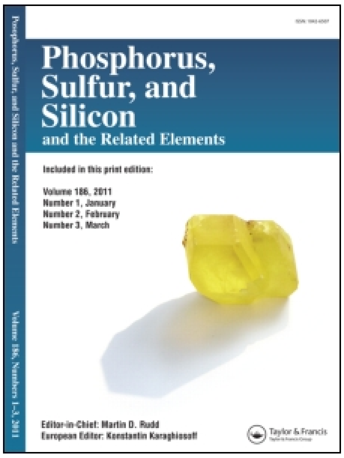

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Synthesis and Multinuclear NMR Study of a New Benzoyl Methylene Triparatolylphosphorine Ylide and its Reactions with Mercury (II) Halides

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The reaction of bromoacetophenone with triparatolylphosphine in chloroform solution gives {Hooch (p-tolyl)$_3$}(I); then reaction of this new ylide with mercury (II) halides ($HgCl_2$, $HgBr_2$, Hgl_2) in equimolar ratio leads to pure compounds of [{(p-tolyl)$_3$PCHCOC$_6$H$_5$}HgCl$_2$]$_2$ (II). [{(p-tolyl)$_3$PCHCOC$_6$H$_5$}. HgBr$_2$]$_2$ (III), and [{(p-tolyl)$_3$PCHCOC$_6$H$_5$}Hgl$_2$]$_2$ (IV) complexes. The IR $^1H^{13}C$, and ^{31}P NMR together, with microanalysis data of the products, were obtained.

Keywords Mercury (II) halides; phosphorus ylide; triparatolylphosphine

INTRODUCTION

Among the phosphorus ylides of general stoichiometry R_3PCR'(R, R$' =$ alkyl, alkoxy, etc.) the α-keto-stabilized ylides $Ph_3PCHCOR$ have shown useful application in organometallic chemistry (due to their ambidentate character as ligands[1]) and as reactants or valuable key intermediates in metal-mediated organic synthesis.[1,2] This ambidentate character facilitates the preparation of stable metal complexes in which the ylide could be O-(A_1, A_2, Scheme 1)[3–7] or C-coordinated (B).[8–10] 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:[3–7]

The phosphorus ylide complexes have been well investigated. They are versatile ligands for catalysts in a very small number of catalytic

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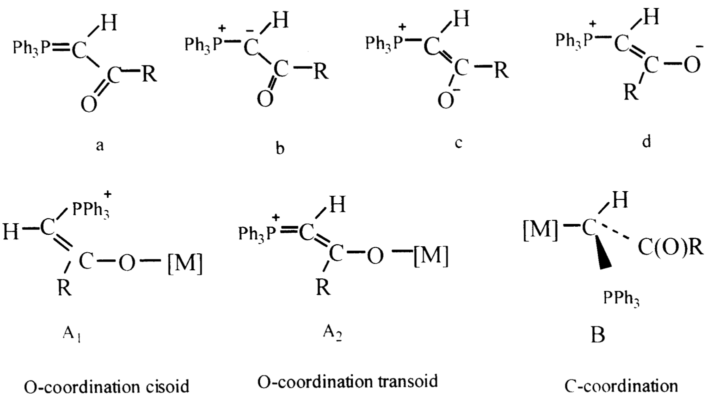

SCHEME 1

reactions, such as, for example, the hydrogenation of olefins and the cyclotrimerization and polymerization of acetylenes, but the most important application is in the industrially used SHOP process.[11] Thus complexes (I), (II), and (III) obtained from the reaction of the new α-carbonyl-stablized ylide (I) with HgX_2 (X = Cl, Br and I).

EXPERIMENTAL

Methanol (MeOH) and diethyl ether (Et_2O) were distilled over Mg or Na and CH_2Cl_2 over CaH_2 just before use. All other solvents were reagent grade and used without further purifications. Melting points were measured with a SMPI apparatus. Solid-state FT-IR spectra in the region of 400–4000 cm^{-1} using KBr pellets were obtained on a (Perkin Elmer) spectrophotometer. ^{1}H and ^{31}P spectra were obtained using a 90 MHz instrument at regional sophisticated instrumentation at Bu-Ali Sina University, and ^{13}C NMR spectra were measured with a BRUKER DRX-500 spectrometer. Elemental analyses were carried out at the Research Institute of Petroleum Industry.

Synthesis

Synthsise of {(p-tolyl)$_3$PCHCOC$_6$H$_5$}

Tri-p-tolylphosphen 0.152 gr(0.5 mmol) was added in a chloroform (25 mL) to a solution of bromoacetophenpon 0.099 gr (0.5 mmol) in chloroform (20 mL) and the mixture was stirred for 4 h. The solution was filtered off and the precipitate was washed with diethylether and collected and dried. Then the reaction mixture was made basic by using NaOH (5%), and a white-yellow precipitate was obtained. Yield: 0.152 gr

(70%). m.p. 188–190°C. Anal. found: C, 77.6; H, 6.1%; $C_{29}H_{27}OP.1.5\,H_2O$ (MW = 449.5 gr). Calc.: C, 77.5; H, 6.68%.

Synthsise of $[\{(p\text{-tolyl})_3PCHCOC_6H_5\}.HgCl_2]_2$

A solution of 0.14 gr (0.5 mmol) of mercury (II) chloride in dry methanol (10 mL) was added to a methanolic solution of 0.211 gr (0.5 mmol) of ylide in dry methanol (10 mL). The white product formed by the slow evaporation of the solvent and dried in vacuum. Yield 0.347 gr (80.11%). m.p. 200–201°C. Anal. fund: C, 48.3; H. 4.1%; $C_{29}H_{27}OPHgCl_2H_2O$ (MW = 711.59). Calc.: C, 48.91; H, 4.07%.

Synthsise of $[\{(p\text{-tolyl})_3PCHCOC_6H_5\}.HgBr_2]_2$

A solution of 0.211 gr(0.5 mmol) of the ylide in dry methanol (10 mL) was added to 0.18 gr of mercury (II) bromide in dry methanol (10 mL) and the mixture was stirred for 4 h. The solvent was then removed in vacuo. The white product obtained was washed with ice-cold methanol and dried in vacuum. Yield 0.294 gr (75.15%). m.p. 193–195°C. Anal. found: C, 43.5; H, 3.7%; $C_{29}H_{27}OPHgBr_2.H_2O$ (MW = 800.39). Calc.: C, 43.48 H, 3.62%.

Synthsise of $[\{(p\text{-tolyl})_3PCHCOC_6H_5\}.HgI_2]_2$

A solution of 0.211 gr (0.5 mmol) of the ylide in methanol (10 mL) was added to a solution of 0.227 gr (0.5 mmol) of mercury (II) iodide in methanol (10 mL). On concentration by removing the solvent in vacuum, a pale yellow, light-sensitive crystalline solid was obtained. The crystals were washed with benzene and dried in vacuo. Yield 0.307 gr (70.2%). m.p. 200–202°C. Anal. found: C, 37.3; H, 3.4%; $C_{29}H_{27}OPHgI_2.2H_2O$ (MW = 912.39). Calc.: C, 38.14; H, 3.39%.

TABLE I υ **(CO) of Selected Compound (I) and Their Complexes With Mercury (II) Halides**

Compound	υ (CO)cm^{-1}	Ref.
$Ph_3PCHCOCH_3$ (APPY)	1530	12
$Ph_3PCHCOPh$ (BPPY)	1525	12
$Ph_3PCHCO\ (p\text{-tolyl})_3$	1528	This article
C-coordination		
$BPPY.HgCl_2$	1635	12
$BPPY.HgBr_2$	1630	12
$[Ph_3PCHCO(p\text{-tolyl})_3HgCl_2]_2$	1597	This article
$[Ph_3PCHCO(p\text{-tolyl})_3HgBr_2]_2$	1633	This article
$[Ph_3PCHCO(p\text{-tolyl})_3HgI_2]_2$	1597	This article

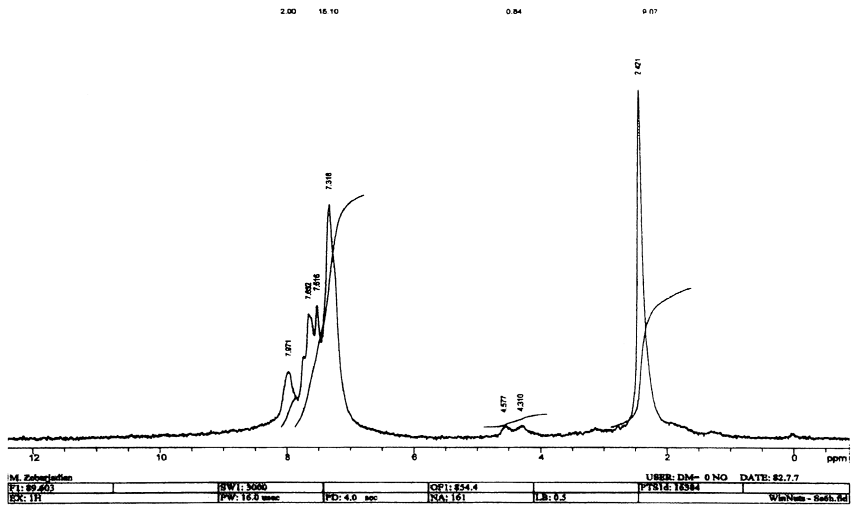

FIGURE 1 ^{1}H NMR $\{(p\text{-tolyl})_3PCHCOC_6H_5\}$ in $CDCl_3$ at 25°C.

RESULTS AND DISCUSSION

The υ (CO), which is sensitive to complexation, occurs at 1528 cm^{-1} in the parent ylide, as in the case of other resonance stabilized ylides. Coordination of the ylide through carbon causes an increase in υ (CO) while for O-coordination a lowering of υ (CO) is expected. The IR absorption

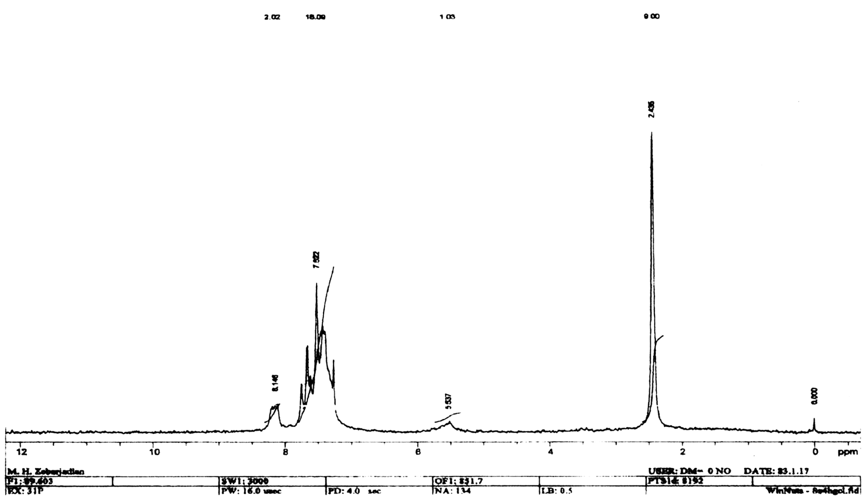

FIGURE 2 ^{1}H NMR $\{(p\text{-tolyl})_3\ PCHCOC_6H_5.HgCl_2\}_2$ in $CDCl_3$ at 25°C.

TABLE II ^{1}H and ^{31}PNMR Data of (I) and Its Complexes With Mercury(II) Halides. s-singlet; d-doublet; m-multiplet; br-broad

Compound	^{1}HNMR			^{31}PNMR
	δ(CH)	$^2J_{(P-H)}$	δPh	
$Ph_3PCHCO(p\text{-}tolyl)_3$	4.4(d)	24.39	7.3–7.95(m)	12.98(s)
$[Ph_3PCHCO(p\text{-}tolyl)_3.HgCl_2]_2$	5.54(br)	—	7.26–8.13(m)	24.4(s)
$[Ph_3PCHCO(p\text{-}tolyl)_3.HgBr_2]_2$	5.2(br)	—	7.25–8.01(m)	22.22(s)
$[Ph_3PCHCO(p\text{-}tolyl)_3.HgI_2]_2$	5.29(br)	—	7.52–8.06(m)	18.5(s)

In $CDCl_3$. 90 MHz. values (ppm) are relative to internal TMS and external 85% phosphoric acid.

bands observed for the three complexes at 1597, 1633, and 1597 cm^{-1} indicate coordination of the ylide through carbon. The υ (P^+—C^-), which is also diagnostic of the coordination, occurs at 879 cm^{-1} in $(p\text{-}tolyl)_3P^+$ —CH (Table I). These assignments were confirmed by comparing the IR spectra of the corresponding ^{13}C substituted ylides.[12] In the present study, the υ(P^+—C^-) values for all three complexes were shifted to lower frequencies and observed at 805 cm^{-1} for three complexes, suggesting some removal of electron density in the P—C bond.

In the ^{1}H NMR spectra for three complexes, the CH ylide proton shifted downfield compared to that of the free ylide (Figures 1 and 2) as a consequence of the inductive effect of the metal center. The expected

TABLE III ^{13}CNMR Data of Benzoylmethelenparatolylephosphoran and Corresponding Complexes With Mercury(II) Halides. s-singlet; d-double; o-ortho; m-meta; p-para; i-ipso carbon. Recorded in $CDCl_3$

Compound	$Ph_3PCHCO(p\text{-}tolyl)_3$	Complex (I)	Complex (II)	Complex (III)
$3CH_3$	22.2(s)	22.2(s)	22.18(s)	22.22(s)
CH	51.8(d)	—	—	44.15(s)
$^2J_{(p-c)}$	113			
CO—Ph(o)	127.38(s)	119.3(s)	119.89(s)	117.87(s)
CO—Ph(m)	128.13(s)	119.87(s)	120.62(s)	118.6(s)
CO—Ph(p)	133.63(s)	133.91(s)	132.53(s)	134.88(s)
CO—Ph(i)	142.58(s)	145.48(s)	145.13(s)	146.34(s)
$P\text{-}(p\text{-}tolyl)_3$(o)	132.5(d)	133.99(d)	134.02(d)	133.83(d)
$^2J_{(p-c)}$	10.6	10.5	10.5	10.6
$P\text{-}(p\text{-}tolyl)_3$(m)	129.57(d)	131.1(d)	130.95(d)	131.38(d)
$^3J_{(p-c)}$	12.25	13	13	13
$P\text{-}(p\text{-}tolyl)_3$(p)	130.67(s)	129.48(s)	133.18(s)	129.56(s)
$P\text{-}(p\text{-}tolyl)_3$(i)	124.49(d)	129.21(s)	128.95(s)	128.92(s)
$^1J_{(p-c)}$	95.6			
CO	184.93(s)	193.93(s)	192.41(s)	192.89

downfield shifts of the ^{31}P and ^{1}H singles for the PCH group upon complexation were observed in their corresponding spectra (Figures 1 and 2, Table II). The appearance of single signals for the PCH group in the ^{31}P and ^{1}HNMR spectra indicates the presence of only one molecule for all three complexes, as expected for C-coordination.

The ^{13}CNMR data of the complexes and the title ylide are listed in Table III along with possible assignments. The ^{13}CNMR shifts of the CO group in the complexes are around 190 ppm, lower than 184 ppm noted for the same carbon in the parent ylide, indicating a much lower shielding of carbon of the CO group in the complexes.

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