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REACTION OF A HETEROTOPIC P,SAs LIGAND WITH GROUP 10 METAL(II) COMPLEXES: A THEORETICAL STUDY

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ABSTRACT. Density functional calculations have been carried out in order to gain some insight into the electronic structure of 1-$Ph_2AsSC_6H_4$-2-PPh_2 (1) and to investigate the reactions of 1 with group 10 metal dihalides. The obtained results explain well the experimentally observed behaviour of 1 during the investigated complexation reactions and support the trends observed for the isomerisation of the resulted trinuclear trimeric compounds.

Keywords: *heterotopic P,SAs ligand, palladium complexes, platinum complexes, structural isomerism, DFT calculations.*

INTRODUCTION

Tertiary phosphine and arsine ligands derived from thiophenol have been shown to be very versatile ligands that form stable complexes with a wide range of transition metals [1]. The coordination chemistry of bidentate HSC_6H_4-2-EPh_2 ligands (E = P, As) was investigated thoroughly mainly due to their mixed-donor chelating compartments [1–3]. For EPh_2(SPh) ligands (E = P, As) [4,5], the metal-mediated E–S bond cleavage was studied in their reactions with metal carbonyls [6–13]. Based on our interest in designing and investigating the coordination properties of a heterotopic P,SAs ligand, the synthesis of 1-$Ph_2AsSC_6H_4$-2-PPh_2 (**1**) and reactions of **1** with group 10 metal dihalides were carried out and reported in a previous study done by our group [14]. Ligand **1** combines the properties of $AsPh_2$(SPh) and HSC_6H_4-2-PPh_2, bearing three donor atoms. However, reactions of **1** with $[PdCl_2(cod)]$ and $[PtI_2(cod)]$ (cod = 1,5-cyclooctadiene) in 1:1 ratio occurred with cleavage of the As–S bond and coordination of the resulting phosphanylthiolato ligand (SC_6H_4-2-PPh_2). Shorter reaction times (4 h, M = Pd; 1 week, M = Pt) led to trinuclear complexes [(*cis*-M{(*μ*-*S*-SC_6H_4-2-PPh_2)-κ^2*S,P*}$_2$)-MX_2-MX{(*μ*-*S*-SC_6H_4-2-PPh_2)-κ^2*S,P*}] [M = Pd, X = Cl (**3**); M = Pt, X = I (**5**)], while the

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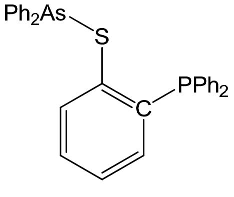
trimeric trinuclear isomers $[MX\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2 S,P\}]_3$ [M = Pd, X = Cl (**2**); M = Pt, X = I (**4**)] were obtained after reaction times of two weeks [14].The central fragments of **2** and **4** are comparable with that of the recently reported $[PtI\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}\kappa^2 S,As\}]_3$ [3] and $[PtI\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}P(Biph)\}\text{-}\kappa^2 S,P\}]_3$ (Biph = 1,1'-biphenyl) [15] complexes. Density functional calculations have been carried out in order to gain some insight into the electronic structure of **1** and to investigate the observed reactions which resulted in the formation of transition metal complexes **2**–**5**.



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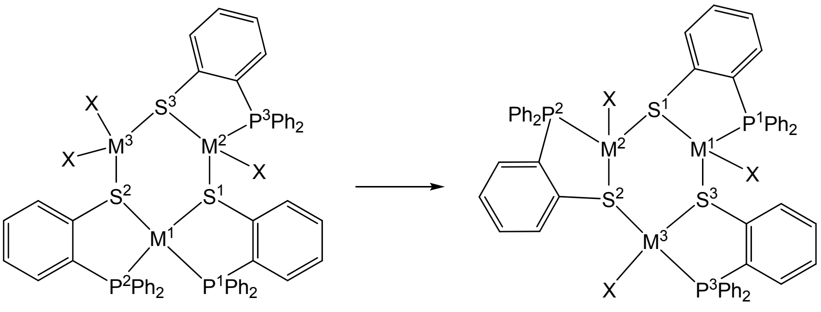
Scheme 1. 1-$Ph_2AsSC_6H_4$-2-PPh_2 (**1**).

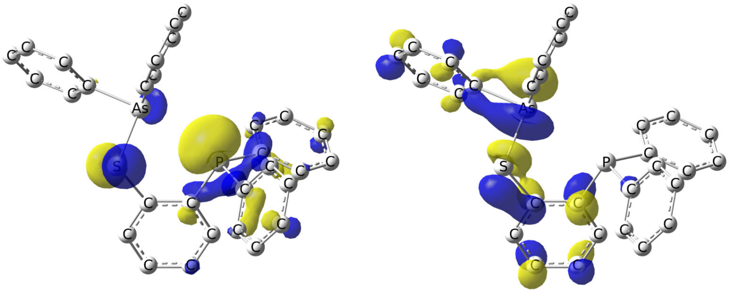


3, **5** **2**, **4**

Scheme 2. Isomerisation of **3** to **2** and **5** to **4**.

RESULTS AND DISCUSSION

The optimised geometry parameters of **1** (Table 1) are in excellent agreement with the experimental values [14]. Figure 1 shows the highest occupied molecular orbital (HOMO) of **1**, which is predominantly made of the phosphorus and sulfur lone pairs. This specific nature of the HOMO makes the P,S chelating pocket of **1** most suitable for an electrophilic attack. This is also supported by the electrostatic potential surface, where the negative regions correspond to the lone pairs at sulfur and phosphorus (Figure 2). The formation of complexes **2–5** undoubtedly proves that only the P,S chelating pocket coordinates to the transition metal centres. The lability of the As–S bond is also suggested by the electronic structure calculations. The lowest unoccupied molecular orbital (LUMO) of **1** is predominantly an As–S antibond (Figure 1). However, the cleavage of the As–S bond might also be induced by the coordination of sulfur to the metal centre, which withdraws an electron from the As–S bond. The eliminated $AsPh_2$ group was observed by MS-ESI spectrometry in the filtrate solutions after isolation of **2**–**5**, which showed different oxidised species of dimerised $AsPh_2$ [1]



HOMO LUMO

Figure 1. Frontier molecular orbitals of **1**. Isovalue: 0.5, positive orbital contour: yellow, negative orbital contour: blue, hydrogen atoms are omitted for clarity.

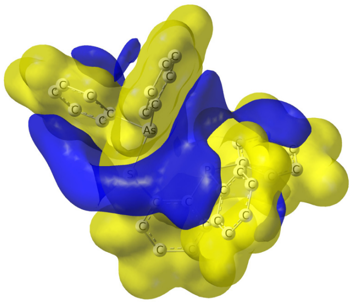


Figure 2. Electrostatic potential surface of **1**. Isovalue: 0.02, positive contours: yellow, negative contours: blue, hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths in pm for **1**.

Bond length	exp. [14]	calcd.
As(1)–S(1)	226.6(1)	228.1
S(1)–C(13)	178.4(4)	180.4
P(1)–C(19)	183.7(4)	185.0
P(1)–C(14)	183.8(4)	186.1
P(1)–C(25)	184.3(4)	185.5

Furthermore, the gas phase As–S and P–C bond dissociation energies for both homolytic and heterolytic bond cleavage were also calculated. In both cases the energy for the homolytic bond cleavage, resulting in two radical fragments (processes 1a and 2a in Table 2), is significantly smaller than the heterolytic bond dissociation energies. Not surprisingly, the P–C homolytic bond dissociation energy is significantly higher than the energy required to cleave the As–S bond. The corrections for the description of the solvation in toluene do not alter these trends. However, the bond dissociation energies are predicted to be lower than without corrections for solvent effects (Table 2).

Table 2. Bond dissociation energies for **1**, in kJ mol^{-1}.

Process	$\Delta G°$ (gas)	$\Delta G°$ (toluene)
1a: **1** → $[AsPh_2]^{\cdot}$ + $[1\text{-}PPh_2\text{-}2\text{-}SC_6H_4]^{\cdot}$	172.5	169.2
1b: **1** → $[AsPh_2]^{-}$ + $[1\text{-}PPh_2\text{-}2\text{-}SC_6H_4]^{+}$	579.5	390.6
1c: **1** → $[AsPh_2]^{+}$ + $[1\text{-}PPh_2\text{-}2\text{-}SC_6H_4]^{-}$	595.0	399.0
2a: **1** → $[PPh_2]^{\cdot}$ + $[S(AsPh_2)C_6H_4]^{\cdot}$	227.5	226.3
2b: **1** → $[PPh_2]^{-}$ + $[S(AsPh_2)C_6H_4]^{+}$	575.8	390.5
2c: **1** → $[PPh_2]^{+}$ + $[S(AsPh_2)C_6H_4]^{-}$	568.8	369.9

The optimised geometry parameters of **2**–**5** (Tables 3 and 4) are in good agreement with the experimental values [14], and the observed covalent and coordinative M–S bonds are correctly reproduced theoretically. Independent of the used metal halide in both cases the trimeric forms **2** and **4** are energetically favoured over their trinuclear counterparts (i.e., **3** and **5**). The relative energy differences between the trinuclear and trimeric forms are very similar: 15.7 kJ mol^{-1} and 10.5 kJ mol^{-1} for **2**/**3** and **4**/**5**, respectively. The corrections for the description of the solvation in tetrahydrofuran predict lower relative energy values for the differences between the trinuclear and trimeric forms (9.2 kJ mol^{-1} and 5.4 kJ mol^{-1} for **2**/**3** and **4**/**5**, respectively). Thus, solvation seems to lower the energy difference between the trinuclear and trimeric forms of both Pd- and Pt- substituted complexes. The trinuclear to trimeric interconversion from **3** to **2** might be facilitated by an intramolecular HOMO-LUMO interaction in **3**. The HOMO of **3** is mainly composed of the Cl(3) lone pair of electrons, which could interact with the σ*(Pd–E) LUMO (E = S, P) located on Pd(1), and trigger the isomeric rearrangement. The HOMO of **5** is composed mainly from the I(2) and I(3) lone pairs of electrons and has a similar character as the HOMO of **3**. However, the LUMO of **5** is shared between all three platinum centres, with the highest atomic orbital coefficient located at Pt(2) (Figure 3).

This might be one of the reasons for the experimentally observed differences between the two isomeric rearrangement reactions [14]. Furthermore, the gas phase Gibbs free energies ($\Delta G°_{gas}$) of the two isomeric rearrangements also suggest differences between the two processes. The conversion from **3** to **2** is more exothermic (ΔG_{gas} = –68.5 kJ mol^{-1}) than the isomerisation from **5** to **4** ($\Delta G°_{\text{gas}}$ = –36.4 kJ mol^{-1}). The corrections for solvent effects do not alter this trend. However, the $\Delta G°_{\text{THF}}$ values are lower (–44.2 kJ mol^{-1} for the conversion from **3** to **2** and –32.1 kJ mol^{-1} for the isomerisation from **5** to **4**). The lower Gibbs free energies for the *trinuclear/trimer* isomerisation in solution, together with the lower relative energy differences between the two isomers in THF, clearly indicate that the solvation effects facilitate the observed isomerisations.

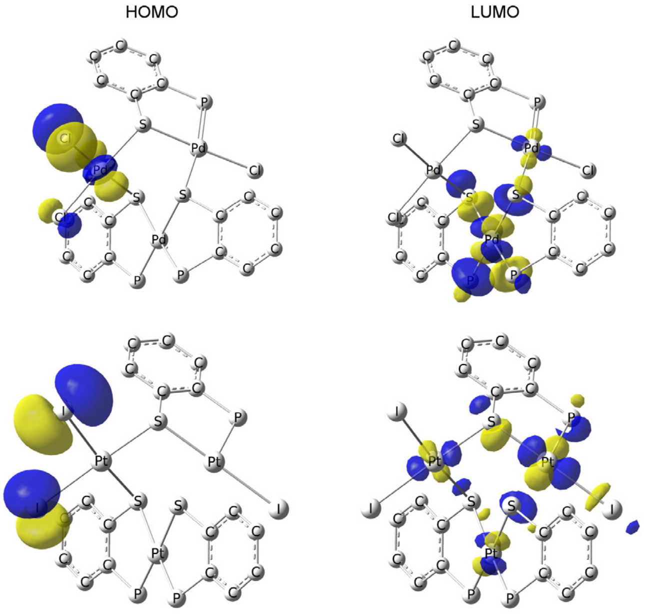


Figure 3. Frontier molecular orbitals of **3** (top) and **5** (bottom). Isovalue: 0.5, positive orbital contour: yellow, negative orbital contour: blue, hydrogen atoms and terminal phenyl rings are omitted for clarity.

Table 3. Selected bond lengths in pm for **2** and **4**.

	2 (M = Pd)		**4 (M = Pt)**	
Bond length	exp. (from [14])	calcd.	exp. (from [14])	calcd.
M(1)–P(1)	223.0(6)	229.9	222.8(1)	229.5
M(1)–S(1)	228.8(6)	237.0	230.2(1)	237.3
M(1)–S(3)	242.5(6)	251.7	242.8(1)	251.5
M(2)–P(2)	223.4(6)	230.0	223.6(1)	228.6
M(2)–S(2)	227.3(5)	235.7	227.3(1)	237.2
M(2)–S(1)	237.3(6)	246.6	237.3(1)	245.8
M(3)–P(3)	223.4(7)	229.3	223.5(2)	229.1
M(3)–S(3)	228.7(6)	237.9	228.8(1)	238.9
M(3)–S(2)	240.5(6)	247.6	238.7(1)	246.8

Table 4. Selected bond lengths in pm for **3** and **5**.

	3 (M = Pd)		**4 (M = Pt)**	
Bond length	exp. (from [14])	calcd.	exp. (from [14])	calcd.
M(1)–P(2)	225.9(2)	233.6	225.3(9)	232.3
M(1)–P(1)	227.5(2)	234.9	225.7(8)	233.1
M(1)–S(1)	234.6(2)	243.9	235.7(8)	242.7
M(1)–S(2)	233.9(2)	240.1	236.1(8)	242.1
M(2)–P(3)	222.3(2)	229.8	222.4(9)	228.6
M(2)–S(3)	227.6(2)	237.6	228.6(8)	238.6
M(2)–S(1)	237.1(2)	246.5	237.8(8)	246.0
M(3)–S(2)	228.6(2)	240.9	230.7(8)	239.7
M(3)–S(3)	230.7(2)	241.0	231.0(8)	240.6

CONCLUSIONS

Theoretical calculations on **1** predict that the P,S chelating pocket will be favoured over the As,S unit during an electrophilic attack, which is in agreement with the previously reported experimental results. The lability of the As–S bond is suggested by the electronic structure of **1** and the bond dissociation energies. The observed trinuclear to trimeric interconversions might be facilitated by intramolecular HOMO-LUMO interactions in the trinuclear isomers. Furthermore, the nature of the metal halide strongly influences the electronic structure of the trinuclear species and the progress of the isomerisation reactions.

EXPERIMENTAL SECTION

Density functional calculations were carried out with the GAUSSIAN 09 program package [16]. The starting geometries of **1**–**5**, obtained from X-ray structure data, have been optimized with the B3LYP density functional [17] using the LANL2DZ basis on Pd, Pt and I (along with the effective core potential of Hay and Wadt [18, 19, 20]) and the 6-31G(d,p) basis set [21] on all other atoms. Corrections for the description of the solvation were carried out by employing the Polarisable Continuum Model (PCM) method of Tomasi and coworkers [22].

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