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# Synthesis and Spectral Characterization of 4-Methoxybenzoylmethylenetri-*p*-tolylphosphorane and It's Reaction with Mercury(II) Halides

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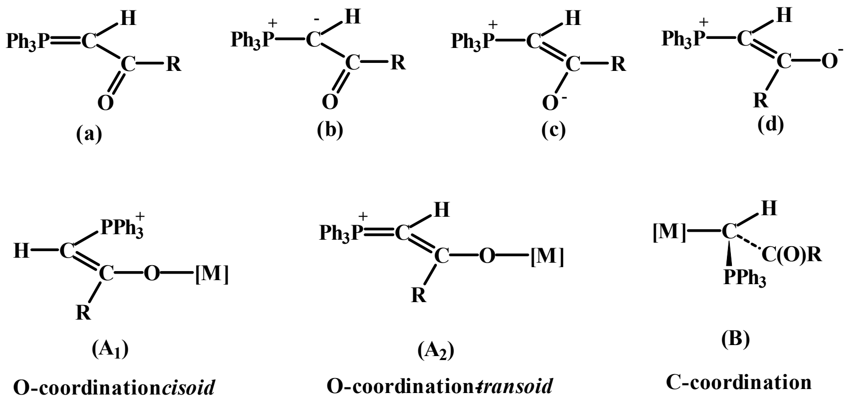
The reaction of the 4-methoxybenzoylmethylenetri-*p*-tolylphosphorane $\{(CH_3C_6H_4)_3PCHCOC_6H_4OCH_3)\}$ (MBPTY) with mercury(II) halide in equimolar ratios using methanol as solvent have yielded $[(MBPTY)\cdot HgCl_2]_2$ (**1**), $[(MBPTY)\cdot HgBr_2]_2$ (**2**), $[(MBPTY)\cdot HgI_2]_2$ (**3**). IR, $^1H$, $^{13}C$ and $^{31}P$ NMR together with microanalysis data of the products were obtained. Analytical data indicate a 1:1 stoichiometry between the ylide and Hg(II) halide in each of the three products.

**Key Words: Mercury(II) halides, Tri-*p*-tolylposphine, Ylide, Phosphorane.**

## INTRODUCTION

Phosphorus ylides are reactive compounds, which take part in many reactions of value in the synthesis of organic products[1-4]. Phosphorus ylides are synthetic targets of interest, because of their value for a variety of industrial, biological and chemical synthetic uses[4-10]. Several methods have been developed for the preparation of phosphorus ylides. These ylides are usually prepared by treatment of a phosphonium salt with a base and phosphonium salts are usually obtained from the phosphine and alkyl halide. Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins in other ways[4]. The phosphonium salts are most often converted to the ylide by treatment with a strong base, though weaker bases can be used if the salt is acidic enough. The coordination chemistry of the phosphoranes of the type α-keto stabilized ylides $Ph_3P = C(H)COR$ have shown useful applications in organometallic chemistry (due to their ambidentate character as ligands) and reactants or valuable key intermediates in metal-mediated organic synthesis. This ambidentate character facilitates the preparation of stable metal complexes in which the ylide could be O-coordinated ($A_1$, $A_2$) or C-coordinated (B) (**Scheme-I**) with both modes rationalized in terms of the resonance forms a-c together with the isomeric formed. However, while a large number of compounds containing C-coordinated ylides are known, very few examples of O-bonded ones have been reported[11-14].



**Scheme-I**

This paper presents the results on the reactivity of $HgX_2$ toward α-keto-stabilized phosphorous ylides, which gives Hg(II) dimeric complexes containing C-bound ylide.

## EXPERIMENTAL

4-Methoxybenzoylmethylenetri-*p*-tolylphosphorane was prepared and characterized according to report procedure[15]. All the solvents were purified before used[16].

Solid-state FT-IR spectra in the region of 4000-200 cm$^{-1}$ using KBr pellets were obtained on a (Perkin Elmer) spectrophotometer. Melting points were measured with a SMPI apparatus. $^{1}$H, $^{31}$P and $^{13}$C NMR spectra were obtained using a 90 and 200 MHz instrument at Regional Sophisticated instrumentation Bu-Ali-Sina and Tarbiat Modaress Universities. Elemental analyses were carried out at Research Institute of Bu-Ali-Sina University.

**Preparation of 4-methoxybenzoylmethylenetri-*p*-tolylphosphorane (A):** Tri-*p*-tolyphosphine (0.152 g, 0.5 mmol) was added to a chloroform solution (25 mL) of 2-bromo-4'-methoxyacetophenone (0.114 g, 0.5 mmol), stirred for 8 h. The solution was filtered off and washed with diethyl ether. The precipitate was collected and dried. The product neutralized by NaOH (0.5 M). Yield (85 %), (m.p. = 161-163°C). IR (KBr, cm$^{-1}$) $\lambda_{max}$: 1527 $\nu$(C = O), 884 $\nu(P^{+}\text{-}C^{-})$. $^{1}$H NMR ($CDCl_3$): 1.251 (s, 9H, $CH_3$), 2.616 (s, 3H, $OCH_3$) 4.664 (d, 1H, $J$ = 15.68, CH), 5.45 -7.37 (m, 16H, Ph) ppm. $^{31}$P NMR ($CDCl_3$): 12.920 (s) ppm. $^{13}$C NMR ($CDCl_3$): 54.76 (s, $OCH_3$), 48.3(d, $J$ = 121.6, CH), 115.28 (d, $J$ = 97.84, P(*p*-tolyl)$_3$(i)), 129.81 (d, $J$ = 13.34, P(*p*-tolyl)$_3$(m)), 131.273 (s, P(*p*-tolyl)$_3$(p)), 132.89 (d, $J$ = 10.9, P(*p*-tolyl)$_3$(o)), 163.59 (s, CO.Ph (i)), 188.861 (s, CO). Anal. (%) Calcd. $C_{27}H_{23}O_2P$: C, 66.05. H, 4.88. Found C, 67.24. H, 4.84.

**Preparation of 4-methoxybenzoylmethylenetri-*p*-tolylphosphorane mercury chloride (B):** A solution of (0.135 g, 0.5 mmol) of mercury(II) chloride in methanol (10 mL) was added to a methanolic solution of (0.226 g, 0.5 mmol) of ylide in dry methanol (10 mL) and the mixture was stirred for 4 h. The white crystals formed by the slow evaporation of the solvent were dried *in vacuo*. Yield (90.0 %) (m.p. = 204-206°C). IR (KBr, $cm^{-1}$) $\nu_{max}$: 1627 ν(C = O), 806 ν($P^+$-$C^-$). $^1H$ NMR (DMSO-$d_6$): 2.393 (s, 9H, $CH_3$), 3.829 (s, 3H, $OCH_3$), 5.403 (d, 1H, CH), 6.82-8.012 (m, 16H, Ph) ppm. $^{31}P$ NMR (DMSO-$d_6$): 23.847(s) ppm. $^{13}C$ NMR (DMSO-$d_6$): 55.43 (s, $OCH_3$), 120.16 (d, *J* = 90.67, P(*p*-tolyl)$_3$(i)), 129.93 (d, *J* = 14.55, P(*p*-tolyl)$_3$(m)), 130.222 (s, P(*p*-tolyl)$_3$(p)), 133.27 (d, *J* = 9.8, P(*p*-tolyl)$_3$(o)), 162.66 (s, CO-Ph(i)), 190.235 (s, CO). Anal. (%) Calcd. $C_{30}H_{29}O_2PCl_2Hg$: C, 49.75; H, 4.01 %. Found C, 49.20; H, 4.13.

**Preparation of 4-methoxybenzoylmethylenetri-*p*-tolylphosphorane mercury bromide (C):** To a solution of (0.226 g, 0.5 mmol) of the above ylide in methanol (10 mL) was added (0.18 g, 0.5 mmol) of mercury(II) bromide and the mixture was stirred for 4 h. The solvent was removed *in vacuo*. The white product obtained was washed with ice-cold methanol and dried in vacuum. Yield (87.2 %) (m.p. = 178-180ºC). IR (KBr, $cm^{-1}$) $\nu_{max}$: 1625 ν(C = O), 805 ν($P^+$-$C^-$). $^1H$ NMR (DMSO-$d_6$): 2.384 (s, 9H, $CH_3$), 3.823 (s, 3H, $OCH_3$), 5.359 (d, 1H, *J* = 15.68, CH), 6.899-8.028 (m, 16H, Ph) ppm. $^{31}P$ NMR (DMSO-$d_6$): 23.622(s) ppm. $^{13}C$ NMR (DMSO-$d_6$): 55.505 (s, $OCH_3$), 123.97 (d, *J* = 109.33, P(*p*-tolyl)$_3$(i)), 130.02 (d, *J* = 12.95, P(*p*-tolyl)$_3$(m)), 130.309 (s, P(*p*-tolyl)$_3$(p)), 133.21(d, *J* = 10.52, P(*p*-tolyl)$_3$(o)), 162.712 (s, CO-Ph(i)), 197.523 (s, CO). Anal.(%) Calcd. $C_{30}H_{29}O_2PBr_2Hg$: C, 44.30; H, 3.56. Found C, 45.20; H, 3.81.

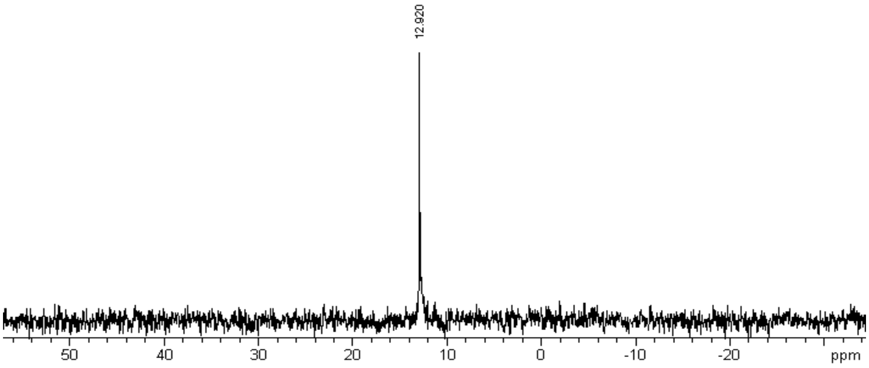
**Preparation of 4-methoxybenzoylmethylenetri-*p*-tolylphosphorane mercury iodide (D):** A soluion of (0.226 g, 0.5 mmol) of the ylide in methanol was added to a solution of (0.227 g, 0.5 mmol) of mercury(II) bromide in methanol (10 mL) and the mixture was stirred for 12 h. On concentration the solvent by removing in vacuum, a pale yellow precipitate was obtained. The products were washed with benzen and dried *in vacuo*. Yield (81 %) (m.p. = 191-193°C). IR (KBr, $cm^{-1}$) $\nu_{max}$: 1620 ν(C = O), 803 ν($P^+$-$C^-$). $^1H$ NMR (DMSO-$d_6$): 2.50 (s, 9H, $CH_3$), 3.941 (s, 3H, $OCH_3$) 5.254 (d, 1H, *J* = 6.988, CH), 7.125-8.164 (m, 16H, Ph)ppm. $^{31}P$ NMR (DMSO-$d_6$): 22.2023 (s) ppm. $^{13}C$ NMR (DMSO-$d_6$): 55.877 (s, $OCH_3$), 115.99 (d, *J* = 91.80, P(*p*-tolyl)$_3$(i)), 130.49 (d, *J* = 13.29, P(*p*-tolyl)$_3$(m)), 131.585 (s, P(*p*-tolyl)$_3$(p)), 133.38 (d, *J* = 11.69, P(*p*-tolyl)$_3$(o)), 164.381 (s, CO-Ph (i)), 190.26 (s, CO). Anal. (%) Calcd. $C_{30}H_{29}O_2PHgI_2$: C, 39.71. H, 3.91. Found: C, 38.06. H, 2.99.

## RESULTS AND DISCUSSION

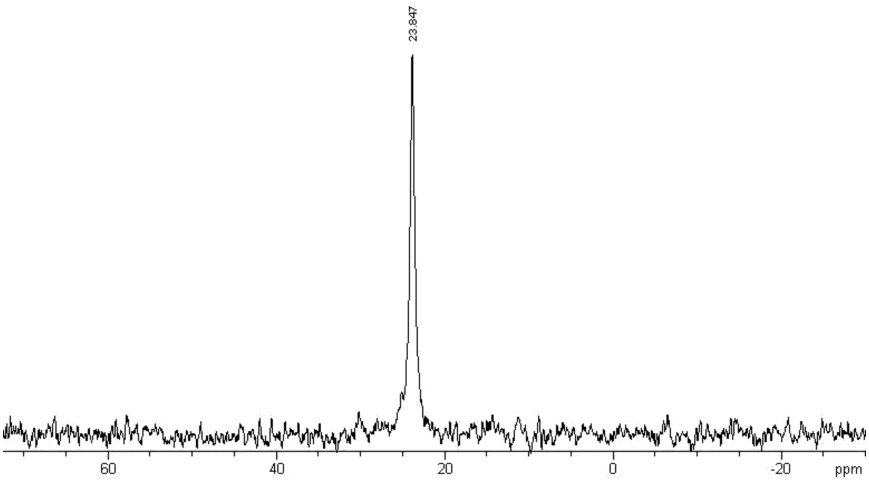
The ν(CO) which is sensitive to complexation occurs at 1527 cm$^{-1}$ in the parent ylide, as in the case of other resonance stabilized ylides[17]. Coordination of ylide through C-coordination causes an increase in ν(CO) while for O-coordination a lowering of ν(CO) is expected. IR absorption bands observed for three complexes at 1627, 1625 and 1620 cm$^{-1}$ indicate coordination of the ylide thorough carbon. The ν($P^+$-$C^-$) which is also suggest of the coordination occurs at 897 cm$^{-1}$ in $(CH_3C_6H_4)_3P^+$-$CH_2$ and at 884 cm$^{-1}$ in $(CH_3C_6H_4)_3PCHCOC_6H_4OCH_3$. These assignments were confirmed by comparing the IR spectra of the corresponding $^{13}C$ substituted ylides. In the present study, the ν($P^+$-$C^-$) values for all three complexes were shifted to lower frequencies and observed at 806, 805 and 803 cm$^{-1}$ for B, C and D, respectively, suggesting some removal of electron density in the P-C bond.

The $^1H$ NMR data of the mercury ylide complexes along with those of the parent ylide are available. The signals due to methine protons, when recorded in $CDCl_3$ was either broad or unobserved probably due to very low solubility of all the complexes in $CDCl_3$. Similar behaviour was observed earlier in the case of ylide complexes of platinum(II) chloride[18]. However, a sharp doublet for the above proton was obtained in DMSO-$d_6$ for each of three complexes in the same region. This indicates that the complexes do not react with DMSO-$d_6$. The expected downfield shifts of $^{31}P$ and $^1H$ signals for PCH group upon complexation were observed in their corresponding spectra (Fig. 1).

The appearance of single signal for PCH group in each of only $^{31}P$ and $^1H$ NMR spectra indicate the presence of only one molecule for all the three complexes, as expected for C-coordination. It must be noted that O-coordination of the ylide generally leads to the formation of *cis* and *trans*



(a)



(b)

Fig. 1. $^{31}$P NMR spectra of (**a**): MBPTY, (**b**): complex (**B**)

isomers giving rise to two different signals in $^{31}$P and $^{1}$H NMR[19]. The $^{13}$C NMR data of the title ylide and the complexes (Fig. 2a and b) are listed with possible assignments. The $^{13}$C NMR shifts of CO group in the complexes are around 190 ppm, lower than 188.2 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of carbon of the CO group in these complexes.

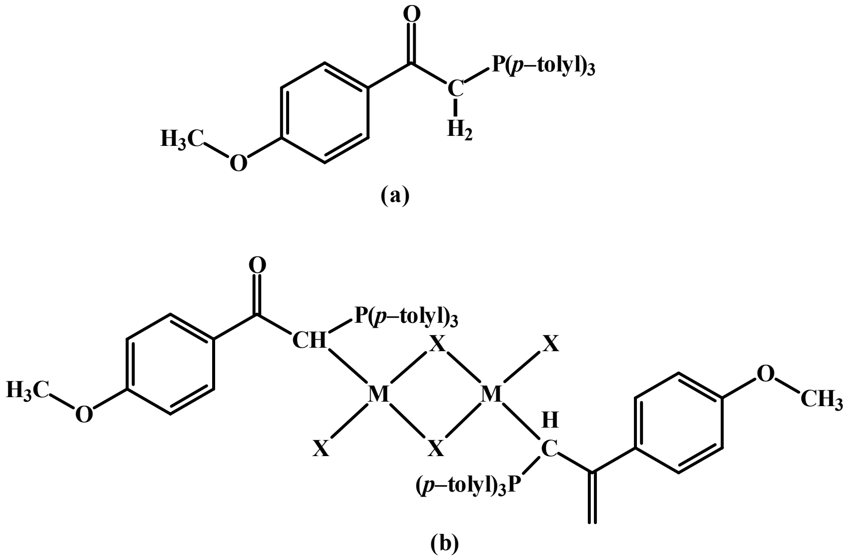


Fig. 2. Suggested structure for (a) ylide (b) mercury halide complexes

## Conclusion

Phosphorus ylides are known to demonstrate rich coordination chemistry. One of the significant aspects of present work has been to ascertion the preferred coordination modes of MBPTY to the mercury(II) metal. Due to the resonance delocalization of the ylide electron density (**Scheme-I**) it is viable for it to coordinate *via* the carbanion (B) or the carbonyl oxygen atom ($A_1$ or $A_2$). Comparing the data collected for the complexes, shifted to higher frequencies in ν(CO) or upfield shift of methine group or phosphorus, to the parent ylide, demonstrate C-coordination had occurred.

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