

## Synthesis and Multinuclear NMR Study of 4-Methylbenzoylmethylene-tri-*p*-tolylphosphorane Ylide and its Related Complexes with Mercury(II) Halides

S.J. SABOUNCHEI\*, A.R. DADRASS and H. NEMATTALAB  
Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran  
Fax: (98)(811)8257407; E-mail: jsabounchei@yahoo.co.uk

The novel  $\alpha$ -phosphorus ylide of (4-methylbenzoylmethylene-tri-*p*-tolylphosphorane) (MBTPPY) (1) is prepared by the reaction of 4-methylacetophenone with tri-*p*-tolylphosphine in chloroform as solvent. The complexes of the type (MBTPPY·HgCl<sub>2</sub>) (2), (MBTPPY·HgBr<sub>2</sub>) (3) and (MBTPPY·HgI<sub>2</sub>) (4) are prepared by the reaction of MBTPPY with mercury(II) halides in moderate to good yields.

**Key Words:** Carbonyl stabilized phosphorus ylide, Mercury(II) halide complexes, Triparatolylphosphine.

### INTRODUCTION

Phosphorus ylides are important reagents in organic chemistry, especially in the synthesis of naturally occurring products with biological and pharmacological activities<sup>1</sup>. The coordination chemistry of the phosphoranes of the type, R<sub>3</sub>P<sup>+</sup>-C<sup>-</sup>H<sub>2</sub> is well known<sup>2-5</sup>. 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<sup>6,7</sup>. Although many bonding modes are possible for the *keto* ylides<sup>8</sup>, the coordination through carbon is more predominant and observed with Pd(II) and Pt(II)<sup>9-11</sup>. The reaction of 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.*<sup>12</sup> to be a mercurated phosphonium salt [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PCHCOC<sub>6</sub>H<sub>5</sub>HgCl]Cl. Weleski *et al.*<sup>13</sup> proposed a symmetrical chloro-bridged dimeric structure for the analogous complex formed by the reaction of CH<sub>3</sub>COCHP(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> 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  $\alpha$ -*keto*-stabilized ylide of (*p*-tolyl)<sub>3</sub>PCHCOC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> and its related mercury(II) halide complexes. In this work, the complexes obtained from the reaction of the new prepared  $\alpha$ -carbonyl-stabilized ylide of (MBTPPY) with HgX<sub>2</sub> (X = Cl, Br and I)

have been reported. All of the products were characterized by IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopic methods and microanalysis.

### EXPERIMENTAL

Methanol was distilled over magnesium powder and diethyl ether over  $\text{CaH}_2$  just before use. All other solvents were reagent grade and used without further purifications.  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  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  $\text{cm}^{-1}$  using KBr pellets were obtained on a FT-IR Perkin Elmer spectrophotometer. Elemental analyses were carried out at Tarbiate Modarres University, Tehran.

**Synthesis of [(*p*-tolyl) $_3\text{PCHCO}_6\text{H}_4\text{CH}_3$ ] (1):** 2-Bromo-4-methylphenylacetophenone (0.213 g, 1 mmol) was dissolved in 20 mL of chloroform, then a solution of tri-*p*-tolylphosphine (0.304 g, 1 mmol) in the same solvent (5 mL) was added to the above solution drop wise and 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 solid formed was filtered off, washed with petroleum benzene ( $2 \times 10$  mL), and dried under reduced pressure. In order to get final product, whole of the crude solid, 0.501 g, (97 %), was transferred to alkaline solution 5 % NaOH and stirred at 40 °C for about 24 h, the pale yellow precipitate of 4-methylbenzoylmethylene-tri-*p*-tolylphosphorane was obtained. The product was washed several times with distilled water and air dried. Yield (95.80 %), (m.p. 192-194 °C). Anal (%) Calcd.  $\text{C}_{30}\text{H}_{29}\text{OP}$ : C, 67.35, H, 5.83. Found: C, 67.00, H, 5.9.

**Synthesis of [(*p*-tolyl) $_3\text{PCHCO}_6\text{H}_4\text{CH}_3$ ] $\cdot\text{HgCl}_2$  complex (2):** A solution of  $\text{HgCl}_2$  (0.135 g, 0.5 mmol) in methanol (15 mL) was added to solution of 4-methylbenzoylmethylenetri-*p*-tolyl-phosphorane (0.218 g, 0.5 mmol) in methanol and stirred for 12 h. The white product formed by slow evaporation of the solvent. The product washed several times with dry diethylether and dried in vacuum. Yield (82.70 %), (m.p. 197-199 °C). Anal. (%) Calcd.  $\text{C}_{30}\text{H}_{29}\text{Cl}_2\text{HgOP}\cdot 2\text{H}_2\text{O}$ : C, 48.14, H, 4.40. Found: C, 47.23, H, 4.09.

**Synthesis of [(*p*-tolyl) $_3\text{PCHCO}_6\text{H}_4\text{CH}_3$ ] $\cdot\text{HgBr}_2$  complex (3):** A solution of  $\text{HgBr}_2$  (0.18 g, 0.5 mmol) in methanol (15 mL) was added to solution of 4-methylbenzoylmethylenetri-*p*-tolylphosphorane (0.218 g, 0.5 mmol) in methanol and stirred for 12 h. The white product formed by slow evaporation of the solvent. The product washed several times with dry diethylether and dried in vacuum. Yield (85 %), (m.p. 203-205 °C). Anal. (%) Calcd.  $\text{C}_{30}\text{H}_{29}\text{Br}_2\text{HgOP}$ : C, 45.21, H, 3.63. Found: C, 45.31, H, 3.80.

**Synthesis of [(*p*-tolyl)<sub>3</sub>PCHCOC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>]<sub>2</sub>HgI<sub>2</sub> complex (4):** A solution of HgI<sub>2</sub> (0.229 g, 0.5 mmol) in methanol (15 mL) was added to solution of 4-methylbenzoylmethylenetri-*p*-tolylphosphorane (0.218 g, 0.5 mmol) in methanol and stirred for 12 h. The white product formed by slow evaporation of the solvent. The product washed several times with dry diethylether and dried in vacuum. Yield (81.87 %), (m.p. 200-202 °C). Anal. (%) Calcd. C<sub>30</sub>H<sub>29</sub>I<sub>2</sub>HgOP: C, 36.85, H, 2.92. Found: C, 35.70, H, 3.02.

## RESULTS AND DISCUSSION

The  $\nu(\text{CO})$  which is sensitive to complexation occurs at 1599 cm<sup>-1</sup> in the parent ylide, as in the case of other resonance stabilized ylides<sup>14</sup>. Coordination of ylide through carbon causes an increase in  $\nu(\text{CO})$  while for O-coordination a lowering of  $\nu(\text{CO})$  is expected (Table-1). Infrared spectra of complexes in the solid state show  $\nu(\text{CO})$  in the range of 1638, 1626 and 1621 cm<sup>-1</sup> indicate coordination of the ylide through carbon at higher wave numbers with the respect to the free ylide (MTBBPY,  $\nu(\text{CO})$  1599 cm<sup>-1</sup> (Table-1). The  $\nu(\text{P}^+-\text{C}^-)$  which is also diagnostic for the coordination, occurs at 881 cm<sup>-1</sup> in (*p*-tolyl)<sub>3</sub>PCHCOC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>. These assignments confirmed by comparing the IR spectra of the corresponding <sup>13</sup>C substituted ylides<sup>10</sup>. In the present study, the  $\nu(\text{P}^+-\text{C}^-)$  values for all three complexes were shifted to lower frequencies and observed at 852, 848 and 837 cm<sup>-1</sup> for **2**, **3** and **4**, respectively, suggesting some removal of electron density in the P-C bond.

TABLE-1  
 $\nu(\text{CO})$  OF SELECTED PHOSPHORANES AND  
 THEIR METAL COMPLEXES

Compound	$\nu(\text{CO})$ cm <sup>-1</sup>	Ref.
Ph <sub>3</sub> PCHCON(CH <sub>3</sub> ) <sub>2</sub>	1530	14
APPY	1530	15
BPPY	1525	16
MBTPPY	1599	Present method
<b>C-Coordination</b>		
MBTPPY·HgCl <sub>2</sub>	1638	Present method
MBTPPY·HgBr <sub>2</sub>	1626	Present method
MBTPPY·HgI <sub>2</sub>	1621	Present method
BPPY·HgCl <sub>2</sub>	1635	17
Au[CH(PPh <sub>3</sub> )CON(CH <sub>3</sub> ) <sub>2</sub> ]	1605	14
<b>O-Coordination</b>		
[(Sn(CH <sub>3</sub> ) <sub>3</sub> ·BPPY)Cl]	1480	7
[(SnPh <sub>3</sub> )·BPPY]Cl	1470	7
[Pd(C <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (APPY)]ClO <sub>4</sub>	1513	9

Ph = C<sub>6</sub>H<sub>5</sub>; APPY = acetylmethylenetriphenylphosphorane;  
 BPPY = benzoylmethylenetriphenylphosphorane.

The  $^1\text{H}$  NMR data of the mercury(II) ylide complexes along with those of the parent ylide are listed in (Table-2). The CH signals of the three complexes are shifted down field compared to that of the free ylide, as a consequence of C-coordination character of the ylide. The expected down field shifts of  $^{31}\text{P}$  signals for the PCH group upon complexation were observed in their corresponding spectra. The appearance of single signals for the PCH group in the  $^{31}\text{P}$  spectra indicates the presence of only one type of molecule for all three complexes.

TABLE-2  
 $^1\text{H}$  AND  $^{31}\text{P}$  NMR DATA OF MBTPPY AND ITS COMPLEXES WITH  
Hg(II) HALIDES (T = 298 K, J IN HZ, TMS  $\delta$  = 0.00 ppm)

Compounds	$\text{CH}_3$	$\delta(\text{CH})$	$^2J_{\text{pH}}$	$\delta(p\text{-tolyl})_3\text{P}$	$\delta(^{31}\text{P})$
MBTPPY	2.385	4.36(d)	23.29	7.25-7.87(m)	12.98(s)
MBTPPY·HgCl <sub>2</sub>	2.417	5.37	–	7.10-8.08(m)	23.65(s)
MBTPPY·HgBr <sub>2</sub>	2.414	5.23	–	7.18-8.01(m)	22.84(s)
MBTPPY·HgI <sub>2</sub>	2.426	5.04(d)	4.21	7.13-7.93(m)	20.41(s)

In CDCl<sub>3</sub>, 90 MHz, values (ppm) relative to internal TMS and external 85 % phosphoric acid s, singlet; d, doublet; m, multiplet.

The resonances of  $^{31}\text{P}$  NMR of complexes **2**, **3** and **4** were observed to occur at a lower field with respect to the free ylide (Table-2), thus suggesting a direct binds of methane carbon with mercury (Fig. 1)<sup>17</sup>. It must be noted that O-coordination of the ylide generally leads to the formation of *cis*- and *trans*-isomers giving rise to two different signals in  $^{31}\text{P}$  and  $^1\text{H}$  NMR<sup>9</sup>.

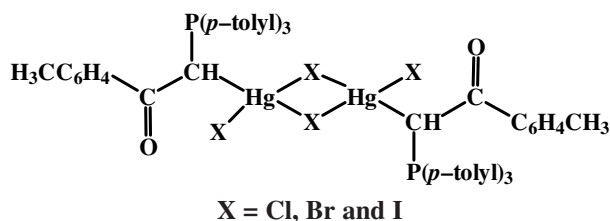


Fig. 1. Suggested structure of complexes

$^{13}\text{C}$  NMR data of the complexes and the title ylide are listed in (Table-3) along with possible assignments. The  $^{13}\text{C}$  NMR shifts of the CO group in the complexes **2** and **3** are higher than 191.34 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of carbon of the CO group in the complexes but this is not in agreement on complex **4** and the reason is not clear yet. Such upfield shift in complexes **2** and **3** also observed in  $[\text{PdCl}(\eta^3\text{-2-XC}_3\text{H}_4)(\text{C}_6\text{H}_5)_3\text{PCHCOR}]$  ( $\text{X} = \text{H, CH}_3$ ;  $\text{R} = \text{CH}_3$ ,

C<sub>6</sub>H<sub>5</sub>) and was attributed to change in hybridization of the ylidic carbon<sup>14</sup>. Similar upfield shifts of 1-2 ppm with reference to the parent ylide were also observed in the case of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PC<sub>5</sub>H<sub>4</sub>·HgI<sub>2</sub>]<sub>2</sub> and in our synthesized mercury complexes<sup>15</sup>. No coupling constant to mercury was observed at room temperature in <sup>1</sup>H and <sup>13</sup>C NMR spectra of complexes **2** and **3** this is due to the broad coupling of proton with mercury and phosphorus atoms (Fig. 1).

TABLE-3  
<sup>13</sup>C NMR DATA OF YLIDE MBTPPY AND ITS COMPLEXES  
WITH MERCURY(II) HALIDES

Possible assignments	MBTPPY	MBTPPY· HgCl <sub>2</sub>	MBTPPY· HgBr <sub>2</sub>	MBTPPY· HgI <sub>2</sub>
CH <sub>3</sub>	21.48(s)	21.79(s)	21.73(s)	20.86(s)
3CH <sub>3</sub>	21.31(s)	21.70(s)	21.67(s)	20.99(s)
CH	42.23(d)	br	br	br
<sup>2</sup> J <sub>PC</sub>	144.22			
CO-Ph(o)	142.31(s)	143.57(s)	143.60(s)	141.07(s)
CO-Ph(m)	145.50(s)	144.74(s)	144.77(s)	143.42(s)
CO-Ph(p)	117.54(s)	121.62(s)	121.51(s)	121.85(s)
CO-Ph(i)	113.48(s)	117.57(s)	117.42(s)	117.65(s)
P-( <i>p</i> -tolyl) <sub>3</sub> (o)	133.62(d)	133.69(d)	133.50(s)	132.26(d)
<sup>2</sup> J <sub>PC</sub>	10.65	10.58	10.36	10.58
P-( <i>p</i> -tolyl) <sub>3</sub> (m)	128.99(d)	130.55(d)	130.51(d)	128.96(d)
<sup>3</sup> J <sub>PC</sub>	12.41	12.88	12.84	12.93
P-( <i>p</i> -tolyl) <sub>3</sub> (p)	130.84(s)	129.75(s)	129.31(s)	127.69(s)
P-( <i>p</i> -tolyl) <sub>3</sub> (i)	127.91(d)	121.62(s)	121.51(s)	121.85(s)
<sup>1</sup> J <sub>PC</sub>	71.45			
CO	191.34(s)	192.94(s)	191.86(s)	188.63(s)

s = singlet, d = doublet, (o) = *ortho*, (m) = *meta*, (i) = ipso carbon, br = broad recorded in CDCl<sub>3</sub>.

#### ACKNOWLEDGEMENTS

This work is financially supported by the Research Council of the University of Bu-Ali Sina. The authors are thankful Mr. Zeberjadian for recording the NMR spectra.

#### REFERENCES

1. G. Wittig, *Science*, **210**, 600 (1980).
2. H. Schmidbaur, *Acc. Chem. Res.*, **8**, 62 (1975).
3. H. Schmidbaur, *Pure Appl. Chem.*, **50**, 19 (1978); **52**, 1057 (1980).
4. H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, **22**, 907 (1983).
5. W.C. Kaska, *Coord. Chem. Rev.*, **48**, 1 (1983).

6. J. Vicente, M.T. Chicote, J.A. Cayuetas, J. Fernandez-Baeza, P.G. Jones, G.M. Sheidriek and P. Espinet, *J. Chem. Soc. Dalton Trans.*, 1163 (1985).
7. S. Kato, T. Kato, M. Mizuta, K. Itoh and Y. Ishii, *J. Organomet. Chem.*, **51**, 167 (1973).
8. J.A. Albanese, A.L. Rheingold and J.L. Burmeister, *Inorg. Chim Acta*, **150**, 213 (1988)
9. R. Uson, J. Fornics, R. Navarro, P. Espinet and C. Mendivil, *J. Organomet. Chem.*, **290**, 125 (1985).
10. H. Koezuka, G. Matsubavashi and T. Tanaka, *Inorg. Chem.*, **15**, 417 (1976).
11. J. Vicente, M.T. Chicote, J. Fernandez-Baeza, J. Martin, I. Saura-Limas, J. Turpin and P.G. Jones, *J. Organomet. Chem.*, **331**, 409 (1987).
12. N.A. Nesmeyanov, V.M. Novikov and O.A. Reutuv, *J. Organomet. Chem.*, **4**, 202 (1965).
13. E.T. Weleski Jr., (The Late) J.I. Silver, M.D. Jasson and J.L. Burmeister, *J. Organomet. Chem.*, **102**, 365 (1975).
14. J. Vicente, M.T. Chicote, M.C. Lagunas and P.G. Jones, *J. Chem. Soc. Dalton Trans.*, 2579 (1991).
15. M. Onishi, Y. Ohama, K. Hiraki and H. Shintan, *Polyhedron*, **1**, 539 (1982).
16. F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1975).
17. M. Kalyanasundari, K. Panchanatheswaran, W.T. Robinson and H. Wen, *J. Organomet. Chem.*, **191**, 103 (1995).

(Received: 23 April 2007;

Accepted: 1 March 2008)

AJC-6388