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Synthesis and characterization of labile ylide of 1-(*p*-tolyl)-2-(tri-*p*-tolylphosphoranylidene)ethanone and its related complexes with mercury(II) halides

Alireza Dadrass[*], **Shahla Ebrahimnezhad, Mahsa Pourmirza and Ahmad Poursattar Marjani**

Faculty of Chemistry, Urmia University, Urmia 57154, Urmia, Iran

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The novel α-phosphorus labile ylide of 1-(*p*-tolyl)-2-(tri-*p*-tolylphosphoranylidene)ethanone (PTTPPY) is prepared by the reaction of 2-bromo-1-(*p*-tolyl)ethanone with tri-*p*-tolylphosphine in chloroform as solvent. The complexes of the type [HgX_2(*p*-tolyl)$_3$$PCHCOC_6H_4CH_3$)] (X = Cl, Br and I) are prepared by the reaction of title ylide with mercury(II) halides in good yields, using methanol as solvent. The final products were characterized by IR, ^1H, ^{13}C, ^{31}P NMR spectroscopic methods and microanalysis.

1. Introduction

Phosphorus ylides are important reagents in organic chemistry, especially in the synthesis of naturally occurring products with biological and pharmacological activities.[1] The organometallic chemistry of phosphorus ylides $R_3P{=}C(R')COR''$ (R, R′, R″ = alkyl or aryl groups) has undergone great growth over the last few years, mainly due to their interesting application as reactants in organometallic and metal-mediated organic synthesis.[2-3] 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.[4] Due to delocalization of electrons in labile ylide, we have an ambidentate ligand and thus bond to a metal center through either the carbanion or the enolate oxygen (Scheme 1). Coordination through carbon is more predominant and observed with soft metal ions, e.g., Pd(II), Pt(II), Hg(II), Au(I), and Au(III),[5-7] whereas, O-coordination dominates when the metals involved are hard, e.g., Ti(IV), Zr(IV), and Hf(IV).[8]

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[*] Corresponding author.
E-mail addresses: dadrassi@yahoo.com (A. Dadrass)

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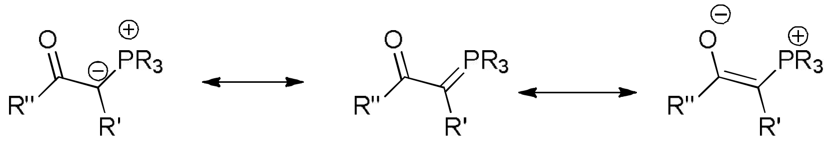


Scheme 1.

The reaction of BPPY ylide with mercury(II) chloride has already been reported by Nesmeyanov *et al.*[9] We are currently interested in synthesis and reactivity of metal derivatives of such ylides as α-keto stabilized ylide of (*p*-tolyl)$_3$PCHCOC$_6$H$_4$CH$_3$ and its related mercury(II) halide complexes.
In this work, the complexes obtained from the reaction of the new prepared α-carbonyl-stabilized ylide of 1-(*p*-tolyl)-2-(tri-*p*-tolylphosphoranylidene)ethanone with HgX$_2$ (X = Cl, Br and I), have been reported. All of the products were characterized by IR, ^{1}H, ^{13}C, ^{31}P NMR spectroscopic methods and microanalysis.

2. *Results and Discussion*

The *ν* (CO) which is sensitive to complexation occurs at 1599 cm^{-1} in the parent ylides, as in the case of other resonance stabilized ylides.[6] Coordination of ylide through carbon causes an increase in ν (CO) while for O-coordination a lowering of ν (CO) is expected. The infrared spectra of complexes in the solid state show ν (CO) in the range of 1638, 1626 and 1621 cm^{-1}, indicate coordination of the ylide through carbon at higher wave numbers with respect to the free labile ylide (PTTPPY *ν* (CO) 1599 cm^{-1}) (Table 1). The ν (P$^+$—C$^-$**)** which is also diagnostic for the coordination, occurs at 881 cm^{-1} in the parent ylide. These assignments confirmed by comparing the IR spectra of the corresponding ^{13}C substituted ylides.[8]

In the present study, the *ν* (P$^+$—C$^-$**)** stretching frequencies for all four complexes were shifted to lower frequencies and observed at 852, 848 and 837 cm^{-1} for **1, 2** and **3,** respectively, suggesting partial removal of electron density of the P−C bond.

Table 1. *ν* (CO) of selected phosphoranes and their metal complexes

Compound	*ν* (CO) cm^{-1}	Ref.
Ph$_3$PCHCON(CH$_3$)$_2$	1530	11
APPY	1530	12
BPPY	1525	13
PTTPPY	1599	This work
C-Coordination		
[HgCl$_2$(PTTPPY)] (**1**)	1638	This work
[HgBr$_2$(PTTPPY)] (**2**)	1626	This work
[HgI$_2$(PTTPPY)] (**3**)	1621	This work
Au[CH(PPh$_3$)CON(CH$_3$)$_2$]	1605	11
O-Coordination		
[(Sn(CH$_3$)$_3$BPPY]Cl	1480	4
[(Snph$_3$)BPPY]Cl	1470	4
[Pd(C$_6$F$_5$(PPh$_3$)$_2$(APPY)]ClO$_4$	1513	6

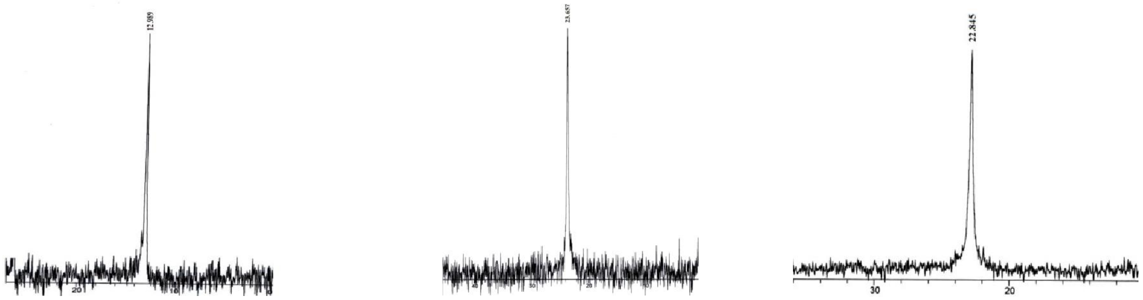
Ph = C$_6$H$_5$; APPY = acetylmethylenetriphenylphosphorane
BPPY = benzoylmethylenetriphenylphosphorane

The ^{1}H and ^{31}P 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 downfield compared to that of the free ylide, as a consequence of C-coordination character. The expected downfield shifts of ^{31}P signals for PCH group upon complexation were observed in their corresponding spectra. The appearance of single signals for PCH group in the ^{31}P NMR indicates the presence of only one molecule for all three complexes. The resonances of ^{31}P NMR complexes **1, 2** and **3** were observed at a lower field with respect to the free ylide (Table 2), thus suggesting a direct bond to methyl carbon with mercury (Fig. 1).[10]

Table 2. ^{1}H and ^{31}P NMR data of PTTPPY and its complexes with Hg(II) halides (T = 298 K, *J* in Hz, TMS δ = 0.00 ppm)

Compound	CH_3	δ(CH)	$^2J_{PH}$	δ(*p*-tolyl)$_3$P	δ(^{31}P)
PTTPPY	2.385	4.36(d)	23.29	7.25-7.87(m)	12.99(s)
[$HgCl_2$(PTTPPY)] (**1**)	2.417	5.37	-	7.10-8.08(m)	23.66(s)
[$HgBr_2$(PTTPPY)] (**2**)	2.414	5.23	-	7.18-8.01(m)	22.85(s)
[HgI_2(PTTPPY)] (**3**)	2.426	5.04(d)	4.21	7.13-7.93(m)	20.41(s)

In $CDCl_3$, 300 MHz, values(ppm) relative to internal TMS and external 85% phosphoric acid s, singlet; d, doublet; m, multiplet



(a) **(b)** **(c)**

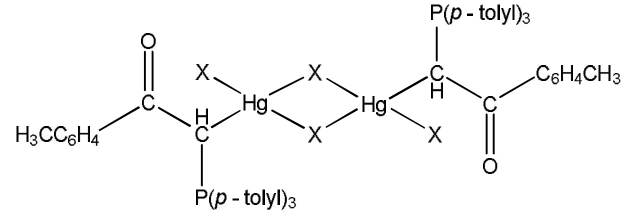
Fig. 1. (a) ^{31}P NMR spectra of ylide PTTPPY in $CDCl_3$ and its selected complexes: (b) [$HgCl_2$PTTPPY] (**1**) (c) [$HgBr_2$PTTPPY] (**2**) in DMSO-*d*$_6$ at 25ºC.

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}P and ^{1}H NMR.[6] The ^{13}C NMR data of the complexes and the title ylide are listed in Table 3 along with possible assignments. The ^{13}C NMR shifts of the CO group in the complexes **1** and **2** are higher than 191.34 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of CO group carbon in the complexes but this is not in agreement with complex **3** and the reason is not clear yet. Such upfield shift in complexes **2** and **3** also observed in [PdCl(η^3-2-XC_3H_4)(C_6H_5)$_3$PCHCOR] (X = H, CH_3; R = CH_3, C_6H_5) and was attributed to change in hybridization of the ylidic carbon.[11] Similar upfield shifts of 1-2 ppm with reference to the parent ylide were also observed in the case of [HgI_2(C_6H_5)$_3$PC_5H_4]$_2$ and in our synthesized mercury complexes.[13] No coupling constant for mercury was observed at room temperature in ^{1}H and ^{13}C NMR spectra of complexes is due to the broad coupling of proton with mercury and phosphorus atoms. The suggested dimeric type structure of complexes are shown in Fig. 2.[14,15]

Table 3. ^{13}C NMR data of ylide PTTPPY and its complexes with Hg(II) halides

Possible assignments	PTTPPY	[$HgCl_2$(PTTPPY)] (**1**)	[$HgBr_2$(PTTPPY)] (**2**)	[HgI_2(PTTPPY)] (**3**)
CH_3	21.48(s)	21.79(s)	21.73(s)	20.86(s)
3CH_3	21.31(s)	21.70(s)	21.67(s)	20.99(s)
CH	42.23(d)	br	br	br
$^2J_{PC}$	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-(*p*-tolyl)$_3$(o)	133.62(d)	133.69(d)	133.50(s)	132.26(d)
$^2J_{PC}$	10.65	10.58	10.36	10.58
P-(*p*-tolyl)$_3$(m)	128.99(d)	130.55(d)	130.51(d)	128.96(d)
$^2J_{PC}$	12.41	12.88	12.84	12.93
P-(*p*-tolyl)$_3$(p)	130.84(s)	129.75(s)	129.31(s)	127.69(s)
P-(*p*-tolyl)$_3$(i)	127.91(d)	121.62(s)	121.51(s)	121.85(s)
$^2J_{PC}$	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 $CDCl_3$



X = Cl, Br and I

Fig. 2. Suggested structure of complexes

3. Conclusion

This work describes the synthesis and characterization of a keto ylides (PTTPPY) and its mercury(II) complexes of the general formula [HgX_2(*p*-tolyl)$_3$$PCHCOC_6H_4CH_3$)] (X = Cl, Br and I). The physical, chemical and spectroscopic data propose that PTTPPY herein exhibits as monodentate C-coordination to the metal center. Theoretical studies on the gas phase structures of the latter complexes, confirm the *trans*-like dimeric structure for all complex compounds. The observation of similar analytical and spectroscopic data after further support the presence of a centrosymmeteric dimeric structure containing the labile ylide and HgX_2.

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4. 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 purification. ^1H, ^{31}P, ^{13}C NMR NMR measurements were recorded on a Bruker 300 spectrometer in DMSO-d_6 and $CDCl_3$ using TMS as the internal reference. Solid state IR spectra in the region 200-4000 cm^{-1} using KBr pellets were obtained on a FT-IR Perkin Elmer spectrophotometer. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer.

4.1 Synthesis of ylide [(p-tolyl)$_3$$PCHCOC_6H_4CH_3$]

2-bromo-1-(*p*-tolyl)ethanone (0.21 g, 1 mmol) was dissolved in chloroform (20 mL), then a solution of tri-paratolylphosphine (0.30 g, 1 mmol) in the same solvent (5 mL) was added to the above solution dropwise, 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 to it. 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 (0.51 g, 97%), was treated with alkaline solution of 5% NaOH, and stirred at 40ºC for about 24 h, the pale yellow precipitate of 1-(*p*-tolyl)-2-(tri-*p*-tolylphosphorane ylidene)ethanone was obtained. The product was washed several times with distilled water and air dried. Yield, 96%, m.p. 192-194 °C. Anal. Calcd. (%) $C_{30}H_{29}OP$: C, 82.54; H, 6.70. Found: C, 81.99; H, 6.02.

4.2 Synthesis of [$HgCl_2$(p-tolyl)$_3$$PCHCOC_6H_4CH_3$]$_2$ complex (1)

A solution of $HgCl_2$ (0.14 g, 0.5 mmol) in dry methanol (15 mL) was treated with 1-(*p*-tolyl)-2-(tri-*p*-tolylphosphoranylidene)ethanone (0.22 g, 0.5 mmol) 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. Yield, 83%, m.p. 197-199 °C.

4.3 Synthesis of [$HgBr_2$(p-tolyl)$_3$PCHCOC$_6$H$_4$CH$_3$]$_2$ complex (2)

A solution of $HgBr_2$ (0.18 g, 0.5 mmol) in dry methanol (15 mL) was treated with 1-(*p*-tolyl)-2-(tri-*p*-tolylphosphoranylidene)ethanone (0.22 g, 0.5 mmol) 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. Yield, 85%, m.p. 203-205 °C. Anal. Calcd. (%) $C_{30}H_{29}Br_2HgOP$: C, 45.21; H, 3.67. Found: C, 45.31; H, 3.80.

4.4 Synthesis of [HgI_2(p-tolyl)$_3$PCHCOC$_6$H$_4$CH$_3$]$_2$ complex (3)

A solution of HgI_2 (0.23 g, 0.5 mmol) in dry methanol (15 mL) was treated with 1-(*p*-tolyl)-2-(tri-*p*-tolylphosphoranylidene)ethanone (0.22 g, 0.5 mmol) 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. Yield, 82%, m.p. 200-202 °C. Anal. Calcd. (%) $C_{30}H_{29}I_2HgOP$: C, 40.44; H, 3.28. Found: C, 40.11; H, 3.02.

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