt	0.01	
	С	-0.70	С	-0.68	
NPA	Cl(2)	-0.37	Cl(2)	-0.37	
	Cl(3)	-0.49	Cl(3)	-0.45	
	[PdCl ₂ DMSO]	-0.41	[PdCl ₂ .DMSO]	-0.43	

Table 5. Wiberg bond indices(WBI) of M–C and M-Cl bonds and natural charges of Pd, Pt, C and Cl atoms as well as total charges of [MCl₂.DMSO] (M=Pd, Pt) fragments.

Donor	Acceptor	Туре	E ² (kcal/mol)
Pd (1) –C l(2)	Pd(1) - C(4)	$\sigma \rightarrow \sigma^*$	25.13
Pd (1) –C(4)	Pd(1) - C(4)	$\sigma \rightarrow \sigma^*$	3.81
Cl (3)	Pd (1) –C(4)	$lp \rightarrow \sigma^*$	82.99
Pd (1) –C(4)	C(6) –O(7)	$\sigma \rightarrow \sigma^*$	4.80
Pt (1) –C (4)	C(6) –O(7)	$\sigma ightarrow \sigma^{*}$	11.73
Pt (1) –C(4)	Pt (1)	$\sigma \to \ lp^*$	5.39
S(6)	Pt (1) –C (4)	$lp \rightarrow \sigma^*$	10.98

Table 6. The most important donor \rightarrow acceptor interactions energy concern to Pd–C bonds at BP86/def2-SVP level of theory.

	[YPdCl ₂ DMSO]	[YPtCl ₂ DMSO]
$\Delta E_{\rm int}$	-72.66	-85.39
ΔE_{Pauli}	192.21	217.97
ΔE_{elstat}	-165.18(62.4%)	-183.46(60.5%)
$\Delta E_{\rm orb}$	-86.16(32.5%)	-100.96(33.3%)
$\Delta E_{\rm disp}$	-13.53(5.1%)	-18.93(6.2%)
		S

Table 7. EDA analysis (BP86/TZ2P(ZORA)//BP86/def2-SVP) of the [YMCl₂DMSO] (M=Pd, Pt) complexes with the C1 symmetry.

	$Cl + B(OH)_{o} - Con$	plexes <i>cis</i> and <i>tran</i> .	s-3	\setminus	
		Conditions, 2 h		/	
Entry	Solvent	Base	Temp. (°C)	Catalyst (<mark>mol%)</mark>	Yield (%) ^b
1	EtOH	K_3PO_4	75	1	38
2	DMF	K_3PO_4	75	1	65
3	Toluene	K_3PO_4	75	1	35
4	EtOH/H ₂ O (1:1)	K_3PO_4	75	1	60
5	DMF/H ₂ O (1:1)	K_3PO_4	75	1	73
6	H_2O	K_3PO_4	75	1	31
7	EtOH	Cs_2CO_3	75	1	51
8	DMF	Cs_2CO_3	75	1	70
9	Toluene	Cs_2CO_3	75	1	40
10	EtOH/H ₂ O (1:1)	Cs_2CO_3	75	1	75
11	DMF/H ₂ O (1:1)	Cs_2CO_3	75	1	86
12	H_2O	Cs_2CO_3	75	1	38
13	EtOH	NEt ₃	75	1	50
14	DMF	NEt ₃	75	1	65
15	Toluene	NEt ₃	75	1	37
16	EtOH/H ₂ O (1:1)	NEt ₃	75	1	52
17	DMF/H ₂ O (1:1)	NEt ₃	75	1	61
18	H_2O	NEt ₃	75	1	25
19	DMF/H ₂ O (1:1)	Cs_2CO_3	75	10	91
20	DMF/H ₂ O (1:1)	Cs_2CO_3	75	0.2	65
21	DMF/H ₂ O (1:1)	Cs ₂ CO ₃	75	0.1	47
22	DMF/H ₂ O (1:1)	Cs_2CO_3	100	1	90
23	DMF/H ₂ O (1:1)	Cs ₂ CO ₃	25	1	42

Table 8. Optimizations for the Suzuki-Miyaura coupling reaction.^a

^a Reaction conditions for Suzuki-Miyaura reaction: chlorobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1 mmol), solvent (2 mL), complexes *cis*- and *trans*-**3**, for 2h in the air. ^b Isolated yield.

R		~~~~	$-B(OH)_2 \xrightarrow{\text{Complexes } cis \text{ and } trans-3}_{\text{Conditions, 2 h}} R$	
Entry	R	R'	Product	Yield (%) ^b
1	NO_2	Н	p-O ₂ N-Ph-Ph (7a)	95
2	COCH ₃	Η	<i>p</i> -CH ₃ OC-Ph-Ph (7b)	93
3	Н	Η	Ph-Ph (7c)	90
4	Me	Η	<i>p</i> -Me-Ph-Ph (7d)	82
5	OCH ₃	Η	<i>p</i> -CH ₃ O-Ph-Ph (7e)	78
6	NO_2	Et	p-O ₂ N-Ph-Ph-Et (7f)	89
7	COCH ₃	Et	<i>p</i> -CH ₃ OC-Ph-Ph-Et (7 g)	90
8	Н	Et	<i>p</i> -Et-Ph-Ph (7h)	85
9	Me	Et	<i>p</i> -Me-Ph-Ph-Et (7i)	73
10	OCH ₃	Et	p-CH ₃ O-Ph-Ph-Et (7j)	70

Table 9. Suzuki-Miyaura reaction of aryl chlorides catalyzed by complexes *cis*- and *trans*-3.^a

^a Reaction conditions: aryl chloride (0.5 mmol), arylboronic acid (0.75 mmol), Cs₂CO₃ (1 mmol), DMF/H₂O (2 mL, 1:1), catalyst (1 mol%), 2 h, at reflux temperature (100 °C) in the air. ^b Isolated yield.

Table 10. Comparison of Suzuki-Miyaura coupling reaction of chlorobenzene and phenylboronic acid using Pd(II) complexes *cis*- and *trans*-**3** and other catalytic system.

<	CI + (HO) ₂ B	Catalyst, Solvent, 7	Base		
Entry	Pd source	Catalyst loading (mol%)	Condition	Yield (%)	Ref.
1	Pd(II) complex of 1-aryl- 3,4,5,6- tetrahydropyrimidine	0.5	<i>t</i> -BuOK, DMF/H ₂ O, 100 °C, 24 h	75	<u>[63]</u>
2	(C^C)-orthopalladated complex of phosphorous ylide	2	Na ₂ CO ₃ , MeOH, 85 °C, 4 h	<mark>49</mark>	<u>[64]</u>
3	(NHC) type Pd(II) complex of N,N-Bis- (2,9-dicyclohexyl-10- phenanthryl)-4,5- dihydroimidazolium chloride	2	KF/18-c-6, THF, 50 °C, 15 h	<mark>96</mark>	<u>[65</u>]
4	(NHC) type Pd(II) complex of <i>trans</i> -(1,3- di(1'-(<i>R</i>)-phenylethyl) imidazolin- 2-ylidene) (phosphine)		Cs ₂ CO ₃ , Xylene, 130 °C, 32 h	<mark>87</mark>	<u>[66]</u>
5	(P^N)- coordinated Pd(II) complex of {8-(di- <i>tert</i> - butylphosphinooxy) quinoline)}	0.1	K ₂ CO ₃ , Toluene, 110 °C, 2 h	<mark>53</mark>	<u>[67]</u>
6	(C^C)-coordinated Pd(II) complex of symmetric diphosphine ylide	0.001	Cs ₂ CO ₃ , DMF, 110 °C, 1.5 h	77	<u>[68]</u>
7	Cα-coordinated Pd(II) complex of sulfur ylide	I	Cs ₂ CO ₃ , DMF/H ₂ O, 100 °C, 2 h	<mark>90</mark>	This work

Pd(II) and Pt(II) complexes of α -keto stabilized sulfur ylide: Synthesis, structural, theoretical and catalytic activity studies

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- Synthesis and characterization of Pd(II) and Pt(II) sulfur-ylide complexes are presented.
- > NMR used to determinate the coordination mode of the ligands.
- X-ray analyses demonstrate the structures are as type cis-[MCl₂(ylide)(DMSO)] (M=Pd, Pt).
- Sulfur ylide Pd(II) Complexes have catalytic activity in Suzuki cross-coupling reactions.
- Theoretical studies on structure and nature of the M–C bonding between the Y ligand (ylide) and [MCl₂.DMSO] fragments are presented.

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