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Synthesis and Spectral Studies of Mercury(II) Complexes of 4-Bromobenzoylmethylenetriphenylphosphorane

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The new α-phosphorus ylide of (4-bromobenzoylmethylenetriphenylphosphorane) (BBPPY) (**1**) is prepared by the reaction of 2,4'-bromoacetophenone with triphenyl phosphine in chloroform as solvent. The mercury(II) complexes of the type (BBPPY· $HgCl_2$) (**2**), (BBPPY·$HgBr_2$) (**3**), (BBPPY·HgI_2) (**4**) and (BBPPY·$Hg(NO_3)_2$ (**5**) are prepared by the reaction of BBPPY with mercury(II) halides and nitrate in moderate to good yields.

Key Words: Triphenylphosphine, Mercury(II), Ylide.

INTRODUCTION

Phosphorus ylides are important reagents in organic chemistry, especially in the synthesis of naturally occurring products with biological and pharmacological activities[1]. The coordination chemistry of the phosphoranes of the type, R_3P^+-C^-H_2 is well known[2-5]. Resonance stabilized ylides, particularly the keto ylides are also successfully used as ligands in organometallic and coordination chemistry owing to their accessibility and stability towards air and moisture[6,7]. Although many bonding modes are possible for the keto ylides[8], the coordination through carbon is more predominant and observed with Pd(II) and Pt(II)[9-11]. The reaction of benzoyl-methylenetriphenylphosphorane (BPPY) ylide with mercury chloride has already been reported along with analytical and IR data of the product. The product was formulated by Nesmeyanow *et al.*[12] to be a mercurated phosphonium salt $[(C_6H_5)_3PCHCOC_6H_5HgCl]Cl$. Weleski *et al.*[13] proposed a symmetrical chloro-bridged dimeric structure for the analogous complex formed by the reaction of $CH_3COCHP(C_6H_5)_3$ and mercury(II) chloride to account for its molecular weight data and negligible electrical conductivity in nitrobenzene solution. We are currently interested in synthesis and reactivity of metal derivatives of such ylide as α-keto-stabilized ylide of $Ph_3PCHCOC_6H_4Br$ and its related mercury halide complexes. In this work, we have reported complexes obtained from the reaction of the newly prepared α-carbonyl stabilized ylide of *i.e.*, 4-bromobenzoylmethylenetriphenylphosphorane (BBPPY) with HgX_2 (X = Cl, Br, I and NO_3^-). All of the products were characterized by IR, ^1H, ^{13}C and ^{31}P NMR spectroscopic methods and microanalysis.

EXPERIMENTAL

Methanol was distilled over magnesium powder and diethyl ether (Et_2O) over CaH_2 just before use. All other solvents were reagent grade and used without further purifications. ^1H, ^{31}P and ^{13}C NMR spectra were obtained using a FT 90 MHz instrument at regional sophisticated instrumentation at Bu-Ali-Sina University, faculty of science. Solid state IR spectra in the region 4000-200 cm^{-1} using KBr pellets were obtained on a FT-IR Perkin Elmer spectrophotometer. Elemental analysis was carried out at Tarbiate Modarres University in Tehran.

Synthesis of ($Ph_3PCHCOC_6H_4Br$) (1): 2,4-Bromophenyl acetophenone (0.278 g, 1 mmol) was dissolved in 20 mL of chloroform, then a solution of triphenylphosphine (0.262 g, 1 mmol) in the same solvent (5 mL) was added to the above solution drop wise and the pale yellow solution was stirred for 4 h. The solution was concentrated under reduced pressure to 10 mL and diethyl ether (20 mL) was added. The white formed solid was filtered off, washed with petroleum benzene (2 × 10 mL) and dried under reduced pressure. In order to get final product, whole of the crude solid 0.388 g yield (72 %), was transferred to 5 % NaOH and stirred at 40ºC for about 24 h, the pale yellow precipitate of 4-bromobenzoylmethylenetriphenylphosphorane was obtained. The product was washed several times with distilled water and air dried.

Synthesis of $Ph_3PCHCOC_6H_4Br{\cdot}HgCl_2$ complex (2): A solution of (0.18 g, 0.5 mmol) of $HgCl_2$ in methanol (15 mL) was added to solution of (0.229 g, 0.5 mmol) of the 4-bromobenzoylmethylenetriphenylphosphorane in dry methanol (15 mL) and stirred for 12 h. The white product formed by slow evaporation of the solvent. The product washed several times with dry diethyl ether and dried in vacuum. Following the same procedure, mercury(II) bromo, iodo and nitrato compounds **3**, **4** and **5** of this series are prepared. Their characterization data are listed in Table-1.

RESULTS AND DISCUSSION

The ν(CO) which is sensitive to complexation occurs at 1578 cm^{-1} in the parent ylide, as in the case of other resonance stabilized ylides[14]. Coordination of ylide through carbon cause an increase in ν(CO) while for O-coordination a lowering of ν(CO) is expected (Table-2). The infrared spectra of complexes in the solid state show ν(CO) in the region of 1657-1619 cm^{-1}, at higher wave numbers with respect to the free ylide (BBPPY, ν(CO) 1578 cm^{-1}). The ($P^+–C^–$) which is also diagnostic for the coordination occurs at 882 cm^{-1} in $Ph_3PCHCOC_6H_4Br$. These assignments confirmed by comparing the IR spectra of the corresponding ^{13}C substituted ylides[10]. In the present study, the ν($P^+–C^–$) values for all four complexes were shifted to lower frequencies and observed at 823, 818, 796 and 829 cm^{-1} for **2, 3, 4** and **5,** respectively, suggesting some removal of electron density in the P–C bond.

TABLE-1
CHARACTERIZATION DATA OF YLIDE AND ITS Hg(II) COMPLEXES

Compd. (m.p.) (ºC)	Yield (%)	m.f. (m.w.)	Found (Calcd.) %		
			C	H	N
BBPPY (194)	95	$C_{29}H_{20}OPBr$ (459.32)	68.94 (67.98)	4.38 (4.38)	–
BBPPY·$HgCl_2$ (201)	85	$C_{29}H_{20}OPBrHgCl_2$ (730.72)	37.07 (38.09)	2.22 (2.45)	–
BBPPY·$HgBr_2$ (217)	83	$C_{29}H_{20}OPBrHgBr_2$ (819.61)	42.87 (42.76)	2.61 (2.75)	–
BBPPY·HgI_2 (195)	86	$C_{29}H_{20}OPBrHgI_2$ (913.71)	35.99 (34.17)	2.07 (2.20)	–
BBPPY·$Hg(NO_3)_2$ (188)	91	$C_{29}H_{20}OPBrHgN_2O_6$ (730.72)	42.07 (39.83)	2.48 (2.57)	3.80 (3.57)

TABLE-2
ν(CO) OF SELECTED PHOSPHORANES AND THEIR METAL COMPLEXES

Compound	ν(CO) cm^{-1}	Ref.
$Ph_3PCHCON(CH_3)_2$	1530	14
APPY	1530	15
BPPY	1525	16
BBPPY	1578	This work
C-Coordination		
BBPPY·$HgCl_2$	1638	This work
BBPPY·$HgBr_2$	1638	This work
BBPPY·HgI_2	1619	This work
BBPPY·$Hg(NO_3)_2$	1657	This work
BPPY·$HgCl_2$	1635	17
$Au[CH(PPh_3)CON(CH_3)_2]$	1605	14
O-Coordination		
$[(Sn(CH_3)_3\cdot BPPY]Cl$	1480	7
$[(SnPh_3)\cdot BPPY]Cl$	1470	7
$[Pd\{C_6F_5)(PPh_3\}_2(APPY)]ClO_4$	1513	9

Ph = C_6H_5·APPY = Acetylmethylenetriphenylphosphorane.
BPPY = Benzoylmethylenetriphenylphosphorane.

^{1}H and ^{31}P NMR data of the mercury(II) ylide complexes along with those of the parent ylide are listed in the Table-3. Signals due to methane protons, when recorded in $CDCl_3$ was either broad or unobserved probably due to very low solubility of all the complexes in $CDCl_3$. However, a sharp doublet for the above proton was obtained in DMSO-d_6 for each of the four complexes in the same region. This indicates that the copmplexes do not react with DMSO-d_6. The expected downfield shifts of ^{31}P and ^{1}H signals for PCH group upon complexation were observed in their corresponding spectra. The appearance of single signals for PCH group in each of ^{31}P and ^{1}H NMR indicates the presence of only one molecule for all of the four complexes, as expected for C-coordination[16]. It must be observed that O-coordination of the ylide generally leads to the formation of *cis* and *trans* isomers giving rise to two different signals in ^{31}P and ^{1}H NMR.

TABLE-3
^{1}H AND ^{31}P NMR DATA OF BBPPY AND ITS Hg(II) COMPLEXES

Compound	δ(CH)	^{2}J(pH)	$\delta(PPh_3)$	$\delta(^{31}P)$
BBPPY	4.39(d)	23.74	7.25-8.0 (m)	14.16 (s)
BBPPY·$HgCl_2$	5.36(d)	8.06	7.66-8.2 (m)	24.23 (s)
BBPPY·$HgBr_2$	5.35(d)	8.96	7.65-8.1 (m)	24.24 (s)
BBPPY·HgI_2	5.14(d)	11.73	7.64-7.9 (m)	22.80 (s)
BBPPY·$Hg(NO_3)_2$	6.47(d)	9.22	7.74-8.2 (m)	30.12 (s)

In $CDCl_3$, 90 MHz, values (ppm) relative to internal TMS and external 85 % phosphoric acid, s = singlet, d = doublet, m = multiplet.

The resonances of ^{31}P NMR complexes **2**, **3**, **4** and **5** were observed to occur at a lower field with respect to the free ylide (Table-3), thus suggesting a direct binds of methane carbon with mercury (Fig. 1)[17].

The ^{13}C NMR data of the complexes and the title ylide are listed in (Table-4) along with possible assignments. The most interesting aspect of the ^{13}C spectra of the complexes is the upfield shift of the signals due ylidic carbon. Such upfield shift observed in PdCl (η^3-2-XC_3H_4) $(C_6H_5)_3PCHCOR$ (X = H, CH_3; R = CH_3, C_6H_5) and was attributed to change in hybridization of the ylidic carbon[14]. Similar upfield shifts of 2-2.5 ppm with reference to the parent ylide were also observed[15] in the case of these mercury(II) halide and nitate complexes. The ^{13}C shifts of CO group in the complexes are around 189 ppm higher than 183.51 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of the carbon of the CO group in the complexes. No coupling to mercury was observed at room temperature in ^{1}H, ^{13}C and ^{31}P NMR spectra of all these complexes.

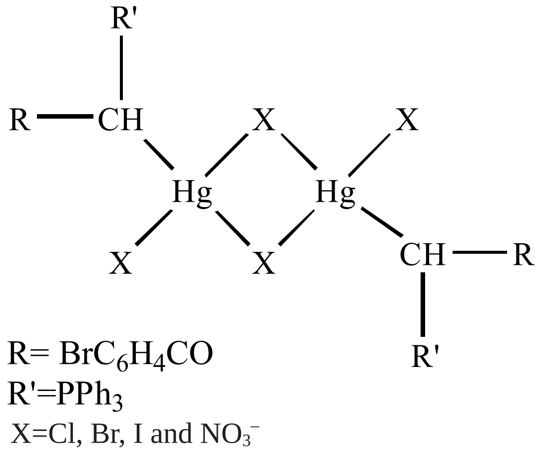

Fig. 1. Suggested structure of complexes

TABLE-4

^{13}C NMR DATA OF BBPPY AND ITS Hg(II) COMPLEXES

Compound	CH	Ar	C=O
BBPPY	50.79 (d)	123.65–133.30 (m)	183.51 (s)
BBPPY·$HgCl_2$	47.25 (d)	122.13–133.71 (m)	189.15 (s)
BBPPY·$HgBr_2$	48.13 (d)	125.44–136.46 (m)	187.44 (s)
BBPPY·HgI_2	48.35 (d)	129.01–133.36 (m)	187.04 (s)
BBPPY·$Hg(NO_3)_2$	br	125.44–134.20 (m)	192.53 (s)

BBPPY, Recorted in $CDCl_3$ and complexes in DMSO-d_6. s, singlet; d, doublet; m, multipilate, br, broad.

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