



Trade Science Inc.

ISSN : 0974 - 746X

Volume 7 Issue 5

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 7(5), 2012 [215-218]

Preparation and multinuclear NMR study of 1-(3-nitrophenyl)-2-(triphenyl-phosphoranydene)ethanone (NBPPY) ylide with its related complexes with mercury (II) salts and silver nitrate

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ABSTRACT

The reaction of the title ylide, Ph₃PCHCOC₆H₄NO₂ (NBPPY) (1), with mercury (II) salts in 1:1 ratios using methanol as a solvent produces the mercurated complexes [(NBPPY).HgCl₂]₂ (2), [(NBPPY).HgBr₂]₂ (3) [(NBPPY).HgI₂]₂ (4) and [(NBPPY).Hg(NO₃)₂] (5) and with silver nitrate in 2:1 as [(NBPPY)₂.AgNO₃] (6) in good yields. Characterization of the obtained compounds was also performed by means of elemental analysis, IR, ¹H, ¹³C and ³¹P NMR data. A theoretical study of some Hg (II) complexes with phosphonium ylides is also reported. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Phosphorus ylides;
Mercury (II) halides;
Silver nitrate;
Complexes;
Triphenylphosphine.

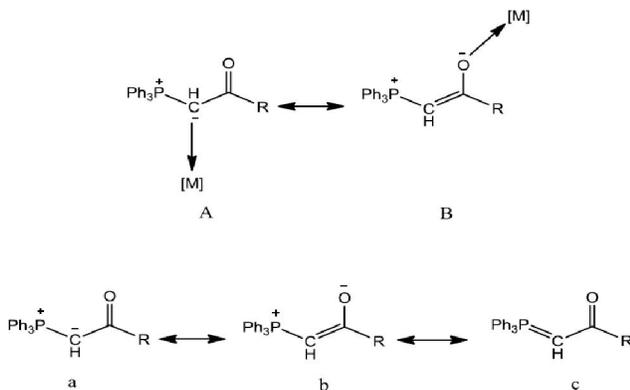
INTRODUCTION

Phosphorus ylides are reactive compounds that take part in many reactions of value in the synthesis of organic products^[1-4]. These compounds are synthetic targets of interest, because of their value for a variety of industrial, biological and chemical synthetic uses^[5-10]. Several methods have been developed for the preparation of phosphorus ylides. These are usually prepared by treatment of a phosphonium salt with a base. Phosphonium salts are usually obtained from the phosphine and alkyl halide. Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins in other ways^[4]. In recent years there have been established a one-pot method for the synthesis of stabilized ylides^[11-14]. The phosphonium salts are most often converted to ylides by treatment with a strong base, though weaker bases can be used if the

salt is acidic enough. The coordination chemistry of the phosphoranes of the type α -ketostabilized ylides Ph₃P=CHCOR have shown useful applications in organometallic chemistry (due to their ambidentate character as ligands) and also they act as reactants or valuable key intermediates in metal-mediated organic synthesis^[6]. This ambidentate character as ligands can be rationalized in terms of the resonance forms (a-c) (where Cis represented by the *cis* and *trans* geometrical isomers). The chemical behavior of carbonyl-stabilized ylide is largely dominated by the C-coordination while very few examples of O-coordinated ylides are known. They have two alternate modes of coordination, A and B which form stable complexes in spite of their low nucleophilicity (arising from electron delocalization through resonance forms (a-c)^[15,16] (Scheme 1). In this work, we describe the preparation, spectroscopic characterization (IR and NMR) of mercury (II) complexes

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and silver nitrate with the title ylide^[17,18].



Scheme 1

EXPERIMENTAL

Starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were measured on a Shimadzu IR-460 spectrometer. ¹H, ¹³C and ³¹P NMR spectra were measured (CDCl₃ solution) with a BRUKER DRX-300 AVANCE spectrometer at 300.13, 75.467 and 62.5 MHz, respectively. Elemental analyses were performed using a Heraeus CHN Rapid analyzer.

Synthesis of [Ph₃PCHCOC₆H₄NO₂] (NBTPPY)(1)

2-bromo-1-(3-nitrophenyl)ethanone (0.244 g, 1 mmol) was dissolved in 20 ml of acetone, with triphenylphosphine in acetone as solvent (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, (0.253 g, 0.5 mmol) of the crud solid was transferred to alkaline solution 5% NaOH and stirred at 40°C for about 24 h, the pale yellow precipitate of 1-(3-nitrophenyl)-2-(triphenylphosphoranylidene)ethanone was obtained. The product was washed several times with distilled water and air dried. The characterization data of the compounds are given below: Pale yellow precipitate; mp: 88-90 °C; Yield: 80%. FT-IR (cm⁻¹):

1522, 1480, 1435, 1107, 910. ¹H NMR (300MHz, CDCl₃, δ ppm): 4.51 (d, *J* = 24Hz, PC-CH H, CH), 7.44-8.69 (m, 19H, Ar); ¹³C NMR(300MHz, CDCl₃, δ ppm): 52.55 (d, *J* = 111.4Hz, PC-CH), 121.94, 132.42, 147.98, 129.92, 128.42 and 143.06 (d, ³*J*_{PC} = 15.3 Hz), 133.14 (d, ¹*J* = 10.1Hz, PC), 129.06 (d, ²*J* = 12.3Hz PC), 128.42, 126.27, and 181.53; ³¹P NMR (62.5 MHz, CDCl₃): 17.42 (s); Anal. Calcd. for C₂₆H₂₀NO₃P: C, 73.41; H, 4.74; N, 3.29. Found: C, 73.66; H, 4.80; N, 3.32.

General procedure for the preparation of mercury (II) complexes of ylide, compounds 2, 3, 4 and 5 (Exemplified for 2)

A solution of (0.082 g, 0.3 mmol) of HgCl₂ in methanol (15 ml) was added to solution of (0.128, 0.3mmol) of the 1-(3-nitrophenyl)-2-(triphenylphosphoranylidene)ethanone in dry methanol (15 ml) and magnetically stirred for 12 h. The brown product formed by slow evaporation of the solvent. The product washed several times with dry diethyl ether and dried in vacuum. The characterization data of the compounds are given below: Brown precipitate; mp: 130-133°C, FT-IR (cm⁻¹): 1645, 1526, 1436, 1348, 828; ¹H NMR (300 MHz, CDCl₃, δ ppm): 5.65 (s, H, CH), 7.27-8.72 (m, 19H, Ar); ¹³C NMR (300 MHz, DMSO-d₆, δ ppm): 47.67 (d, *J* = 111.4 Hz, PC-CH), 121.29, 134.24, 148.19, 128.42, 127.24 and 137.24 (d, ³*J* = 15.3 Hz PC), 133.80 (d, ¹*J* = 10.1 Hz, PC), 130.02 (d, ²*J* = 12.3 Hz PC), 130.63, 123.07, and 190.97; ³¹P NMR (62.5 MHz, CDCl₃): 22.14 (s); Anal. Calcd. for C₅₂H₄₀Cl₂Hg₂N₂O₆P₂: C, 47.21; H, 3.03; N, 2.12. Found: C, 47.64; H, 3.14; N, 2.18.

Selected data for [Ph₃PCHCOC₆H₄NO₂. HgBr₂]₂ Complex (3)

Brown precipitate; mp: 154-156°C; Yield: 75%. FT-IR (cm⁻¹): 1635, 1523, 1434, 1345, 878. ¹H NMR(300 MHz, CDCl₃, δ ppm): 5.33 (d, ²*J* = 11.1 Hz, PH-CH), 7.62-8.74 (m, 19H, Ar); ¹³C NMR(62.5 MHz, DMSO-d₆, δ ppm): 49.63 (d, ¹*J* = 88.8Hz, PC-CH), 122.57, 134.30, 148.23, 131.86, 129.28, 131.86 and 140.92 (d, ³*J* = 10.0Hz, PC); 133.63 (d, ²*J* = 10.3Hz PC), 130.06, 124.83 (d, ¹*J* = 89.9Hz, PC) and 185.17. ³¹P NMR (300 MHz, DMSO-d₆, δ ppm): 22.17 (s); Anal. Calcd. for C₅₂H₄₀Br₂Hg₂N₂O₆P₂: C, 44.24; H, 2.86; N, 1.98.

Found: C, 44.64; H, 3.04; N, 1.99.

Selected data for $[\text{Ph}_3\text{PCHCOC}_6\text{H}_4\text{NO}_2, \text{HgI}_2]_2$ Complex (4)

Grey precipitate; mp: 156-158°C; Yield: 76%. FT-IR (cm^{-1}): 1633, 1523, 1435, 1349, 827. ^1H NMR (300 MHz, CDCl_3 , δ ppm): 5.15 (d, $^2J = 15.1$ Hz, PH-CH), 7.60-8.69 (m, 19H, Ar); ^{13}C NMR (62.5 MHz, DMSO-d_6 , δ ppm): 50.30 (d, $^1J = 94.50$ Hz, PC-CH), 122.27, 130.14, 148.22, 130.28, 129.27 and 138.61 (d, $^3J = 12.1$ Hz, PC); 133.55 (d, $^1J = 10.0$ Hz, PC), 129.77 (d, $^2J = 12.2$ Hz, PC), 129.99, 125.29 (d, $^1J = 91.2$ Hz, PC) and 183.86. ^{31}P NMR (300 MHz, CDCl_3 , δ ppm): 22.06 (s). Anal. Calcd. for $\text{C}_{52}\text{H}_{40}\text{I}_2\text{Hg}_2\text{N}_2\text{O}_6\text{P}_2$: C, 41.46; H, 2.68; N, 1.86. Found: C, 41.65; H, 2.71; N, 1.90.

Synthesis of $[\text{Ph}_3\text{PCHCOC}_6\text{H}_4\text{NO}_2, \text{Hg}(\text{NO}_3)_2]$ Complex (5)

A solution of (0.108 g, 0.3 mmol) of $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in methanol (15 ml) was added to solution of (0.128, 0.3 mmol) of the 1-(3-nitrophenyl)-2-(triphenylphosphoranylidene)ethanone in dry methanol (15 ml) and stirred for 12 h. The pale grey product formed by slow evaporation of the solvent. The product washed several times with dry diethyl ether and dried in vacuum. The characterization data of the compounds are given below: Pale grey precipitate; mp: 198-200°C; Yield: 73%. FT-IR (cm^{-1}): 1662, 1530, 1435, 1362, 830. ^1H NMR (300 MHz, CDCl_3 , δ ppm): 6.17 (br, H, CH), 7.56-8.82 (m, 19H, Ar); ^{13}C NMR (62.5 MHz, DMSO-d_6 , δ ppm): 50.30 (d, $^1J = 96.50$ Hz, PC-CH), 124.11, 134.90, 148.32, 129.15, 128.52 and 140.23 (d, $^3J = 12.11$ Hz, PC); 134.21 (d, $^1J = 10.3$ Hz, PC), 130.30 (d, $^2J = 12.7$ Hz, PC), 130.73, 121.73 (d, $^1J = 89$ Hz, PC) and 192.25. ^{31}P NMR (300 MHz, CDCl_3 , δ ppm): 29.32 (s). Anal. Calcd. for $\text{C}_{26}\text{H}_{20}\text{HgN}_2\text{O}_6\text{P}$: C, 45.39; H, 2.93; N, 4.07. Found: C, 46.05; H, 3.03; N, 4.23.

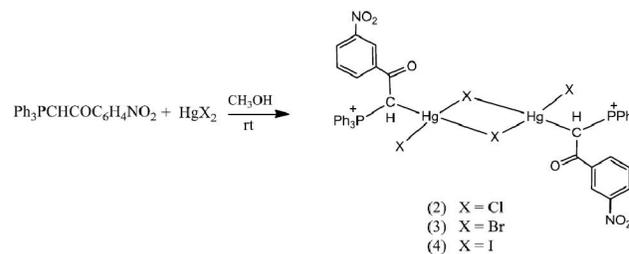
Synthesis of $[(\text{Ph}_3\text{PCHCOC}_6\text{H}_4\text{NO}_2)_2, \text{AgNO}_3]$ Complex (6)

A solution of (0.051 g, 0.3 mmol) of AgNO_3 in methanol (15 ml) was added to solution of (0.256 g, 0.6 mmol) of the 1-(3-nitrophenyl)-2-(triphenylphosphoranylidene)ethanone in dry methanol (15 ml) and stirred for 12 h. The greyish product formed by slow

evaporation of the solvent. The product washed several times with dry diethyl ether and dried in vacuum. The characterization data is given below: Greyish precipitate; mp: 148-150°C; Yield: 80%. FT-IR (cm^{-1}): 1609, 1525, 1436, 1347, 860. ^1H NMR (300 MHz, CDCl_3 , δ ppm): 4.78 (br, H, CH), 7.57-8.60 (m, 19H, Ar); ^{13}C NMR (62.5 MHz, DMSO-d_6 , δ ppm): 49.12 (d, $^1J = 105.8$ Hz, PC-CH), 121.46, 133.06, 148.24, 129.12, 127.01 and 142.51 (d, $^3J = 15.1$ Hz, PC); 133.33 (d, $^1J = 10.2$ Hz, PC), 130.30 (d, $^2J = 12.2$ Hz, PC), 129.92, 125.19 (d, $^1J = 92.4$ Hz, PC) and 182.10. ^{31}P NMR (300 MHz, CDCl_3 , δ ppm): Anal. Calcd. for $\text{C}_{52}\text{H}_{40}\text{AgN}_3\text{O}_7\text{P}_2$: C, 63.17; H, 4.08; N, 4.25. Found: C, 63.51; H, 4.71; N, 4.28.

RESULT AND DISCUSSION

Reactions of HgX_2 (X = Cl, Br and I) with ylides in 1:1 stoichiometry afforded halide-bridged dimeric structures 2-4 (Scheme 2) containing C-coordinated ylide ligands^[8]. The complex 5 may be having neutral inner coordination sphere type structure and ylide in 2:1 stoichiometry with silver nitrate, probably gives linear structure of complex 6.



Scheme 2

The $\nu(\text{CO})$ band, which is sensitive to complexation, occurs at 1522 cm^{-1} for the parent ylide, as in the case of other resonance stabilized ylides. Coordination of the ylide through carbon causes an increase in $\nu(\text{CO})$, while for O-coordination a lowering of $\nu(\text{CO})$ is expected. The infrared absorption bands observed for the all complexes at 1640, 1635, 1633, 1662 and 1609 cm^{-1} indicate coordination of the ylide through carbon^[9-14]. The $\nu(\text{P}^+-\text{C}^-)$ value, which is also diagnostic for the coordination, occurs at 928 cm^{-1} in $\text{Ph}_3\text{P}^+-\text{CH}_2$ and at 910 cm^{-1} in NBPPY. In the present study, the $\nu(\text{P}^+-\text{C}^-)$ values for all complexes were shifted to lower frequencies and were observed at 828, 878, 827, 830 and 860 cm^{-1} for 2, 3, 4, 5 and 6 respectively, suggesting

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some removal of electron density from the P–C bond^[15].

The ¹H NMR data for all the complexes, along with those of the parent ylide, are analyzed. The signals due to the methine protons, when recorded in CDCl₃, were either broad or unobserved, probably due to the very low solubility of all the complexes in CDCl₃. Similar behavior was observed earlier in the case of ylide complexes of mercury (II) halides.^{16,17} The expected downfield shifts of ³¹P and ¹H signals for the PCH group upon complexation were observed in their corresponding spectra. The appearance of single signals for the PCH group in both the ³¹P and ¹H NMR spectra at ambient temperature indicates the presence of only one molecule for all the complexes, as expected for C-coordination. It must be noted that O-coordination of the ylide leads to the formation of cis and trans isomers which would give rise to two different signals in the ³¹P and ¹H NMR spectra^[6]. The resonances in the ³¹P NMR spectra and ¹³C-NMR data of the complexes and the title ylides along with possible assignments are characterized. The ¹³C-NMR shifts of the C=O group in the complexes are around 182.10–192.25 ppm i.e., at lower field than for the free phosphonium ylides, indicating a much lower shielding of the C-atom of the C=O group in the complexes.

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