In The Name of Allah,

The Most Beneficent, The

Most merciful

Bu-Ali Sina University
Faculty of Chemistry

Thesis for the Degree of Doctor of Philosophy in Inorganic Chemistry

Title:

Synthesis and characterization of some new phosphorus ylides and their metal complexes with spectroscopy and X-ray crystallography methods

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Thesis submitted in partial fulfillment of the requirements for the degree of doctor of philosophy (Ph.D.) in Inorganic Chemistry

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To my Wife,

Samira

And my Daughter,

Hasti

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Abstract

After presentation of a history of phosphorus ylides and their metal complexes, the synthesis of 12 keto-stabilized phosphorus ylides with general formula of $Ar_3PCHCOR$ (α type) and $Ar_3PCO_2R^1CHR^2CO_2R^1$ (β-type) (Ar = aryl group; R=aryl or alkyl groups; $R^1$and R^2=alkyl groups) are presented. Characterization of above ylides were performed with elemental analysis, IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy methods. Variable temperature ^1H and ^{31}P NMR study on one of the β-type, shows that the two rotamers equilibrate rapidly at higher temperatures. The crystal structure of one of the α types is also discussed.

The synthesis of thirteen binuclear, three mononuclear and four polynuclear complexes of α-ylides are reported. Characterization of these compounds were performed with elemental analysis, IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy methods. The existence of satellites due to coupling between ^{199}Hg and ^{31}P centers at room temperature and disappearing of them in ^{31}P NMR spectra at higher temperatures and lower concentrations is a new observation in Hg(II) complexes of phosphorus ylides.

The crystal structure of three binuclear, three mononuclear and one polynuclear Hg(II) complexes of these ylides are discussed. Furthermore, the crystal structure of two previously known binuclear complexes and one orthopalladated complex are also studied. These studies show that:

1- C-coordination is occurred for all ligands coordinated to Hg(II), Cd(II) and Pd(II) centers.
2- An unprecedented O-coordination of DMSO to a soft Hg(II) center is occurred.
3- Presentation of a coordination number of 7 for Hg(II) in polymeric complex with bridged nitrate anions is interesting and unusual.
4- Comparing of bond lengths in free ylide and coordinated ylide in Hg(II) complex indicates that ylide resonance forms are destroyed upon complexation.

Ab initio calculations were made on the mercury(II) complexes of phosphorus ylides. Following results were obtained:

1- Calculations on binuclear Hg(II) complexes show that the observed trans-like isomers are always more stable than cis-like ones. This stability is calculated to be 4-12 Kcal.mol^{-1}.

2- The results of calculation show that the bridge-splitting exothermic reaction in DMSO solution is potentially possible for all dimeric complexes in which DMSO acts as a ligand. The data show that in the case of iodine complexes, the formation of mononuclear complexes is relatively more favorable than corresponding chlorine and bromine complexes.

3- We were interested to compare the relative stability of two possible C- and O-coordinated isomers in binuclear Hg(II) complexes of phosphorus ylides. Thus we optimized an O-coordinated structural isomer for one of compounds. The results showed that this structure is 49.63 Kcal/mol less stable than its observed C-coordinated isomer indicating that C-coordination is significantly preferred with all ligands in present complexes.

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