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Comparative study of 1,4-P$^{\cdots}$Ointramolecular interaction in hybrid phosphine-phosphoniumylide and their Hg(II) derivatives

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ABSTRACT

Inter and intramolecular interactions are important in the context of conformational preferences, molecular reactivity and supramolecular chemistry. The extent of 1, 4 P$^{\cdots}$O intramolecular interaction present in the solid state structures of a special class of phosphine appended phosphorus ylide ligand and its Hg(II) derivatives were examined. While halogen ligands around mercury ion seem to affect the P, O nonbonding distances, the P-C-C-O torsion angles are less influenced. Comparison of the geometrical parameters indicates the preference for cisoid conformation in solid state.

Keywords: Phosphorus ylides, Hg(II) complexes, conformational analysis.

INTRODUCTION

Molecular interactions are a subject of immense studies in the realm of supramolecular chemistry. Biological implications of noncovalent interactions such as hydrogen bonding is ubiquitous, for example, in protein folding, structure of nucleic acids, drug-receptor interactions etc [1]. Apart from hydrogen bonding there are several weak forces like π-π stacking, arene-perfluoroarene interactions and more recently halogen bonding that have been found beneficial in chemistry, material science, biology and medicine at large. From a synthetic chemistry point of view, it is still a great challenge to control such noncovalent interactions [2].

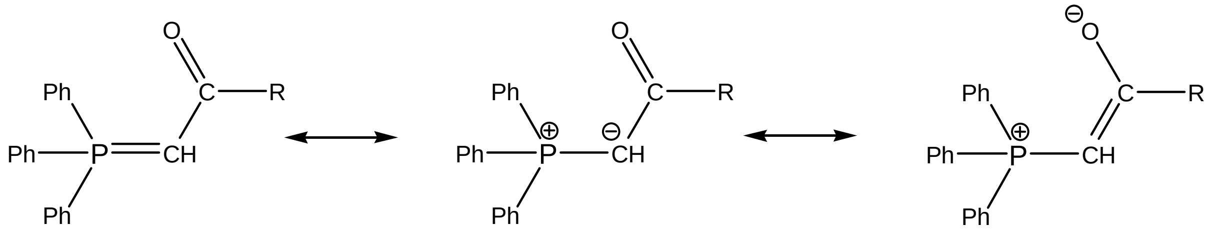
Phosphorus ylides are compounds containing a carbanion directly attached to a positively charged phosphorus atom. They are widely used reagents in organic chemistry to install a double bond in specific location of a molecule with specific stereochemistry (Wittig reaction) [3]. The α-stabilized phosphorus ylides of the type Ph_3PCRR' (where R = $COCH_3$, COPh, COOEt, $CONH_2$, CN and R' = H, $COCH_3$, COPh) have been employed as useful ligands in coordination chemistry [4]. An attractive force between P^+ and O^- centres, termed as 1,4-P$^{\cdots}$O interaction, is theoretically predicted in α-stabilized ylides, and it is expected to have influence on the conformational preferences and reactivity [5].The coordination chemistry of mercury(II) complexes has been studied in a variety of contexts [6]. In this paper, we examine the molecular structures of eight phosphorus ylides and their mercury(II) derivatives to throw light into the geometric parameters of 1,4-P$^{\cdots}$O intramolecular interaction.

MATERIALS AND METHODS

PLATON crystallographic software was used for computing geometrical parameters pertinent to the present study using the CIF files of the following compounds. $PPh_2CH_2PPh_2{=}CHCOPh$ [4], $[HgCl_2(\mathit{P}Ph_2CH_2PPh_2\mathit{C}HCOPh)]$ [4], $[HgBr_2\ (\mathit{P}Ph_2CH_2PPh_2\mathit{C}HCOPh)]$ [4], $[HgI_2\ (\mathit{P}Ph_2CH_2PPh_2\mathit{C}HCOPh)]$ [4], $[HgCl_3\ (\mathit{P}Ph_2CH_2PPh_2CH_2COPh)]$ [7], $[HgCl_2\ (Br)\ (\mathit{P}Ph_2CH_2PPh_2CH_2COPh)]$ [7], $[HgBr_3\ (\mathit{P}Ph_2CH_2PPh_2CH_2COPh)]$ [7], $[HgBr_2\ (I)\ (\mathit{P}Ph_2CH_2PPh_2CH_2COPh)]$ [7].

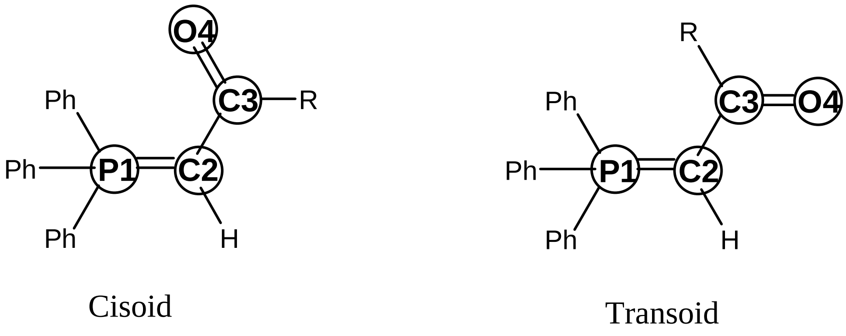
RESULTS AND DISCUSSION

The α-carbonyl substituted resonance stabilized ylides show delocalization of negative charge as shown in Scheme 1. Depending on the metal ion, this type of ylide can act as either C-donor or O-donor ligand.



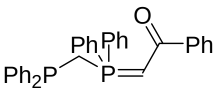
Scheme 1. Resonance delocalization in carbonyl stabilized ylides

Molecular structures of α-carbonyl ylides can essentially display two types of conformations, cisoid and transoid (Scheme 2). Both the rotational isomers have been observed in different ylides. While $Ph_3P{=}CHCO_2CH_3$ shows both isomers [8], $Ph_3P{=}CHCOCH_3$ shows only cisoid isomer [9]. In this study, hybrid ylides containing both phosphine and phosphorus ylide are chosen for examining the conformational preferences.



Scheme 2. Possible rotational isomers in α-carbonyl ylides

Scheme 3 shows the chemical diagrams of selected ylide and its mercury derivatives along with compound number. Relevant geometrical parameters such as P, O nonbonding distances and P-C-C-O torsion angles are given in Table 1. The results indicate the P, O nonbonding distance ranges from 2.855(1) to 3.107(2)Å. The sum of van der Waals radii of P and O atoms is 3.35 Å and the observed distances are within this range. While the free ylide **1** shows the longest interaction, the shortest distance is observed for bromo complex **3**.



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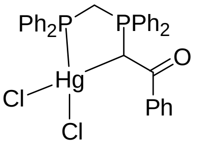

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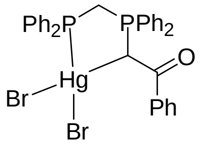

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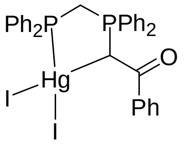

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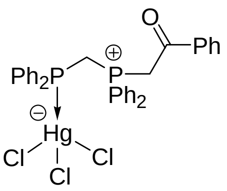

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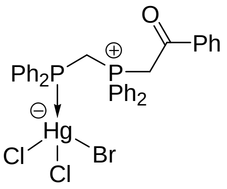

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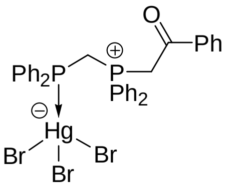

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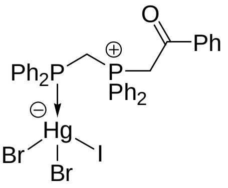

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Significantly, the iodo complex **4** having two molecules in the asymmetric unit exhibit two different distances, 2.907(1), 2.976(1)Å, respectively. Comparing this distance with the P, O distances observed in other two chelate complexes **2** and **3** demonstrates the influence of different halogen atoms upon 1, 4 $P^{\cdots}O$ intramolecular interaction. The zwitterionic complexes, **5-8**, all have the P, O distance in a similar range. But in this case also a clear influence of different halogen atoms is visible. When all the halogen atoms around mercury ion is same, like in the case of compound **5** having three chlorides (2.957(3)Å) or in the case of compound **7** having three bromides (2.933(3)Å), the P, O distance is higher. Whereas in mixed halogeno compound **6** having two chlorides and one bromide (2.917(5)Å) or compound **8** containing two bromides and one iodide (2.913(9)Å), the P, O distance is shorter.

The P-C-C-O torsion angle (θ) is also a good indicator of strength of P, O interaction. If the θ angle is close to 0^o, the resulting conformation is called cisoid (strong P, O interaction) and if the θ angle is close to 180^o transoid (no P, O interaction) isomer results. The free ylide **1** has the lowest θ value -2.7(3)^o although the P, O nonbonding distance is the highest. The zwitterionic compound **5** shows the θ value of 9.3(4)^o. For most of the compounds the θ angle is in the range of 20^o. With compound **3**and **8** having the θ angle 18.2(17)^o and -14.6(15)^o, respectively. This comparison makes it clear that different halogens have no significant influence on the P-C-C-O torsion angles. On the other hand, the overall θ angle values of all the compounds definetly point out that the cisoid is the favoured conformation.

Table 1. P….O nonbonding distances and P-C-C-O torsion angles

Compound	**P···O (Å)**	**P-C-C-O (θ, °)**
1	3.107(2)	-2.7(3)
2	2.885(1)	21.0(10)
3	2.855(1)	18.2(17)
4*	2.907(1), 2.976(1)	-28.1(10), -25.2(10)
5	2.957(3)	9.3(4)
6	2.917(5)	21.7(8)
7	2.933(3)	24.7(5)
8	2.913(9)	-14.6(15)

**Asymmetric unit contains two independent molecules*

CONCLUSION

In conclusion, an analysis of conformational preferences in certain phosphorus ylide derivatives has been made. The results suggest that all the derivatives have a clear preference for cisoid conformation due to 1, 4 P···O intramolecular interaction. Both the P, O nonbonding distances and P-C-C-O torsion angles indicate that a moderate 1,4 P···O influence is operative in solid state.

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