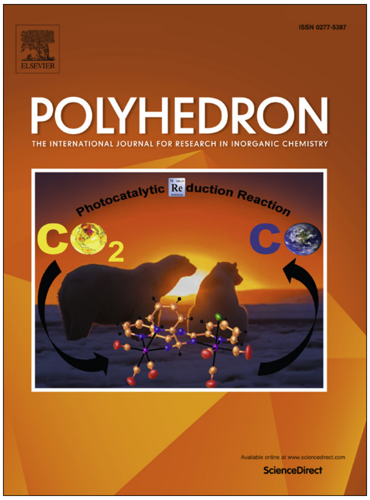

A new Pd(II) complex of a sulfur ylide; Synthesis, X-ray characterization, theoretical study and catalytic activity toward the Suzuki-Miyaura reaction

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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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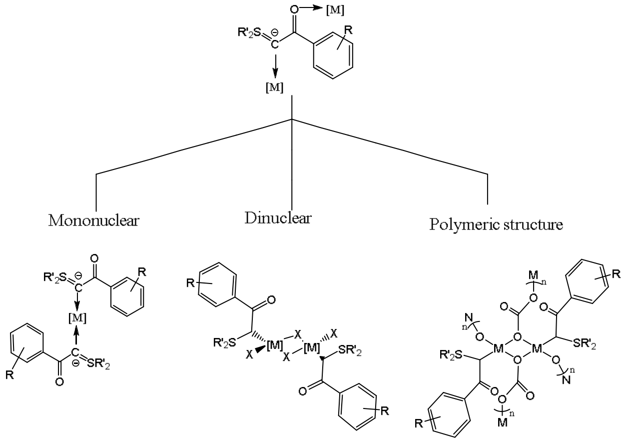
Abstract: The new sulfonium salt [$SMe_2CH_2C(O)C_6H_4$-*m*-OCH_3]Br (**1**) was synthesized from the reaction of dimethyl sulfide and 2-bromo-3'-methoxyacetophenone. Further treatment with NaOH 10% gave the α-keto stabilized sulfur ylide $SMe_2C(H)C(O)C_6H_4$-*m*-OCH_3 (**2**). This ligand was reacted with the dichloro(1,5-cyclooctadiene)palladium(II) complex, [$PdCl_2$(cod)], in a 2:1 ratio to give the new Cα-coordinated complexes *cis*- and *trans*-[$PdCl_2(SMe_2C(H)C(O)C_6H_4$-*m*-$OCH_3)_2$] (**3a** and **3b**). Characterization of the obtained compounds was performed by elemental analysis, IR, ^{1}H, ^{13}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 [$PdCl_2(SMe_2C(H)C(O)C_6H_4$-*m*-$OCH_3$).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 thestructure and nature of the Pd–C bond in complex **4** is reported here at the BP86/def2-SVP level of theory.

Keywords: Sulfur ylide, Palladium(II) complex, X-ray characterization, Suzuki-Miyaura reaction, Theoretical study.

1. Introduction:

Sulfur ylides, $R_2S=C(R')(R'')$, 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 Cα 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 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, $AgNO_3$ interacts with the Cα 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].



Scheme 1. The canonical bonding modes of $R'_2SCHC(O)C_6H_4R$ to metal ions.

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 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 [25]. 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 [26]. 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 [27,28].

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 α-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 [$PdCl_2$(cod)], was prepared according to the published procedures [29]. Melting points were measured on a SMP3 apparatus. IR spectra were recorded in the range 4000-400 cm^{-1} on a Shimadzu 435-U-04 spectrophotometer from KBr pellets. NMR spectra (^1H and ^{13}C) were recorded on 500 MHz and 250 MHz Bruker and 90 MHz Jeol spectrometers in DMSO-d_6 or $CDCl_3$ 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 [$Me_2SCH_2C(O)C_6H_4$-*m*-OMe]Br (1): Dimethyl sulfide (0.06 g, 1 mmol) was added to an acetonic solution (5 ml) of the ketone [$BrCH_2C(O)C_6H_4$-*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 [$Me_2SCH_2C(O)C_6H_4$-*m*-OMe]Br: Yield: 0.26 g, 0.93 mmol, 93%. Anal. Calc. for $C_{11}H_{15}O_2SBr$ (%): 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) ν(cm^{-1}): 1676 (CO); 787 (C^--S^+). ^1H NMR (DMSO-d_6, ppm) δ: 2.97 (s, 6H, $S(CH_3)_2$); 3.84 (s, 3H, OCH_3); 5.49 (s, 2H, CH_2); 7.50 (Br, 4H, Ph). ^{13}C NMR (DMSO-d_6, ppm) δ: 24.44 (s, $S(CH_3)_2$); 52.68 (s, CH_2); 55.67 (s, OCH_3); 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).

2.3.2. Synthesis of the sulfur ylide [$Me_2SCHC(O)C_6H_4$-*m*-OMe] (2): Treatment of compound **1** (0.29 g, 1 mmol) with H_2O (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 benzine and dried.

2.2.4. Data for [$Me_2SCHC(O)C_6H_4$-*m*-OMe]: Yield: 0.18 g, 0.86 mmol, 86%. Anal. Calc. for $C_{11}H_{14}O_2S$ (%):C, 62.84; H, 6.66; S, 15.26. Found: C, 62.94; H, 6.7; S, 15.27. IR (KBr disk) ν(cm^{-1}): 1596 (CO); 847 (C^--S^+). ^1H NMR ($CDCl_3$, ppm) δ: 2.90 (s, 6H, $S(CH_3)_2$); 3.79 (s, 3H, OCH_3); 4.99 (s, 1H, CH); 6.89-7.23 (mm, 4H, Ph). ^{13}C NMR ($CDCl_3$, ppm) δ: 28.53 (s, $S(CH_3)_2$); 52.79 (s, CH_2); 55.24 (s, OCH_3); 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$_2$(Me$_2$SCHC(O)C$_6$H$_4$-*m*-OMe)$_2$] (3a and 3b): A dichloromethane solution of ylide **2** (0.21 g, 1 mmol, 5 ml) was added to a dichloromethane solution of [PdCl$_2$(cod)] (0.14 g, 0.5 mmol, 5 ml). The mixture was stirred for 4 h at room temperature. The yellow solid that formed was filtered, washed with diethyl ether and dried.

2.2.6. Data for *cis*- and *trans*-[PdCl$_2$(Me$_2$SCHC(O)C$_6$H$_4$-*m*-OMe)$_2$]: Yield: 0.27 g, 0.46 mmol, 92%. Anal. Calc. for $C_{22}H_{28}O_4Cl_2S_2Pd$ (%): C, 43.65; H, 4.68; S, 10.70. Found: C, 43.71; H, 4.84; S, 10.74. Melting point: 198–201 ºC. Far-IR ν(cm^{-1}): 255 (Pd-Cl) (*cis* isomer); 333 (Pd-Cl) (*trans* isomer). IR (KBr disk) ν(cm^{-1}): 1625 (CO); 843 (C^--S^+). ^{1}H NMR (DMSO-*d*$_6$, ppm) δ: 2.77-3.16 (*cis* and *trans* isomers, 12H, S(CH$_3$)$_2$); 3.84 (s, 3H, OCH$_3$); 5.08-5.38 (*trans* isomer, 1H, CH); 5.66 (*cis*, major diastereoisomer, 1H, CH); 5.75 (*cis*, minor diastereoisomer, 1H, CH); 7.18-7.98 (*cis* and *trans* isomers, m, 8H, Ph). ^{13}C NMR (DMSO-*d*$_6$, ppm) δ: 26.42-27.74 (s, S(CH$_3$)$_2$); 49.52, 49.86 (s, CH); 55.66, 55.91 (s, OCH$_3$); 113.47 (s, Ph); 119.05 (s, Ph); 121.10 (s, Ph); 129.39 (s, Ph); 138.60 (s, Ph); 159.38 (s, Ph); 194.21 (s, CO).

2.2.7. Synthesis of the Pd(II) complex [PdCl$_2$(Me$_2$SCHC(O)C$_6$H$_4$-*m*-OMe).DMSO] (4): 0.06 g (0.1 mmol) of the mononuclear complexes **3a** and **3b** were dissolved in DMSO (2 ml). Pale yellow crystals were formed by the slow diffusion of methanol into the DMSO solution over two weeks.

2.2.8. Data for [PdCl$_2$(Me$_2$SCHC(O)C$_6$H$_4$-*m*-OMe).DMSO]: Yield: 0.057 g, 0.12 mmol, 95%. Decomposition: 170-175 ºC. IR (KBr disk) ν(cm^{-1}): 1624 (CO); 1186 (SO); 833 (C^--S^+). ^{1}H NMR (DMSO-*d*$_6$, ppm) δ: 2.77-3.16 (cis and trans isomers, 12H, S(CH$_3$)$_2$); 3.84 (s, 3H, OCH$_3$); 5.08-5.38 (*trans* isomer, 1H, CH); 5.66 (cis, major diastereoisomer, 1H, CH); 5.75 (cis, minor diastereoisomer, 1H, CH); 7.18-7.98 (*cis* and *trans* isomers, m, 8H, Ph). ^{13}C NMR (DMSO-*d*$_6$, ppm) δ: 26.44-27.76 (s, $S(CH_3)_2$); 49.53, 49.88 (s, CH); 55.67, 55.93 (s, OCH_3); 113.48 (s, Ph); 119.06 (s, Ph); 120.93 (s, Ph); 129.40 (s, Ph); 138.74 (s, Ph); 159.32 (s, Ph); 194.55 (s, CO).

2.3. X-ray crystallography:

A suitable crystal was 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 [30], the structure was solved with the ShelXT [31] structure solution program using direct methods and refined with the ShelXL [32] refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters; H atoms were constrained to geometrical estimates, with an isotropic displacement parameter of 1.5 times (Me) or 1.2 times (other) that of the parent carbon atom.

2.4. Computational details (theoretical studies):

The geometry of the [$Y.PdCl_2.DMSO$] complex (**4**) (Y: [$SMe_2C(H)C(O)C_6H_4$-*m*-OCH_3]) was fully optimized at the BP86 [33,34] /def2-SVP [35] level of theory. It has been shown that BP86 is a suitable level for calculation of the M←L bonding situation in complexes such as these [36-41]. All calculations were performed using the Gaussian 09 set of programs [42]. Natural bond orbital (NBO) analyses [43] were also carried out with the internal model Gaussian 09. Bonding analysis in terms of energy-decomposition were carried out at BP86/TZ2P(ZORA)//BP86/def2-TZVPP with C_1 symmetry. The basis sets for all elements are triple-ζ quality augmented by one set of polarization functions (ADF basis set TZP(ZORA)) with the program package ADF2009.01.

2.5. General experimental procedure for the Suzuki-Miyaura cross-coupling reactions: A one-pot mixture of aryl halide (0.75 mmol), arylboronic acid (1 mmol), catalyst (0.005 mol%), Cs_2CO_3 (1.5 mmol) and EtOH (2 ml) was heated to 78 °C for 4 h. The reactions progress was monitored by thin layer chromatography (TLC). After completion of the reaction, the mixture was cooled to room temperature and diluted with n-hexane (15 ml) and water (15 ml). The resulting organic layer was twice washed with brine (15 ml) and dried over $CaCl_2$, filtered and purified by recrystallization or silica gel column chromatography (n-hexane:EtOAc, 80:20) and analyzed by NMR spectroscopy (^{1}H and ^{13}C).

Characterization of the products of the Suzuki-Miyaura cross-coupling reactions:

Data for biphenyl: Melting point: 67-69 °C. ^{1}H NMR (89.6 MHz, $CDCl_3$, ppm) δ= 7.47-7.64 (m, 10H, biphenyl). ^{13}C NMR (100.62 MHz, $CDCl_3$, ppm) δ= 127.21-141.29 (m, biphenyl)

Data for 4-nitro biphenyl: Melting point: 112–113 °C. ^{1}H NMR (89.6 MHz, $CDCl_3$, ppm) δ: 7.26-8.34 (m, 9H, biphenyl). ^{13}C NMR (250 MHz, $CDCl_3$, ppm) δ: 124.10-146.97 (m, biphenyl).

Data for 4-methoxy biphenyl: Melting point: 90-91 °C. ^{1}H NMR (89.6 MHz, $CDCl_3$, ppm) δ: 3.86 (s, 3H, methyl), 6.93-7.50 (m, 10H, biphenyl). ^{13}C NMR (250 MHz, $CDCl_3$, ppm) δ: 55.41 (s, OCH_3), 114.18-159.19 (m, biphenyl).

Data for 4-carboxaldehyde biphenyl: Melting point: 89-91 °C. ^{1}H NMR (400.61 MHz, $CDCl_3$, ppm) δ: 7.40-7.86 (m, 9H, biphenyl), 9.98 (s, 1H, CHO). ^{13}C NMR (100.62 MHz, $CDCl_3$, ppm) δ: 127.39-147.23 (m, biphenyl), 191.94 (s, CO).

Data for 4-biphenyl carboxylic acid: Melting point: 223-226 °C. ^{1}H NMR (89.6 MHz, $CDCl_3$, ppm) δ: 7.32-7.88 (m, phenyl, 9H), 11.04 (s, COOH, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 124.37-144.81 (m, biphenyl), 163.39 (s, C=O).

Data for 1-phenyl naphthalene: Oil. ^{1}H NMR (89.6 MHz, CCl_3, ppm) δ: 7.23-7.49 (m, phenyl, 8H), 7.51-8.28 (m, phenyl, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 125.34-140.70 (m, aromatic).

Data for 2-phenyl thiophene: Melting point: 34-35 °C. ^{1}H NMR (89.6 MHz, $CDCl_3$, ppm) δ: 6.95-7.29 (m, phenyl, 5H), 7.29-7.55 (m, thiophene, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 123.01-144.43 (s, aromatic).

Data for 4-nitro-4′-ethyl biphenyl: Melting point: 82-83 °C. ^{1}H NMR (89.6 MHz, $CDCl_3$) δ: 1.34 (t, 3H, CH_3), 2.73 (q, 2H, CH_2), 7.26-8.34 (m, 8H, biphenyl). ^{13}C NMR (250 MHz, $CDCl_3$, ppm) δ: 15.56 (s, CH_3), 28.49 (s, CH_2), 124.12-145.37 (m, biphenyl).

Data for 4-methoxy-4′-ethyl biphenyl: Melting point: 73-75 °C. ^{1}H NMR (89.6 MHz, $CDCl_3$): δ = 1.29 (t, 3H, CH_3), 2.67 (q, 2H, CH_2), 3.86 (s, 3H, OCH_3), 6.92-7.46 (m, 8H, biphenyl). ^{13}C NMR (250 MHz, $CDCl_3$, ppm) δ: 15.56 (s, CH_3), 31.14 (s, CH_2), 55.23 (s, OCH_3), 114.03-158.66 (m, biphenyl).

Data for 4-acetyl-4′-ethyl biphenyl: Melting point: 105-108 °C. ^{1}H NMR (400.61 MHz, $CDCl_3$, ppm) δ: 1.24 (t, 3H, CH_3), 2.51 (s, 3H, CH_3), 2.59 (q, 2H, CH_2), 7.25-8.01 (m, 8H, biphenyl). ^{13}C NMR (100.62 MHz, $CDCl_3$, ppm) δ: 15.52 (s, CH_3), 26.64 (s, CH_3), 28.55 (s, CH_2), 126.90-154.74 (m, biphenyl), 197.76 (s, CO).

Data for 4-ethyl-4′-biphenyl carboxylic acid: Melting point: 195-197 °C. ^{1}H NMR (89.6 MHz, $CDCl_3$, ppm) δ: 1.30 (t, CH_3, ^3J = 7.8 Hz, 3H), 2.68 (q, CH_2, ^3J = 6.5 Hz, 2H), 6.92-7.81 (m, phenyl, 8H), 11.1 (s, COOH, 1H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ: 14.93 (s, CH$_3$), 30.66 (s, CH$_2$), 127.78-141.62 (m, biphenyl), 169.34 (s, C=O).

Data for 1-(4-ethylphenyl) naphthalene: Oil. ^{1}H NMR (89.6 MHz, CDCl$_3$, ppm) δ: 1.45 (t, CH$_3$, ^3J = 7.3 Hz, 3H), 2.83 (q, CH$_2$, ^3J = 7.6 Hz, 2H), 7.11–8.50 (m, phenyl, 11H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ: 15.53 (s, CH$_3$), 28.67 (s, CH$_2$), 125.35-143.13 (s, aromatic).

Data for 2-(4′-ethyl phenyl) thiophene: Melting point: 48-49 °C. ^{1}H NMR (89.6 MHz, CDCl$_3$, ppm) δ: 1.16 (t, CH$_3$, ^3J = 7.2 Hz, 3H), 2.62 (q, CH$_2$, ^3J = 8.1 Hz, 2H), 6.91-7.80 (m, phenyl, H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ: 15.52 (s, CH$_3$), 28.53 (s, CH$_2$), 122.57-131.84 (m, aromatic).

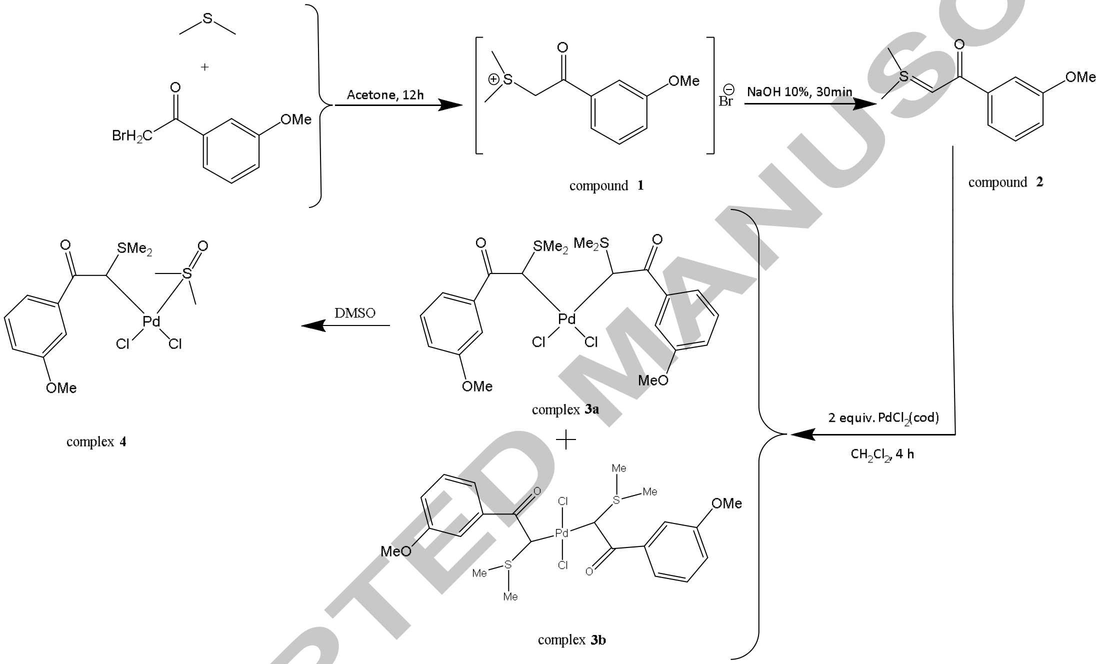
Data for 3-(4′-ethyl phenyl) pyridine: Oil. ^{1}H NMR (250 MHz, DMSO-d$_6$) δ: 1.27 (t, CH$_3$, 3 H), 2.69 (q, CH$_2$, 2H), 7.29 (m, aromatic, 3H), 7.50 (d, aromatic, 2H), 7.84 (d, aromatic, 1H), 8.57 (d, aromatic, 1H), 8.85 (s, aromatic, 1H); ^{13}C NMR (63 MHz, DMSO-d$_6$) δ: 15.63 (s, CH$_3$), 21.10 (s, CH$_3$), 28.57 (s, CH$_2$), 123.56-148.15 (s, aromatic).

The following compounds gave data consistent with those published, see Table 9: 4-methyl-biphenyl (entry 2) [44], 4-acetylbiphenyl (entry 6) [45], 4-ethyl-biphenyl (entry 11) [46], 4-meyhyl-4′-ethyl biphenyl (entry 12) [20], 4-carboxaldehyde-4′-ethyl-biphenyl (entry 15) [20], 3-phenyl pyridine (entry 10) [47].

3. Results and discussion

3.1. Synthesis

Dimethyl sulfide, SMe$_2$, reacts with 2-bromo-3'-methoxyacetophenone in an equimolar ratio forming the new sulfonium salt **1** in 93% yield. Further treatment of this salt with NaOH led to elimination of HBr, giving the new sulfur ylide **2** in 86% yield. Reaction of this ligand with [$PdCl_2$(cod)] in a 2:1 ratio yielded the new mononuclear complexes **3a** and **3b** (Scheme 2). Crystallization of these complexes from DMSO solution led to a ligand replacement reaction and afforded the DMSO coordinated complex *cis*-[$PdCl_2$(ylide).DMSO] (**4**). These complexes are insoluble in most of organic solvents, such as chloroform, acetone and toluene. Therefore, we chose DMSO as a suitable solvent for the NMR spectroscopies and crystallization.



Scheme 2: Synthesis of the Pd(II) complexes **3a/3b** and **4**.

3.2. Spectroscopy:

The structures were characterized successfully by ^{1}H, ^{13}C NMR and MS spectroscopies and other conventional techniques, as well as IR spectroscopy and elemental analysis. Also, the structure of complex **4** was determined unequivocally by single crystal X-ray diffraction. Table 1 shows a brief summary of these spectroscopic data.

Table 1. Spectroscopic data for compounds **1**-**3** and the starting ketone.

Compound	IR; ν(CO) cm^{-1}	^1H NMR; δ(SCH) ppm	^{13}C NMR; δ(CO) ppm
Ketone	1702	4.45	192.16
1	1676	5.46	191.33
2	1596	4.29	182.69
3a and **3b**	1630	5.08-5.88	194.21

The CHNS elemental analysis of the palladium complexes **3a** and **3b** indicates a 2:1 stoichiometry between the sulfur ylide and $PdCl_2$. Also, the mononuclear structure of complexes **3a** and **3b** was confirmed by mass spectroscopy, with m/z values of 179.0, 210.0 and 598.0 for the $PdCl_2$ and ylide fragments and $PdCl_2(ylide)_2$ molecular ion, respectively.

In the far-IR spectra of complexes **3a** and **3b**, two Pd-Cl stretching bands were observed at 333 and 255 cm^{-1}, which are in accord with both *cis*- and *trans*- dichlorobis(sulfur ylide) structures in the solid state [11]. Also, the ν(CO) and in the mid-IR spectrum of sulfur ylide **2** was observed at around 1596 cm^{-1}, occurring at a lower frequency than the related sulfonium salt **1** (1676 cm^{-1}). This is due to the fact that the electron density on the C=O bond in the ylide is somewhat removed. Moreover, the coordination of the ylide through the Cα atom (carbanion mode) causes a significant increase in the ν(CO) frequencies of complexes **3a** and **3b**, as if the coordination of the ylide occurred from an O atom, we would expect a decrease of the ν(CO) frequency [14]. Furthermore, the ν(S=C) band of the ylide **2** is also sensitive to the coordination.

It was seen that coordination of the ylide **2** to the Pd(II) ion has caused a shift of ν(S=C) to lower frequencies, which is consistent with some removal of electron density from the S–C bonds.

The ^{1}H NMR spectrum of the sulfur ylide **2** shows an upfield shift in the SCH signal compared to that of the sulfonium salt **1**. This upfield shift is due to the presence of a formal negative charge on the methinic carbon, which can increase the electron density in the C-H bond. Also, the methinic signals of complexes **3a** and **3b** show a downfield shift compared to the ylide **2**, indicating that coordination of the ylide through the Cα atom has happened. The coexistence of the *cis* and *trans* isomers is confirmed by the ^{1}H NMR spectra. DMSO-d_6 solutions of these complexes displayed four signals for the SMe_2 group and four signals for the methine group. The higher field pair of SMe_2 and the methinic proton signals may be assigned to the *trans* isomer [48]. Since the methinic carbons are chiral, two (RR/SS or RS/SR) diastereoisomers are expected for these complexes [11]. The presence of two such dynamic diastereoisomers was observed in the ^{1}H NMR spectrum of complexes **3a** and **3b**. The *trans* diastereoisomers exhibit the signals of the methinic protons as one singlet and one doublet peak around 5.08-5.38 ppm, whereas, the *cis* diastereoisomers exhibit two singlet peaks around 5.66-5.75 ppm.

In the ^{13}C NMR spectrum of sulfur ylide **2**, removal of the formal negative charge on the sulfonium salt makes the methinic carbon atom deshielded. Thus, a downfield shift for the signal of the SCH group and a decrease of the electron density in the S=C bond in the sulfur ylide was expected. Contrariwise, coordination of the sulfur ylide through the Cα atom causes an upfield shift in the ^{13}C NMR signal of methinic group [11], from 52 ppm in ylide **2** to 49 ppm in complexes **3a** and **3b**. This upfield shift of the SCH signal for these complexes is the most important aspect of the ^{13}C NMR spectra and this is due to the change in the hybridization of the ylidic carbon atom from sp^2 to sp^3 [49]. Downfield shifts for the CO and OCH_3 signals were also observed for complex **3**, indicating a much lower shielding of the carbon atoms of the CO and OCH_3 groups in this complex [11]. The presence of two nearby singlet peaks for SCH, OCH_3 and four CH_3 signals for two SMe_2 groups in the ^{13}C NMR spectra of complexes **3a** and **3b** confirmed the diastereoisomerism of these complexes.

3.3. DMSO as ligand:

Evaluation through literature data on the coordination of dimethylsulfoxide (DMSO) to relatively soft metal atoms showed that the coordination mode of this ligand is highly dependent on both electronic and steric factors [50]. However, steric demands play a more significant role in determining the coordination mode, rather than the moderate π-acceptor properties of S-bonded DMSO [51]. Recently, the synthesis and characterization of a mononuclear Hg(II) complex of a phosphorus ylide containing one DMSO molecule as a ligand was reported by our group [51,52]. The O-coordination mode of DMSO was revealed by single crystal X-ray analysis of the mononuclear complex [$HgCl_2$.(P-ylide).DMSO], in which P-ylide is a bulky phosphorus ylide of the type of $Ph_3PCHC(O)C_6H_4Cl$. Although on the basis of the Hard-Soft-Acid-Base principle [53], the S-bonding mode is preferred in the specific case of the Hg(II) soft metal ion, the steric hindrance of a bulky ligand, like phosphorus ylides, may affect the coordination mode of the DMSO ligand and induce the O-bonding mode.

Crystallization of DMSO solutions of complexes **3a** and **3b** led to formation of a yellow single crystal of complex **4** and, as mentioned above, such a ligand replacement reaction was expected. Also, the presence of non-bulky sulfur ylide ligands and the soft metal Pd(II) ion in complexes **3a** and **3b** led to the preferential S-bonding coordination mode of the DMSO ligand [54]. Although attempts to achieve suitable single crystals of complexes **3a** and **3b** were unsuccessful, we obtained a single crystal of the new DMSO coordinated complex **4**. This is good confirmation of complex formation between the Pd(II) ion and the sulfur ylide. The molecular structure of complex **4** is shown in Figure 1. Relevant parameters concerning data collection and refinement are given in Table 2. Selected bond distances and angles for the unit cell of complex **4** are displayed in Table 3.

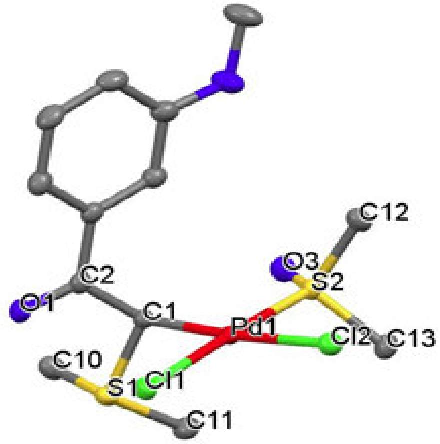


Figure 1: The molecular structure of complex **4**.

Table 2: Crystal data and refinement details for complex **4**.

Compound	**Compound**
Empirical formula	$C_{15}H_{24}Cl_2O_3PdS_2$
Formula weight	465.71
Temperature/K	130.00(10)
Crystal system	Orthorhombic
Space group	Pbca
a/Å	15.51248(13)
b/Å	9.19756(8)
c/Å	24.14916(16)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3445.53(5)
Z	8
ρ calc./ g cm^{-3}	1.796
μ/mm^{-1}	13.865
F(000)	1872.0

Crystal size/mm^3	0.1138 × 0.07 × 0.03
Radiation	CuK$_\alpha$ (λ = 1.54184)
2Θ range for data collection/°	7.322 to 154.18
Index ranges	$-19 \leq h \leq 19$, $-11 \leq k \leq 10$, $-26 \leq l \leq 30$
Reflections collected	34284
Independent reflections	3632 [R_{int} = 0.0258, R_{sigma} = 0.0142]
Data/restraints/parameters	3632/0/196
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0183, wR_2 = 0.0500
Final R indexes [all data]	R_1 = 0.0198, wR_2 = 0.0507
Largest diff. peak/hole / e Å^{-3}	0.41/-0.53

Table 3: Selected bond lengths [Å] and bond angles [°] for complex **4**.

Bond type	**Bond Length/Å**	**Angle type**	**Angle/°**
Pd1 - Cl1	2.3272(4)	Cl1- Pd1 - Cl2	93.355(15)
Pd1 - Cl2	2.3757(4)	S2 - Pd1 - Cl1	175.983(15)
Pd1 - S2	2.2515(4)	S2 - Pd1 - Cl2	87.886(14)
Pd1 - C1	2.0673(17)	C1 - Pd1 - Cl1	89.01(5)
S1 - C1	1.7981(16)	C1 - Pd1 - Cl2	175.50(5)
S1 - C10	1.8000(19)	C1 - Pd1 - S2	90.01(5)
S1 - C11	1.791(2)	C1 - S1 - C10	101.36(8)
S2 - O3	1.4842(13)	C11 - S1 - C1	100.93(9)
S2 - C12	1.7848(18)	O3 - S2 - Pd1	118.12(6)
S2 - C13	1.7753(18)	S1 – C1 - Pd1	111.50(8)
O1 - C2	1.225(2)	C2 - C1 - Pd1	110.36(11)
C1 – C2	1.500(2)	C2 - C1 - S1	107.07(11)

The Pd atom is in a square planar environment, coordinated by one ylide ligand, two chlorides and a DMSO molecule, [Y.PdCl$_2$.DMSO]. The methoxy substituted aromatic ring is oriented such that the methoxy group is trans to the ketone oxygen atom, the O2-C5...C2-O1 torsion angle being -164.8(2)°. There exist π-π interactions between the aromatic rings related by

(1-x, 1-y, 1-z), C5 is superimposed above C7’ and C6 lies above the center of the other aromatic ring. There are a number of weak C-H…X intra- and inter-molecular interactions, the latter link the molecules into a 3D network.

2.4. Computational details (theoretical studies):

A theoretical study on the structure and nature of the metal-ligand bond for complex **4** has been reported at the BP86/def2-SVP level of theory. The X-ray crystal structure confirmed that complex **4** exhibits a square planar structure in which two chloride atoms are in *cis*-like positions (Figure 2).

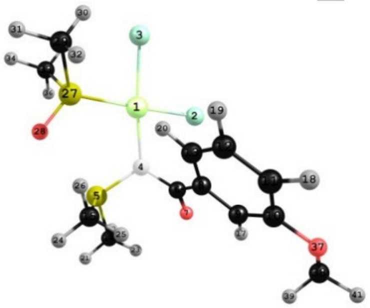


Figure 2. Optimized structure of complex **4** at the BP86/SVP level of theory.

Thus further calculations, including the structure and nature of the C–Pd bond in complex **4**, were performed on the *cis*-like structure. The optimized structure of complex **4** at the BP86/def2-SVP level of theory is shown in Figure 2 and trends for the variation of the corresponding bond lengths and bond angles extracted from optimized geometry are given in Table 4. The calculated bond lengths and bond angles of complex **4** are in good agreement with the X-ray experimental values (Table 4).

Table 4. Selected bond lengths (Å) and bond angles (°) of complex **4** at the BP86/def2-SVP level of theory.

Bond Lengths	Value/Å	Bond angles	Value/°
Pd(1)-S(27)	2.38(2.25)[a]	Cl(2)-Pd(1)-C(4)	170.99(175.50)
Pd(1)-C(4)	2.08(2.06)	Cl(1)-Pd(1)-S(27)	177.77(175.98)
Pd(1)-Cl(2)	2.33(2.32)	Cl(2)-Pd(1)-S(27)	92.31(87.88)
Pd(1)-Cl(3)	2.39(2.37)	C(1)-Pd(1)-S(27)	102.58(90.01)

[a] The experimental values are given in parenthesis.

To studying the nature of the metal-ligand bond and/or possible interactions in this complex, natural bond orbital (NBO) analysis was performed and used to estimate the delocalization of the electron density between the occupied Lewis-type orbitals and the formally unoccupied non-Lewis NBOs (antibonding or Rydberg), which corresponds to stabilizing the donor-acceptor interaction [55]. The values of the WBI (Wiberg bond indices) and partial charges on the Pd, C and Cl atoms involved in the bonding interactions between $PdCl_2$.DMSO and Y of complex **4**, as well as the total charge of the ligand Y and [$PdCl_2$.DMSO] fragment, were evaluated through natural population analysis and the results are given in Table 5. The calculated partial charges on both the Pd and C atoms of the Pd−C bond carry negative charges in the Pd−C bond, but the results show that the q(C) is greater than q(Pd) and this may come from σ donation between the C and Pd atoms of the Pd−C bond (Table 5). Also, the negative value of the total charge of the [$PdCl_2$.DMSO] fragment shows that there is a charge transfer of about 0.4 from the Y ligand to the [$PdCl_2$.DMSO] fragment in complex **4** and this data could confirm that the nature of the Pd−C bond in this complex is more electrostatic.

Table 5. Wiberg bond indices (WBI) of the Pd–C and Pd-Cl bonds and natural charges of the Pd, C and Cl atoms as well as the total charge of the Y ligand and the [$PdCl_2$.DMSO] fragment.

WBIs	Pd-C	0.50
	Pd-Cl(2)	0.68
	Pd-Cl(3)	0.61
NPA	Pd	-0.018
	C	-0.670
	Cl(2)	-0.289
	Cl(3)	-0.422
	[$PdCl_2$.DMSO]	-0.413
	Y	0.413

Second-order perturbation theory analysis of the Fock matrix was carried out to evaluate the donor-acceptor interactions on the basis of the NBO analysis. The values of the donor-acceptor interactions in the compounds are given in Table 6. The important donor-acceptor interactions in the case of the Pd–C bond were from σ(Pd–C) and the lone pair (LP) of the Cl and S atoms as donors to σ* (Pd–C) and σ* (Pd–Cl) as acceptors (Table 6).

Table 6. The most important donor→ acceptor interactions concerning the Pd─C bond at the BP86/def2-SVP level of theory.

Donor	Acceptor	Type	E^2 (kcal/mol)
Pd(1)–C (4)	Pd(1)–Cl(2)	σ → σ*	19.44
Pd(1)–C(4)	Pd(1)–C(4)	σ → σ*	4.02
Cl(3)	Pd(1)–C(4)	Lp → σ*	62.70
S(27)	Pd(1)–C(4)	lp → σ*	6.32

To better understand the nature of the Pd–C bonding between the Y ligand and the [PdCl$_2$.DMSO] fragment in complex **4**, quantum chemical calculations in the terms of energy-decomposition analysis at the BP86/TZ2P(ZORA)//BP86/def2-SVP level with C$_1$ symmetry, using the program package ADF2009.01, was carrying out. The ΔE_{int} value between the two investigated fragments in complex **4** is about 73 kcal/mol (Table 7). The breakdown of the ΔE_{int} values into Pauli repulsion ΔE_{Pauli} and two attractive components shows that roughly 62% comes from the electrostatic attraction, ΔE_{elstat}, while ~32% comes from the orbital term, ΔE_{orb}, and the remaining concern is from $\Delta E_{\text{dispersion}}$. Thus the values of ΔE_{elstat} show that the nature of the Pd–C bonding in complex **4** is more electrostatic.

Table 7. EDA analysis (BP86/TZ2P(ZORA)//BP86/def2-SVP) of complex **4** with C$_1$ symmetry.

ΔE_{int}	-73.39
ΔE_{Pauli}	190.42
ΔE_{elstat}	-164.65(62.4%)
ΔE_{orb}	-85.64(32.5%)
ΔE_{disp}	-13.51(5.1%)

This data is in good agreement with the NBO analysis which shows about a 0.4 e charge transfer from the Y ligand to the [PdCl$_2$.DMSO] fragment (Table 6) and 0.5 WBI in the Pd–C bonding (Table 6).

The covalent bonding between the [PdCl$_2$.DMSO] fragment and the Y ligand in complex **4** becomes visible by calculated deformation densities (Δρ). Figure 3 show the important deformation densities and the associated energy values which provide about 90 % of the overall orbital interactions for the complex **4**. Visual inspection of Figure 3a, indicates Δρ1, which shows the contribution to ΔE_{orb} and comes from the DMSO.Cl$_2$Pd←Y σ donation. Figure 3b displays the deformation density Δρ2 which comes from the Pd–Cl bond to Y ligand charge transfer. Also Figures 3c-e display the deformation densities Δρ3, Δρ4 and Δρ5 which come from the [$PdCl_2$.DMSO] fragment to Y ligand π-back donation.

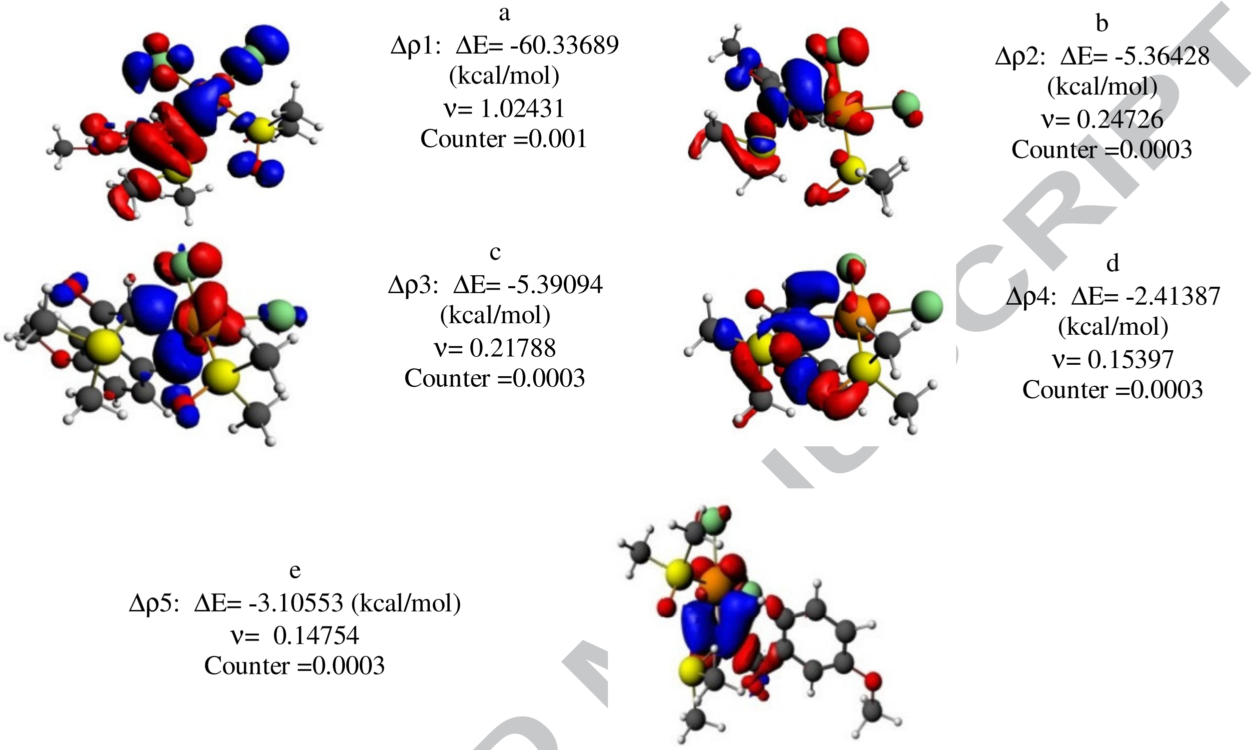


Figure 3. Deformation densities Δρ associated with the most important orbital interactions in complex **4**. Note that the colour in this Figure, denotes the charge flow, which is from the red to the blue region.

3.4. Suzuki-Miyaura cross-coupling reactions of aryl halides and boronic acid:

The catalytic performance of the palladium complexes **3a** and **3b** in the Suzuki-Miyaura cross-coupling reaction was examined. Initially, we performed a model reaction to optimize the reaction conditions, including the catalyst loading, base, solvent and temperature (Table 8). Reaction of phenylboronic acid with bromobenzene in ethanol at 78 °C in the presence of Cs_2CO_3 (1.5 mmol) was chosen as a model reaction. The reaction provided the coupled product in 90% yield (Table 8, entry 1). Then, a series of experiments was performed to find optimum conditions.

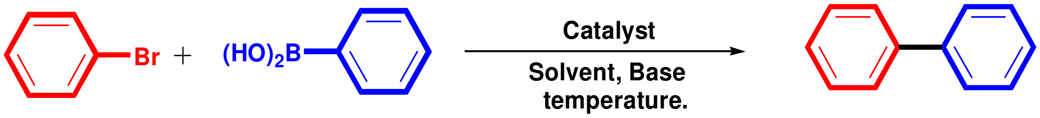
At the first stage of optimization, we studied the efficiency of the catalyst loading on the reaction. As expected, varying the catalyst concentration has a considerable effect on the activity of the catalyst. When the reaction was carried out with 0.001 mmol of catalyst, the reaction proceeded very slowly and running the reaction in the absence of catalyst resulted in no conversion (Table 8, entries 3 and 4). If the loading of the catalyst was increased to 0.005 mmol, the yield of the coupled products for the reactions showed a rise (Table 8, entry 2). At a high loading of the catalyst (> 0.05 mmol), the maximum efficiency was observed. Also, an excessive amount of catalyst did not increase the yield dramatically (Table 8, entry 5). Therefore, due to an economic aspect, a low catalyst loading of 0.005 mmol was chosen as the best concentration of the catalyst.

The solvent optimization stage was done with several commonly used solvents. Polar aprotic solvents such as DMF and NMP were tested and the results showed that the conversion for the desired coupling product was good at reflux temperature (Table 8, entries 6 and 7, respectively). Using of ethanol as a green solvent gave the highest yield for this reaction (Table 8, entry 2). However, water required additional time for completing the coupling reaction (Table 8, entry 8). Also, non-polar solvents such as toluene and hexane gave low conversions (Table 8 entries 9 and 10).

Next, we optimized the conditions to select the best base from the commonly used ones. A base usually plays an important role in such cross-coupling reactions and has a striking accelerating effect on the reaction time. Thus, we investigated a series of reactions to screen the influence of the base on the catalytic system. Among the tested bases, Cs_2CO_3 and K_2CO_3 were the most effective base for the reactions (Table 8, entries 2 and 12), while other bases, such as Na_2CO_3 and NaOAc, proved to be less active (Table 8, entries 11 and 13). Using of the organic bases NEt_3 and pyridine instead of inorganic bases decreased the catalyst activity and lowered the conversion (Table 8, entries 14 and 15).

Finally, we optimized the reaction temperature. The reaction at reflux gives the coupled products with the highest yield. Decreasing the temperature led to an increased reaction time and decreased yields (Table 8, entries 16, 17).

Table 8. Optimizations for the Suzuki-Miyaura cross-coupling reaction.



Entry	Base	Cat. loading (mmol)	Solvent	Temp. (°C)	Yield (%)[b]
1	Cs_2CO_3	0.05	Ethanol	Reflux	90
2	Cs_2CO_3	0.005	Ethanol	Reflux	88
3	Cs_2CO_3	0.001	Ethanol	Reflux	35
4	Cs_2CO_3	-	Ethanol	Reflux	-
5	Cs_2CO_3	0.1	Ethanol	Reflux	93
6	Cs_2CO_3	0.005	NMP	Reflux	82
7	Cs_2CO_3	0.005	DMF	Reflux	79
8	Cs_2CO_3	0.005	H_2O	Reflux	61
9	Cs_2CO_3	0.005	Toluene	Reflux	70
10	Cs_2CO_3	0.005	Hexane	Reflux	75
11	Na_2CO_3	0.005	Ethanol	reflux	69
12	K_2CO_3	0.005	Ethanol	reflux	80
13	NaOAc	0.005	Ethanol	reflux	54
14	NEt_3	0.005	Ethanol	reflux	40
15	Pyridine	0.005	Ethanol	reflux	40
16	Cs_2CO_3	0.005	Ethanol	25	51
17	Cs_2CO_3	0.005	Ethanol	50	78

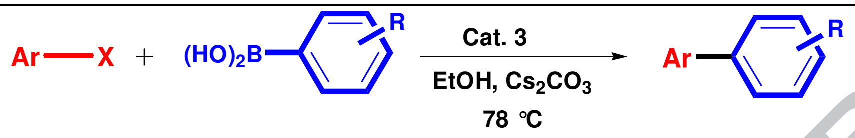
[a] Reaction conditions for the Suzuki-Miyaura cross-coupling reaction: bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol), solvent (2 ml), catalyst, 4 h, in the air.

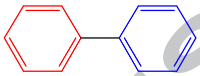
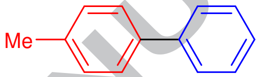
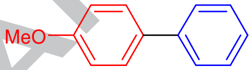
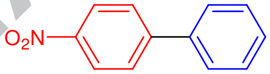
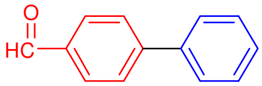
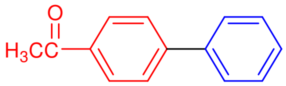
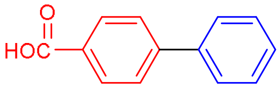
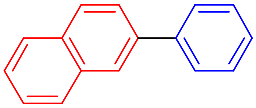
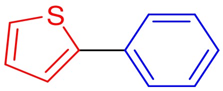
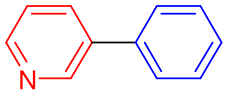
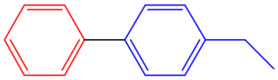
[b] Isolated yield.

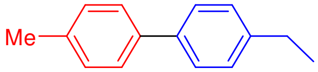
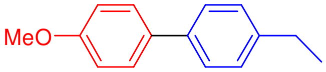
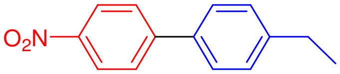
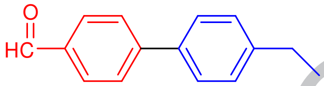
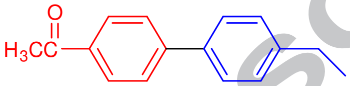
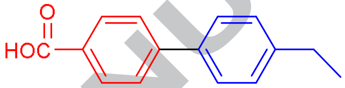
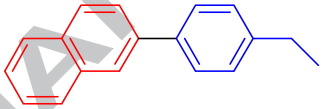
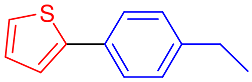
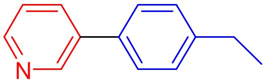
According to the optimized reaction conditions (EtOH, Cs_2CO_3 and 0.005 mmol of catalyst at reflux temperature) various types of functionalized aryl halides reacted with arylboronic acid and were converted into the corresponding coupled products in high to excellent yields (Table 9).

A range of aryl halides bearing electron-withdrawing and electron-donating groups was studied in the Suzuki-Miyaura reaction. It is well known that the type of aryl halide substituent is important for catalytic activity. The reaction of aryl halides containing electron-withdrawing substituents, such as $-NO_2$, -CHO and $-COCH_3$ groups, with phenylboronic acid gives the required products in good to excellent yields (Table 9, entries 4-6). Conversely, the catalyst activity is lowered by increasing the electron density on the aryl halides, e.g. using 4-bromoanisole and 4-bromotoluene (Table 9, entries 2 and 3). Also among the aryl halides reagents, aryl iodides and bromides were more reactive than aryl chlorides [56]. The small C–I bond dissociation energy and easy oxidative addition to the Pd(0) species causes the aromatic iodides to have a higher reactivity compared to other aryl halides in the coupling reactions. Aryl chlorides are less reactive than the other aryl halides because of the large C–Cl bond dissociation energy and they showed little or no activity in the coupling reactions. However, due to the economical aspect of aryl chlorides and the challenge of activating the C–Cl bond, more applications of aryl chlorides in cross-coupling reactions have resulted [57]. In this regard, both electron neutral and electron rich 4-chlorobenzene and 4-chlorotoluene show relatively low reactivity in coupling reactions compared with the analogous aryl bromides and aryl iodides (Table 9, entries 1 (70%), 2 (69%)). However, 4-chlorobenzaldehyde is a bit more reactive than the other aryl chlorides (Table 9, entry 5). The electronically neutral benzene halides produced a good amount of the desired product when coupled with arylboronic acids (Table 9, entry 11).

Table 9: Suzuki-Miyaura cross-coupling reaction of aryl halides and arylboronic acids.



Entry	Ar	R	X	Product	Yield %
1	PhX	H	Cl Br I		70 88 93
2	*p*-Me-PhX	H	Cl Br		69 84
3	*p*-OMe-PhX	H	Br I		81 90
4	*p*-NO_2-PhX	H	Br		89
5	*p*-C(O)H-PhX	H	Cl Br		74 84
6	*p*-C(O)CH_3-PhX	H	Br		84
7	*p*-COOH-PhX	H	Cl Br		76 86
8	1- naphthalene	H	Cl Br		73 81
9	2- thiophene	H	Cl Br		71 84
10	3-pyridine	H	Cl Br		67 79
11	PhX	*p*-Et	Cl Br I		68 84 94

12	*p*-Me-PhX	*p*-Et	Cl Br		67 83
13	*p*-OMe-PhX	*p*-Et	Br I		79 90
14	*p*-NO_2-PhX	*p*-Et	Br		85
15	*p*-C(O)H-PhX	*p*-Et	Cl Br		70 83
16	*p*-C(O)CH_3-PhX	*p*-Et	Br		83
17	*p*-COOH-PhX	*p*-Et	Cl Br		70 81
18	1- naphthalene	*p*-Et	Cl Br		76 85
19	2- thiophene	*p*-Et	Cl Br		73 81
20	3-pyridine	*p*-Et	Cl Br		69 80

[a] Reaction conditions for the Suzuki-Miyaura cross-coupling reaction: arylhalide (0.5 mmol), arylboronic acid (0.75 mmol), Cs_2CO_3 (1.5 mmol), ethanol (2 ml), catalyst (0.005 mmol), 4 h, in the air.

[b] Isolated yield.

To extend the scope of our work, we next investigated the cross-coupling of various electron rich and deficient aryl halides with 4-ethyl-phenylboronic acid. As expected, electron-donating substituents on the arylboronic acid have a decreasing effect on the yield of the reaction. However, activated aryl halides, such as aryl iodides and aryl bromides containing electron-withdrawing substituents, advance the reactions to give excellent yields (Table 9, entries 11-16).

4. Conclusion

In summary, the present study describes the synthesis and characterization of the new sulfonium salt **1**, sulfur ylide **2** and the new mononuclear palladium(II)-ylide complexes **3a**, **3b** and **4**. On the basis of the physico-chemical and spectroscopic data, we propose the C-coordinated mode for these mononuclear complexes, which is further confirmed by the X-ray crystal structures. X-ray analysis showed that the Pd atom is coordinated by one ylide ligand, two chloride ions and a DMSO molecule. Also a theoretical study on the structure and nature of the Pd–C bond in complex **4**, investigated here at the BP86/def2-SVP level of theory, is reported. The NBO analysis showed that a charge transfer about 0.4 occurred from the Y ligand to the [$PdCl_2$.DMSO] fragment in complex **4**. This result proved that the electrostatic character of the Pd–C bonding in this complex is greater than the covalent character. The EDA results also show that the nature of the Pd–C bonding in complex **4** is more electrostatic and ETS-NOCV analyses confirms that the main contribution to ΔE_{orb} in the Pd–C bonding in complex **4** comes from DMSO.$Cl_2Pd \leftarrow Y$ σ donation. The catalytic activity of complexes **3a** and **3b** toward the Suzuki-Miyaura cross-coupling reaction between various aryl halides and arylboronic acids in EtOH as the solvent at reflux temperature was investigated. The ease of preparation of the complexes, low catalyst loading and stability toward air and moisture make these complexes ideal catalysts for the Suzuki-Miyaura cross-coupling reaction.

Acknowledgements

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Supplementary material

Physical measurements and selected ^{13}C and ^{1}H NMR spectra of compounds can be found in the online version. CCDC 1438733 contains the supplementary crystallographic data for the complex **4**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK. Tel.: +44 (0)1223 762911; or deposit@ccdc.cam.ac.uk.

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Graphical abstract-pictogram

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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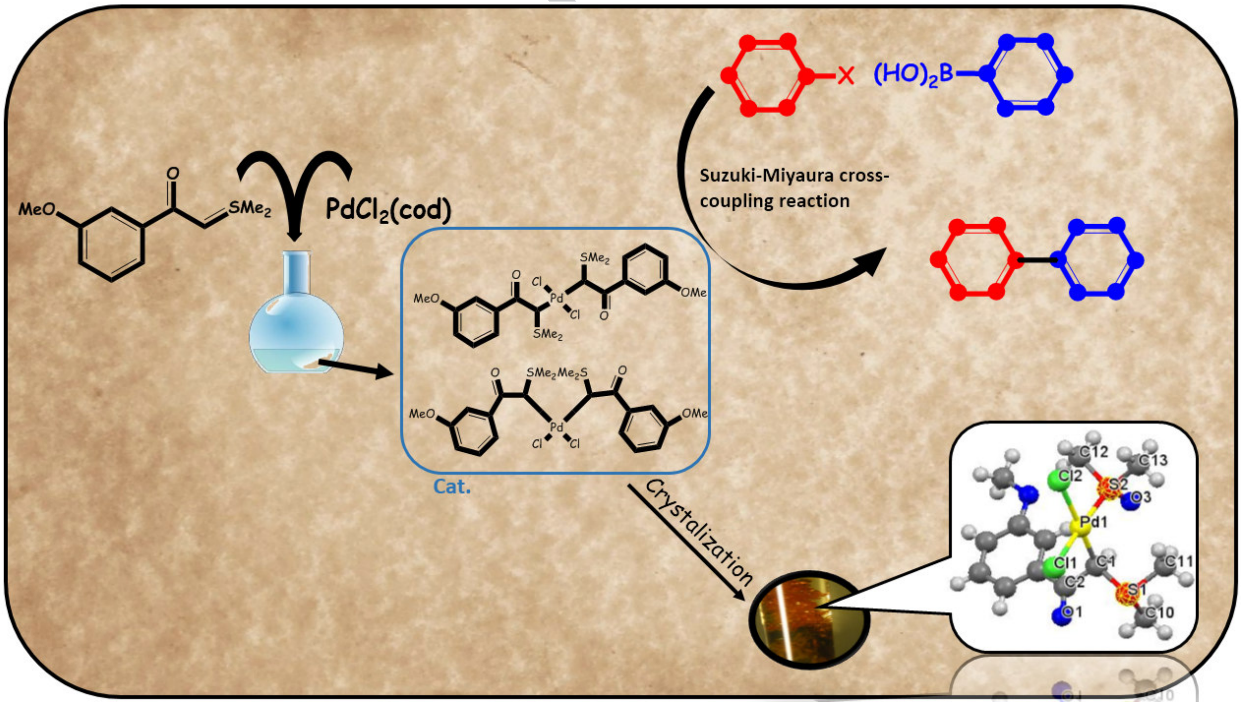

Graphical abstract-synopsis

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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The new sulfonium salt [$SMe_2CH_2C(O)C_6H_4$-*m*-OCH_3]Br (**1**) was synthesized from the reaction of dimethyl sulfide and 2-bromo-3'-methoxyacetophenone. Further treatment with NaOH 10% gave the α-keto stabilized sulfur ylide $SMe_2C(H)C(O)C_6H_4$-*m*-OCH_3 (**2**). This ligand was reacted with the dichloro(1,5-cyclooctadiene)palladium(II) complex, [$PdCl_2$(cod)], in a 2:1 ratio to give the new Cα-coordinated complexes *cis*- and *trans*- [$PdCl_2(SMe_2C(H)C(O)C_6H_4$-*m*-$OCH_3)_2$] (**3a** and **3b**). The X-ray analysis results revealed that complex **3a** has undergone a ligand replacement reaction in DMSO solution and the complex [$PdCl_2(SMe_2C(H)C(O)C_6H_4$-*m*-$OCH_3$).DMSO] (**4**) was formed. The air/moisture stable complexes **3a** and **3b** were employed as efficient catalysts for the Suzuki-Miyaura cross-coupling reaction of several aryl halides. 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.