



Trade Science Inc.

March 2010

ISSN : 0974 - 746X

Volume 5 Issue 1

# Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 5(1), 2010 [15-18]

## Investigation of reactivity of phosphorus ylides as hard donar ligands, with Ag(I), Cd(II), and Pd(II) as soft metal centers: A multinuclear NMR study

A.R.Dadrass<sup>1\*</sup>, Ali Souldozi<sup>2</sup>, Simin Khorsand<sup>3</sup>, S.J.Sabounchei<sup>4</sup>

<sup>1</sup>Chemistry Department, Urmia University, Urmia - 57159-165, (IRAN)

<sup>2</sup>Department of Chemistry, Islamic Azad University, Urmia Branch, PO Box 969, Urmia, (IRAN)

<sup>3</sup>Chemistry Department, Urmia University, Urmia - 57159-165, (IRAN)

<sup>4</sup>Faculty of Chemistry, Science, Bu-Ali Sina University, Hamadan - 65174, (IRAN)

E-mail : Dadrassi@yahoo.com

Received: 5<sup>th</sup> January, 2010 ; Accepted: 15<sup>th</sup> January, 2010

### ABSTRACT

The reaction between oxophilic group of 3 metal salts and the ambidentate  $\alpha$ -keto ylides (4-bromobenzoylmethylene triphenylphosphorane (BBPPY) and (4-bromobenzoylmethyl-phenetriparatolyl phosphorane (BBTPPY) in dry methanol and acetonitrile as solvents lead to formation of C-bound metal-ylide complexes. The compounds were characterized by IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopic methods microanalysis.

© 2010 Trade Science Inc. - INDIA

### KEYWORDS

Hard donar ligand;  
Phosphorus ylide reaction;  
Phosphorus ylide complexe.

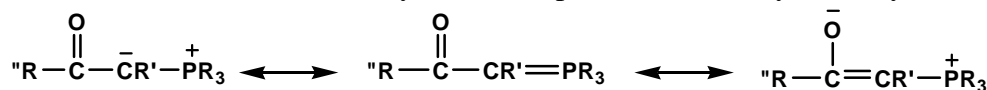
### INTRODUCTION

The coordination chemistry of ambidentate ligands have been investigated<sup>[1]</sup>. One of our goals was to find an ambidentate ligand wherein control of the bonding mode (C vs O) would reside, at least in part, in variables that were found within the ligand itself<sup>[2]</sup>. Although many bonding modes are possible for keto ylides, coordination through ylides methine carbon is more predominant and observed with soft metal ions, e.g., Pd(II), Pt(II), Hg(II) Au(I), and Au(III)<sup>[3-8]</sup>, whereas, O-coordination dominates when the metals involved are hard, e.g., Ti(IV), Zr(IV), and Hf(IV)<sup>[9]</sup>. The ease of system-

atic variation of the R, R' and/or R'' groups in the phosphorus ylides of the type R<sub>3</sub>PCR'C(O)R'' suggested that these are ideal candidates.

The keto-stabilized ligand can coordinate to a metal center through the ylide's methine carbon atom (2) or the carbonyl oxygen atom(3) wherein (R = C<sub>6</sub>H<sub>5</sub>, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, R' = H, and R'' = BrC<sub>6</sub>H<sub>4</sub>) (Scheme 1).

Our initial efforts were therefore directed toward the use of the soft metal centers, such as Ag(I), Cd(II), and Pd(II), that would preferentially bond to the ylide's methine carbon. The aims of our present work are (i) to determine and compare the molecular structure of the products formed by the title ylides with these kinds



Scheme 1

## Full Paper

of soft metals, and (ii) to characterize all the products by FT-IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra.

### RESULTS AND DISCUSSION

The  $\nu(\text{CO})$  which is sensitive to complexation occurs at 1578 and 1598 $\text{cm}^{-1}$  in the parent ylides, as in the case of other resonance stabilized ylides<sup>[14]</sup>. Coordination of ylide through carbon cause an increase in  $\nu(\text{CO})$  while for O-coordination a lowering of  $\nu(\text{CO})$  is expected (TABLE 1). The infrared spectra of complexes in the solid state show  $\nu(\text{CO})$  in the range of 1608 and 1680 $\text{cm}^{-1}$ , at higher wave numbers with respect to the free ylide (BBPPY,  $\nu(\text{CO})$  1578 and 1598 $\text{cm}^{-1}$ ). The  $(\text{P}^+ - \text{C}^-)$  which is also diagnostic for the coordination occurs at 882 and 883 $\text{cm}^{-1}$  in the parent ylides. These assignments confirmed by comparing the IR spectra of the corresponding  $^{13}\text{C}$  substituted ylides<sup>[16]</sup>. In the present study, the  $\nu(\text{P}^+ - \text{C}^-)$  values for all four complexes were shifted to lower frequencies and observed at 845, 816, 807, 808 and 884 $\text{cm}^{-1}$  for 2, 3, 4, 5 and 6 respectively, suggesting some removal of electron density in the P-C bond.

The  $^1\text{H}$  and  $^{31}\text{P}$  NMR data of the mercury (II) ylide complexes along with those of the parent ylides are listed in the (TABLE 2). Signals due to methane protons, when

**TABLE 1 :  $\nu(\text{CO})$  of selected phosphoranes and their metal complexes**

Compound	$\nu(\text{CO})\text{cm}^{-1}$	Ref.
$\text{Ph}_3\text{PCHCON}(\text{CH}_3)_2$	1530	11
APPY	1530	12
BPPY	1525	13
BBPPY	1578	10
BBTPPY	1578	This work
<b>C-coordination</b>		
BBTPPY. $\text{AgNO}_3$	1608	This work
BBPPY. $\text{AgNO}_3$	1619	This work
BBPPY. $\text{Cd}(\text{NO}_3)_2$	1590	This work
BBPPY. $\text{CdCl}_2$	1680	This work
BBPPY. $\text{PdCl}_2$	1619	This work
$\text{Au} [\text{CH}(\text{PPh}_3)\text{CON}(\text{CH}_3)_2]$	1605	11
<b>O-coordination</b>		
$[(\text{Sn}(\text{CH}_3)_3.\text{BPPY})\text{Cl}]$	1480	14
$[(\text{SnPh}_3).\text{BPPY}]\text{Cl}$	1470	14

Ph =  $\text{C}_6\text{H}_5$ , APPY = acetylmethylenetriphenylphosphorane, BPPY = benzoylmethylenetriphenyl-phosphorane

recorded in  $\text{CDCl}_3$  was either broad or unobserved probably due to very low solubility of all the complexes in  $\text{CDCl}_3$ . However, a sharp doublet for the above proton was obtained in  $\text{DMSO}-d_6$  for each of the four complexes in the same region. This indicates that the complexes do not react with  $\text{DMSO}-d_6$ . The expected downfield shifts of  $^{31}\text{P}$  and  $^1\text{H}$  signals for PCH group upon complexation were observed in their corresponding spectra. The appearance of single signals for PCH group in each of  $^{31}\text{P}$  and  $^1\text{H}$  NMR indicates the presence of only one molecule for all of the four 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* isomers giving rise to two different signals in  $^{31}\text{P}$  and  $^1\text{H}$  NMR.

The resonances of  $^{31}\text{P}$  NMR complexes 2, 3, 4, 5 and 6 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 soft metal center. The  $^{13}\text{C}$  NMR data of the complexes and the title ylide are listed in (TABLE 3) along with possible assignments. The most interesting aspect of the  $^{13}\text{C}$  spectra of the complexes is the up field shift of the signals due ylidic carbon. Such up field shift observed in  $\text{PdCl}_2$  ( $\eta^3\text{-}2\text{-XC}_3\text{H}_4$ ) ( $\text{C}_6\text{H}_5$ ) $_3\text{PCHCOR}$  ( $\text{X} = \text{H}, \text{CH}_3$ ;  $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$ ) and was attributed to change in hybridization of the ylidic carbon<sup>[14]</sup>. Similar up field shifts of 2-7.6ppm with reference to the parent ylides BBPPY and BBTPPY were also observed in the case of these metal complexes<sup>[15]</sup>. The  $^{13}\text{C}$  shifts of CO group in the complexes are around 189-191ppm higher than 183.51 in BBPPY and 183.28ppm noted for the same carbon in the BBTPPY, indicating much lower shielding of the carbon of the CO group in the complexes. No coupling with these metal ions was observed at room temperature in  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of all these complexes.

### EXPERIMENTAL

Methanol was distilled over magnesium powder and diethyl ether ( $\text{Et}_2\text{O}$ ) 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 instrument- tation at Bu-Ali-Sina Univer-

TABLE 2 :  $^1\text{H}$  and  $^{31}\text{P}$ NMR data of BBPPY and BBTPPY with their metal complexes

Compd.	$\delta(\text{CH})$	$^2\text{J}_{(\text{PH})}$	$\delta\text{CH}_3$	$\delta(\text{PPh}_3)$	$^{31}\text{P}\{^1\text{H}\}$
BBTPPY	4.48 (d)	br	2.35(s)	7.26-7.88 (m)	13.28 (s)
BBTPPY. $\text{AgNO}_3$	4.38 (d)	21.00	2.40(s)	7.31-7.76 (m)	16.45 (s)
BBPPY. $\text{AgNO}_3$	5.14 (d)	11.64		7.65-8.10 (m)	18.19 (s)
BBPPY. $\text{Cd}(\text{NO}_3)_2$	6.22 (d)	12.00		7.64-7.90(m)	27.00 (s)
BPPY. $\text{CdCl}_2$	4.21 (d)	4.50		7.74-8.20 (m)	17.68 (s)
BBPPY. $\text{PdCl}_2$	6.12 (d)	15.00		6.98-8.08 (m)	25.19(s)

In  $\text{CDCl}_3$ , 90 MHz, values (ppm) relative to internal TMS and external 85% phosphoric acid. s, singlet; d, doublet; m, multiplet; br, broad

sity, faculty of science. Solid state IR spectra in the region  $200\text{-}4000\text{cm}^{-1}$  using KBr pellets were obtained on a FT-IR Perkin Elmer spectrophotometer. The ylide ( $\text{Ph}_3\text{PCHCOC}_6\text{H}_4\text{Br}$ ) was prepared according to published procedure<sup>[10]</sup>. Elemental analysis was carried out at Tarbiate Modarres University in Tehran.

#### Synthesis of ylide [ $(p\text{-tolyl})_3\text{PCHCOC}_6\text{H}_4\text{Br}$ ]

2,4-Bromophenyl acetophenone (0.278g, 1 mmol) was dissolved in 20ml of chloroform, then a solution of tri-paratolyphosphine (0.304g, 1 mmol) in the same solvent (5ml) 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 (20ml) was added. The white formed solid was filtered off, washed with petroleum benzene ( $2 \times 10\text{ml}$ ), and dried under reduced pressure. In order to get final product, whole of the crud solid (0.547g), (94%), was transferred to alkaline solution 5% NaOH and stirred at  $40^\circ\text{C}$  for about 24 h, the pale yellow precipitate of 4-bromobenzoylmethylene triparatolylyl-phosphorane was obtained. The product was washed several times with distilled water and air dried. Yield (85%), (m.p.  $176\text{-}178^\circ\text{C}$ ). Anal. (%) Calcd.:  $\text{C}_{29}\text{H}_{26}\text{BrOP}$ : C, 69.47, H, 5.23. Found: C, 69.46, H, 5.22.

#### Synthesis of [ $(p\text{-tolyl})_3\text{PCHCOC}_6\text{H}_4\text{Br}$ ] $\cdot\text{AgNO}_3$ ] complex(1)

A solution of (0.084g, 0.5 mmol) of  $\text{AgNO}_3$  in methanol (15ml) was added to solution of (0.5g, 1 mmol) of the 4-bromobenzoylmethylenetriparatolylyl phenylphosphorane in dry methanol (15ml) and stirred for 24 h. The white product formed by slow evaporation of the solvent. The product washed several times with dry diethylether and dried in vacuum. Yield (68%),

TABLE 3 :  $^{13}\text{C}$  NMR data of BBTPPY and metal complexes

Compound.	CH	$^2\text{J}_{\text{p-c}}$	$\text{CH}_3$	$\text{PPh}_3$	C=O
BBTPPY	51.17	107.34	21.36	123.24-142.70 (m)	183.28 (s)
BBTPPY. $\text{AgNO}_3$	49.11	110.25	19.45	122.07-141.07 (m)	186.21 (s)
BBPPY. $\text{AgNO}_3$	43.57	86.02		124.41-133.42 (m)	185.12 (s)
BBPPY. $\text{Cd}(\text{NO}_3)_2$	(br)	-		117.32-134.84 (m)	191.63 (s)
BBPPY. $\text{CdCl}_2$	49.73 (d)	110.92		123.25-142.89 (m)	189.93 (s)
BBPPY. $\text{PdCl}_2$	(br)	-		124.42-143.50 (m)	191.53 (s)

BBPPY, Recorted in  $\text{CDCl}_3$ , and complexes in  $\text{DMSO}-d_6$ , s, singlet; d, doublet; m, multipilate, br, broad

(m.p.  $157\text{-}159^\circ\text{C}$ ). Anal. (%) Calcd.:  $\text{C}_{58}\text{H}_{50}\text{Br}_2\text{AgNO}_5\text{P}_2$ : C, 59.51, H, 4.47. Found: C, 59.75, H, 4.52.

#### Synthesis of [ $(\text{Ph}_3\text{PCHCOC}_6\text{H}_4\text{Br})_2\text{AgNO}_3$ ] complex(2)

A solution of (0.084g, 0.5 mmol) of  $\text{AgNO}_3$  in methanol (15ml) was added to solution of (0.458g, 1 mmol) of the 4-bromobenzoylmethylenetriphenyl phosphorane in dry methanol (15ml) and stirred for 24 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%), (m.p.  $163\text{-}165^\circ\text{C}$ ). Anal. (%) Calcd.:  $\text{C}_{52}\text{H}_{40}\text{Br}_2\text{AgNO}_5\text{P}_2$ : C, 57.38, H, 3.70. Found: C, 56.78, H, 3.54.

#### Synthesis of [ $(\text{Ph}_3\text{PCHCOC}_6\text{H}_4\text{Br})\cdot\text{Cd}(\text{NO}_3)_2$ ] complex(3)

A solution of (0.154g, 0.5 mmol) of  $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  in methanol (15ml) was added to solution of (0.229g, 0.5 mmol) of the 4-bromobenzoyl methylenetriphenylphosphorane in dry methanol (15ml) 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 (79%), (m.p.  $185\text{-}187^\circ\text{C}$ ). Anal. (%) Calcd.:  $\text{C}_{52}\text{H}_{40}\text{Br}_2\text{CdN}_2\text{O}_8\text{P}_2$ : C, 54.07, H, 3.49, N, 2.43. Found: C, 54.35, H, 3.62, N, 2.51.

#### Synthesis of [ $(\text{Ph}_3\text{PCHCOC}_6\text{H}_4\text{Br})\cdot\text{CdCl}_2$ ] complex(4)

A solution of (0.088g, 0.5 mmol) of  $\text{CdCl}_2$  in methanol (15ml) was added to solution of (0.229g, 0.5 mmol) of the 4-bromobenzoylmethylenetriphenylphosphorane in dry methanol (15ml) and stirred for 12 h. The white product formed by slow evaporation of the solvent. The product washed several times with dry diethylether and

## Full Paper

dried in vacuum. Yield (74%), (m.p. 165-167°C). Anal. (%) Calcd.: C<sub>29</sub>H<sub>20</sub>BrCdCl<sub>2</sub>OP: C, 48.59, H, 3.14. Found: C, 49.08, H, 3.26.

### Synthesis of Trans-[PdCl<sub>2</sub>{CH(PPh<sub>3</sub>)COC<sub>6</sub>H<sub>4</sub>Br}<sub>2</sub>](5)

The new ylide of (Ph<sub>3</sub>P)CHCOC<sub>6</sub>H<sub>4</sub>Br (0.252g, 0.55 mmol) was added to a saturated solution of PdCl<sub>2</sub> (0.49g, 0.28 mmol) in CH<sub>3</sub>CN (10cm<sup>3</sup>) and the suspension stirred for 15 min, then filtered. The pale yellow solid washed with diethyl ether and dried in vacuum. Yield (82%), (m.p. 175-177°C). Anal. (%) Calcd.: C<sub>52</sub>H<sub>40</sub>Br<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Pd: C, 56.99, H, 3.67. Found: C, 49.08, H, 3.26.

### ACKNOWLEDGEMENTS

This work is financially supported by the Research Concil of the University of Urmia. We are thankful Mr. Zeberjadian for recording the NMR spectra.

### REFERENCES

- [1] J.L.Burmeister; *Curr.Contents*, **28**, 16 (1988).
- [2] J.L.Burmeister, J.L.Silver, E.T.Weleski; *Proc. Int.Conf.Coord.Chem.*, 14<sup>th</sup> (Toronto, Ontario, Canada) 442-444 (1972).
- [3] E.T.Weleski, J.L.Silver, M.D.Janson, J.L.Burmeister; *J.Organomet.Chem.*, **102**, 365 (1975).
- [4] R.Uson, J.Fornies, R.Navarro, P.Espinet, C.Mendivil; *J.Organomet.Chem.*, **290**, 125 (1985).
- [5] H.Koezuka, G.Matsubayashi, T.Tanaka; *Inorg. Chem.*, **25**, 417 (1976).
- [6] J.Vicente, M.T.Chicote, J.Fernandez-Baeza, J.Martin, I.Saura-Llamas, J.Turpin, P.G.Jones; *J.Organomet.Chem.*, **331**, 409 (1987).
- [7] M.Kalyanasundari, K.Panchanatheswaran, W.T.Robinson, H.Wen; *J.Organomet.Chem.*, **91**, 103.
- [8] J.Vicente, M.T.Chicote, I.Saura-Llamas, J.Turpin, J.Fernandez-Baeza; *J.Organomet.Chem.*, **333**, 129 (1987).
- [9] J.A.Albanese, D.L.Staley, A.L.Rheingold, J.L.Burmeister; *Inorg.Chem.*, **29**, 2209 (1990).
- [10] S.J.Sabounchei, A.R.Dadrass; *Asian Journal of Chemistry*, **19**(7), 5471 (2007).
- [11] J.Vicente, M.T.Chicote, M.C.Lagunas, P.G.Jones; *J.Chem.Soc.Dalton Trans*, 2579 (1991).
- [12] M.Onishi, Y.Ohama, K.Hiraki, H.Shintan; *Polyhedron*, **1**, 539 (1982).
- [13] M.Kalyanasundari, K.Panchanatheswaran, Ward T.Robinson, H.Wen; *J.Organomet.Chem.*, **191**, 103-109 (1995).
- [14] S.Kato, T.kato, M.Mizuta, K.Itoh, Y.Ishii; *J.Organomet.Chem.*, **5**, 167 (1973).
- [15] R.Uson, J.Fornics, R.Navarro, P.Espinet, C.Mendivil; *J.Organomet.*, **290**, 125 (1985).
- [16] H.Koezuka, G.Matsubavashi, T.Tanaka; *Inorg. Chem.*, **15**, 417 (1976).