

# Binuclear mercury (II) complexes of ambidentate sulfonium ylides in comparison with analogous phosphonium-based complexes; synthesis, characterization and a comprehensive theoretical study

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## ABSTRACT

The dehydrobromination reaction of a new sulfonium salt [(Me)<sub>2</sub>SCH<sub>2</sub>(O)C<sub>10</sub>H<sub>7</sub>]Br (**1**) with sodium hydroxide solution led to formation of sulfonium ylide (Me)<sub>2</sub>SCHC(O)C<sub>10</sub>H<sub>7</sub> (**2**) which was used to synthesize three binuclear complexes [(Me)<sub>2</sub>SCHC(O)C<sub>10</sub>H<sub>7</sub>]<sub>2</sub>HgX<sub>2</sub> (X = Cl (**3**), Br (**4**) and I (**5**)). Characterization of all compounds was thoroughly performed by elemental analysis, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic methods. Also the structure of complex (**4**) was characterized by X-ray crystallography method. The structure of prepared complexes was also compared with analogous phosphonium complexes [(Ph<sub>3</sub>PCHC(O)C<sub>10</sub>H<sub>7</sub>)]<sub>2</sub>HgX<sub>2</sub> (X = Cl, Br and I) using DFT calculations with the M06/def2-SVP level of theory. Based on the theoretical studies of geometry-optimized bidentate structures, the interaction energy values, ΔE<sub>int</sub>, for C→M bonds in [(Me)<sub>2</sub>SCHCOC<sub>10</sub>H<sub>7</sub>]<sub>2</sub>HgX<sub>2</sub> complexes are larger than those in [(Ph<sub>3</sub>PCHCOC<sub>10</sub>H<sub>7</sub>)]<sub>2</sub>HgX<sub>2</sub> (X = Cl, Br and I) complexes. Obviously, in comparison to the phosphonium ylide, the sulfonium ylide forms a stronger bond with Hg<sub>2</sub>X<sub>4</sub> (X = Cl, Br and I) fragments in aforementioned complexes.

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## 1. Introduction

Ylides are reactive compounds, in which a carbanion directly bonded to a heteroatom with a high degree of formal positive charge [1–3]. Different synthetic methods for the preparation of ylides have yet been used. Most of these methods include two steps: reaction of an alkyl/aryl halide RCH<sub>2</sub>X with a E<sub>Z</sub><sub>n</sub> nucleophile (NR<sub>3</sub>, PR<sub>3</sub>, AsR<sub>3</sub>, SR<sub>2</sub>, etc); and (2) dehydrohalogenation of the “onium” salt [RCH<sub>2</sub>-EZ<sub>n</sub>]X to form the ylide RCH = EZ<sub>n</sub> [4–6]. The utilization of α-keto stabilized phosphonium and sulfonium ylides RC(O)CH=PR<sub>3</sub> and RC(O)CH=SR<sub>2</sub> as ambidentate ligands towards various transition metal ions has aroused considerable interest in organometallic chemistry researches [7–12]. In both kind of phosphonium and sulfonium ylides, coordination to the soft metal ions is more dominated by the Cα-coordinated complexes than those of O-coordinated ylides [13–17]. This fact arises from the Hard-Soft-Acid-Base principle (HSAB) [18], which indicates that the

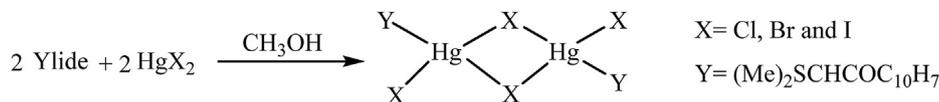
coordinatively active carbanion atom is more suitable site for donation of electron density to the soft metal ions and formation of strong metal-carbon bonds in ylidic complexes [19,20].

The synthesis of complexes derived from sulfonium ylides and mercury (II) halides was first published in 1975 by Weleskiet *al.* and they proposed symmetric halide-bridged binuclear structure for these complexes [21]. Also, in 2013 our research group extended the synthesis and characterization of phosphonium ylides to some new α-keto stabilized sulfonium ylide and their transition metal complexes [16]. Based on single crystal X-ray diffraction studies, some of the mercury (II) halide complexes with both of phosphonium and sulfonium ylide ligands were found to be halide-bridged binuclear compounds [16,22]. For example, the reaction of phosphonium ylide Ph<sub>3</sub>PCHCOC<sub>10</sub>H<sub>7</sub> with mercury (II) halides gave the [(Y). HgX<sub>2</sub>]<sub>2</sub> (Y = Ph<sub>3</sub>PCHCOC<sub>10</sub>H<sub>7</sub> and X = Cl, Br and I) binuclear complexes [23].

In the present study, we aimed to report the synthesis of new analogous sulfonium ylide (Me)<sub>2</sub>SCHCOC<sub>10</sub>H<sub>7</sub> and its mercury (II) halide complexes (Scheme 1). Because of the similarity in structure and also the same coordinated group (-C<sub>10</sub>H<sub>7</sub>) on ylidic carbon in

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**Scheme 1.** Reaction of the ylide (Y) with HgX<sub>2</sub> in (1:1) ratio.

both group of phosphonium and sulfonium ylides, we tried to compare these two group of complexes with each other with use of theoretical studies. In this regard, DFT calculations with MO6/def2-SVP level of theory were applied using a quantitative bonding analysis. In terms of orbital interactions, this investigation as the first comprehensive theoretical study compares the bonding behavior of three binuclear sulfonium complexes  $[(\text{Me})_2\text{SCHCOC}_{10}\text{H}_7]_2\text{Hg}_2\text{X}_4$  (X = Cl, Br and I) with those of binuclear phosphonium ylide complexes  $[\text{Ph}_3\text{PCHCOC}_{10}\text{H}_7]_2\text{Hg}_2\text{X}_4$  (X = Cl, Br, I). The main objective of this study is to investigate the differences between the bonds which monodentate sulfonium ylide and monodentate phosphonium ylides form with mercury (II) halides, although both kinds of bonds are donor-acceptor and both ligands are two-electron donor.

## 2. Experimental

### 2.1. Physical measurements and materials

All the chemicals were purchased from Merck or Fluka Chemical Companies. NMR spectra were obtained on 250 MHz broker spectrometers in DMSO-d<sub>6</sub> or CDCl<sub>3</sub> as the solvent. Chemical shifts ( $\sigma$ ) are reported relative to internal TMS (<sup>1</sup>H and <sup>13</sup>C). Melting points were measured on a Stuart SMPI apparatus. Elemental analysis for C, H, N and S were performed using a Perkin–Elmer 2400 series analyzer. Fourier transform infra-red spectra were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets.

### 2.2. X-ray crystallography

Colourless single crystals of  $[(\text{Me})_2\text{SCHCOC}_{10}\text{H}_7]_2\text{Hg}_2\text{Br}_2$  were crystallized by solvent diffusion of methanol into DMSO. Data collection was carried out on a Rigaku Oxford Diffraction Super Nova diffractometer using mirror monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 130 K. Using Olex2 [24], the structure was solved with the ShelXT [25] structure solution program using Intrinsic Phasing and refined with the ShelXL [26] refinement package using Least Squares minimization on F<sup>2</sup>, using all data. Gaussian absorption corrections were applied to the data. All non-hydrogen atoms were refined with anisotropic displacement parameters, while all hydrogen atoms were placed at geometrical estimates and refined using the riding model. Details of the structure are given in Table 2.

### 2.3. Computational methods

A theoretical study on structures and nature of metal-ligand bonds in some binuclear mercury (II) complexes of both phosphonium and sulfonium ylides with general formula  $[\text{Ph}_3\text{PCHCOC}_{10}\text{H}_7]\text{HgX}_2$  and  $[(\text{Me})_2\text{SCHCOC}_{10}\text{H}_7]\text{HgX}_2$  (X = Cl, Br and I) have been reported. In this context, the X-ray crystal structures of some derivatives of latter complexes which recently reported, were used as a basis for the DFT calculations [16,23]. The geometries of the binuclear mercury (II) complexes in the presence of two various kinds of ylide, phosphonium and sulfonium ylides, have been optimized without symmetry constraints at both MO6/

def2-SVP and BP86/def2-SVP levels of theory by using Gaussian 09 [27]. Vibrational frequency analyses, calculated at the same level of theory, indicate that the optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. NBO analyses were also carried out with the internal model GAUSSIAN 09 [28]. The bonding analyses, in terms of energy-decomposition analysis (EDA), were conducted at BP86-D3/TZ2P (ZORA)//M06/def2-SVP with C1 symmetry. The basis sets for all elements have triple-f quality augmented by one set of polarization functions (ADF basis set TZ2P (ZORA)) with the program package ADF2009.01 [29]. EDA calculations were carried out to analyze the nature of the metal-ligand bonds in latter compounds.

The IR frequency and <sup>13</sup>C NMR shielding results were obtained at the same level of theory. The <sup>13</sup>C isotropic shielding constant was calculated using the CSGT method and also TMS isotropic shielding constant was calculated through B3LYP/6-311 + G (2d,p) using the GIAO method.

**Table 1**

Selected spectroscopic data for compounds 1–5 (the data in parenthesis are related to the phosphonium analogues).

Compound	IR; $\nu(\text{CO}) \text{ cm}^{-1}$	<sup>1</sup> H NMR; $\delta\{\text{SCH}\} \text{ ppm}$	<sup>13</sup> C NMR; $\delta\{\text{CO}\} \text{ ppm}$
<b>1</b>	1665 (1660)	5.59 <sup>a</sup> (6.29) <sup>b</sup>	191.64 (190.12)
<b>2</b>	1596 (1594)	4.59 (4.58) <sup>c</sup>	178.61 (184.62)
<b>3</b>	1640 (1631)	5.71 (5.73) <sup>c</sup>	192.59 (191.12)
<b>4</b>	1638 (1626)	5.56 (5.66) <sup>c</sup>	191.59 (190.42)
<b>5</b>	1631 (1620)	5.43 (5.39) <sup>c</sup>	190.92 (188.83)

<sup>a</sup>  $\delta\{\text{SCH}_2\}$ .

<sup>b</sup>  $\delta\{\text{PCH}_2\}$ .

<sup>c</sup>  $\delta\{\text{PCH}\}$ .

**Table 2**

Crystal data and structure refinement for  $[\text{HgBr}_2((\text{Me})_2\text{SCHCOC}(\text{O})\text{C}_{10}\text{H}_7)]_2$ .

Identification code	rwg2018_12cGau
Empirical formula	C <sub>28</sub> H <sub>28</sub> Br <sub>4</sub> Hg <sub>2</sub> O <sub>2</sub> S <sub>2</sub>
Formula weight	1181.44
Temperature/K	130.00 (10)
Crystal system	triclinic
Space group	P-1
a/Å	7.5659 (3)
b/Å	9.5668 (5)
c/Å	12.0666 (6)
$\alpha/^\circ$	107.724 (4)
$\beta/^\circ$	106.491 (4)
$\gamma/^\circ$	97.796 (4)
Volume/Å <sup>3</sup>	773.78 (7)
Z	1
$\rho_{\text{calc}}/\text{cm}^3$	2.535
$\mu/\text{mm}^{-1}$	15.233
F (000)	544.0
Crystal size/mm <sup>3</sup>	0.252 × 0.178 × 0.084
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^\circ$	6.464 to 64.762
Index ranges	−5 ≤ h ≤ 11, −14 ≤ k ≤ 14, −17 ≤ l ≤ 15
Reflections collected	9265
Independent reflections	4931 [R <sub>int</sub> = 0.0269, R <sub>sigma</sub> = 0.0481]
Data/restraints/parameters	4931/0/174
Goodness-of-fit on F <sup>2</sup>	1.043
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0284, wR <sub>2</sub> = 0.0546
Final R indexes [all data]	R <sub>1</sub> = 0.0349, wR <sub>2</sub> = 0.0574
Largest diff. peak/hole/e Å <sup>−3</sup>	1.67/−1.37

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