Synthesis and Characterization of Transition Metal (Hg(II), Ag(I) and Cd(II)) Complexes of Some New Phosphorus Ylides

S. Javad Sabounchei*, Vida Jodaian and Hassan Nemattalab

Faculty of Chemistry, University of Bu-Ali Sina, Hamedan 65174, Iran

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ABSTRACT

Reaction of two new phosphorus ylides Ph₃PCHCOC₆H₄ (Y¹) and Ph₃PCHCOC₄H₃S (Y²) with mercury(II) halides and a previously reported ylide (p-tolyl)₃PCHCOOCH₂Ph (Y₃) with CdCl₂ in equimolar ratios using methanol as solvent yielded binuclear complexes of the type [(Y).HgX₂]₂ (Y = Y¹ and Y², X = Cl, Br and I) and a complex of [(Y³).HgCl₂]₂. The latter ylide reacts with Hg(NO₃)₂.H₂O in the same solvent with equimolar ratios to give a polynuclear complex [Hg(Y³)(NO₃)(µ-NO₃)]ₙ. Also, the reaction between ylides and AgNO₃ in 1:2 molar ratios gave mononuclear complexes. Characterization of these products was carried out by elemental analysis, IR and multinuclear NMR techniques.

KEYWORDS

Phosphorus ylides, triphenylphosphine, mercury(II) nitrate, silver nitrate.

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 utility of metalated phosphorus ylides in synthetic chemistry has been well documented.²⁻⁵ Juxtaposition of the keto group and carb-anion in phosphorus ylides allows for the resonance delocalization of the ylidic electron density while providing additional stabilization to the ylide species. The α-keto-stabilized phosphorus ylides R₃P=C(R')COR" (R, R' and R" = alkyl or aryl groups) show interesting properties such as their high stability and their ambidentate character as ligands (C-versus O-coordination). This ambidentate character can be rationalized in terms of the resonance forms A–C, together with the isomeric form D (Fig. 1). Form B can be considered as leading to coordination by the carbon atom to give a complex of form E, whereas isomers C and D would both lead to coordination by the oxygen atom, affording structures F (transoid) and G (cisoid), respectively. Although many coordination modes are possible for keto ylides,⁶ coordination through carbon is more predominant and observed with soft metal ions, e.g. Pd(II), Pt(II), Ag(I), Hg(II), Au(I) and Au(III),⁷⁻¹¹ whereas O-coordination dominates when the metals involved are hard, e.g., Ti(IV), Zr(IV) and Hf(IV).¹² Only W(0) complexes of the type W(CO)₅L (L = ylide)¹³ and Pd(II) complexes of stoichiometry [Pd(C₆F₅)L₂)(APPY)](ClO₄)⁸ [APPY = Ph₃PCHCOMe; L = PPh₃ and PBu₃; L₂ = bipy] contain stable ylides O-linked to a soft metal centre.

In this work, we describe the synthesis and spectroscopic (IR and NMR) characterization of Hg(II), Cd(II) and Ag(I) complexes of the above ylides.

2. Results and Discussion

Reaction of the ligands with HgX₂ (X = Cl, Br and I) and CdCl₂ in methanol (1:1) yielded the binuclear complexes (see Scheme 1).⁷⁻¹⁴⁻¹⁶ On the other hand, the reaction of ylides with AgNO₃ in a 1:2 ratio...
molar ratio in dichloromethane as solvent gave mononuclear complexes (see Scheme 2).\textsuperscript{17}

According to our previous work\textsuperscript{18} the compounds derived from phosphorus ylides and Hg(NO\textsubscript{3})\textsubscript{2}.H\textsubscript{2}O form polynuclear structures with nitrate anions in the bridges (see Scheme 3).

2.1. IR Spectra

The IR data of the ligands as well as those of the corresponding metal complexes are listed in Table 1. The ν(CO) absorption, which is sensitive to complexation, occurs at 1523, 1527 and 1615 cm\textsuperscript{-1} for Y\textsubscript{1}, Y\textsubscript{2} and Y\textsubscript{3}, respectively, as in the case of other resonance-stabilized ylides.\textsuperscript{19} Coordination of the ylides through the carbon atom 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 1588–1735 cm\textsuperscript{-1}, at higher wavenumbers with respect to the free ylide. The ν(P\textsuperscript{+}\textsubscript{–}C–\textsubscript{y}) mode, which is also diagnostic for the coordination modes, occurs at 873 and 874 cm\textsuperscript{-1} for Y\textsubscript{1} and Y\textsubscript{2}. In the present study, the ν(P\textsuperscript{+}\textsubscript{–}C–\textsubscript{y}) values for Hg(II) complexes were shifted to lower wavenumbers and were observed in the range of 811–818 cm\textsuperscript{-1}, suggesting some removal of electron density from the P–C bond.\textsuperscript{14,15,18}

2.2. $^1$H and $^{31}$P NMR Spectra

The signals due to methinic protons, when recorded in CDCl\textsubscript{3} or DMSO-d\textsubscript{6} were broad or unobserved, probably due to the very low solubility of the complexes. The expected higher field shifts of $^{31}$P and $^1$H signals for the PCH group upon complexation were observed in their corresponding spectra. The higher field shifts of the CH proton upon coordination in the $^1$H NMR spectra show the coordination of the ylides through methinic carbon atoms. The proton-decoupled $^{31}$P NMR spectra show only one sharp singlet between δ 16.4 and 24.5 ppm in these complexes. $^{31}$P chemical shift values for complexes appear to higher field by about δ 3–11 ppm with respect to the parent ylides (δ 14.2, 13.8 and 13.9 ppm for Y\textsubscript{1}, Y\textsubscript{2} and Y\textsubscript{3} respectively), indicating that coordination of the ylide has occurred. Appearance of one set of signals for the PCH group in both the $^{31}$P and $^1$H NMR spectra indicates the presence of only one molecule for all complexes,\textsuperscript{7} as expected for C-coordination. It must be noted that O-coordination of the ylides generally leads to the formation of cis and trans isomers, giving rise to two different signals in the $^{31}$P and $^1$H NMR spectra (see Fig. 1).\textsuperscript{8,12}

2.3. $^{13}$C NMR Spectra

The most interesting aspect of the $^{13}$C NMR spectra of the complexes is the low field shift of the signals due to the ylidic carbon. Such a low field shift was observed in PdCl$_2(η^2$-2-CH$_3$) (C$_2$H$_4$)$_2$PCHCOR (X = H, CH$_3$, R = CH$_3$, C$_6$H$_5$), and was attributed to a change in hybridization of the ylidic carbon.\textsuperscript{23} Similar low field shifts of δ 3–7 ppm with reference to the parent ylide were observed in the carbon atom of the P–C bond of the complexes.
were also observed in the case of [(C₆H₅)₃PC₅H₄HgI₂]₂ and in our synthesized mercury complexes. The δC shifts of the CO group in the complexes are lower than noted for the same carbon in the parent ylides, indicating much lower shielding of the CO group in the complexes.

3. Experimental

Methylnaphthyl ketone, methyl-2-thienyl ketone and triphenylphosphine with a chloroform solution of 2-bromomethylketone and 2-bromomethyl-2-thienyl ketone were synthesized by the reaction of Y³ with the parent ylides, indicating much lower shielding of the CO group in the complexes. No coupling to the carbon in the parent ylides, indicating much lower shielding of the carbon of the CO group in these complexes. Failure to observe satellites in the above spectra was previously noted in the ylide complexes of Hg(II) and Ag(I), which had been assigned to fast exchange of the ligand with the metal complex.

3.1. Synthesis of Y¹ (general procedure)

To a chloroform solution (25 mL) of triphenylphosphine (0.131 g, 0.5 mmol) was added 2-bromomethylnaphthyl ketone (0.129 g, 0.5 mmol) and the mixture was stirred for 12 h. The solid product (phosphonium salt) was filtered off, washed with diethyl ether and dried under reduced pressure. Further treatment with aqueous NaOH solution led to elimination of HBr, giving the free ligand Y¹. Yield: 84 %. M.p. 193–194 °C. % Anal. calcd. (found) for C₈₇H₇₉OP: C, 83.70 (83.46); H, 5.39 (5.31). IR (KBr disk): ν (CO) = 1577 (CO) and 873 (P-C) cm⁻¹. ¹H NMR (CDCl₃): δ 4.58 (d, JPC = 25.26 Hz, 1H, CH) and 7.23–8.49 ppm (m, 22H, arom.). ³¹P NMR (CDCl₃): δ 14.11 ppm. ¹³C NMR (CDCl₃): δ 50.77 (d, JPC = 108.92 Hz, CH), 126.76 (d, JPC = 92.27 Hz, PPh₃ (i)), 128.72 (d, JPC = 129.39 Hz, PPh₃ (m)), 131.97 (d, JPC = 2.32 Hz, PPh₃ (p)), 134.32 (d, JPC = 10.29 Hz, PPh₃ (o)), 138.20 (d, JPC = 14.10 Hz, Cl₁), 125.58, 126.12, 126.58, 127.01, 128.81, 132.89, 133.96 (C₂–C₁₀) and 184.62 ppm (s, CO).
3.7. Data for [(Y1)2.HgI2]2 (4)
Yield: 71 %. M.p. 202–204 °C. % Anal. calc'd. (found) for C48H38Br4Hg2O2P2S2: C, 38.60 (39.65); H, 2.56 (2.51); IR (KBr disk): ν123.64, 127.10 and 127.44 (C1–C10), 124.51 (d, 13C). H NMR (DMSO-d6): δ 56.23 (d, 13C). 1H NMR (DMSO-d6): δ 19.69 Hz (C1) and 190.42 ppm (s, CO).

3.8. Data for [(Y2)2.Ag]NO3 (5)
Yield: 74 %. M.p. 198–199 °C. % Anal. calc'd. (found) for C48H38AgNO5P2S2: C, 40.72 (42.22); H, 2.62 (2.61). IR (KBr disk): ν 1611 (CO) and 813 cm –1 (P-C). 1H NMR (DMSO-d6): δ 19.46 (d, 13C). 13C NMR (DMSO-d6): δ 21.59 (s, CH3), 24.46 (d, 13C). PPh3 (s, (C2)), 129.24 (d, 13C). 13C NMR (DMSO-d6): δ 133.18 (d, 13C). 31P NMR (DMSO-d6): δ 11.74 Hz (C1) and 183.43 ppm (s, CO).

3.9. Data for [(Y3)2.Ag]NO3 (6)
Yield: 66 %. M.p. 197–198 °C. % Anal. calc'd. (found) for C60H38AgNO7P2: 2H2O: C, 64.87 (64.64); H, 5.63 (5.35). IR (KBr disk): ν 3403 (OH) and 3488 cm –1 (OH). 1H NMR (DMSO-d6): δ 6.89–7.94 ppm (m, 18H, arom.). 31P NMR (DMSO-d6): δ 144.98 (d, 13C). 13C NMR (DMSO-d6): δ 21.59 (s, CH3), 68.27 (s, CH2).

3.10. Synthesis of [(Y1)2.AgNO3(NO3)(µ-NO3)]n (7)
A solution of CdCl2.H2O (0.057 g, 0.3 mmol) in methanol (15 mL) was added to a solution of Y (0.14 g, 0.3 mmol) in dry methanol (15 mL) and stirred for 14 h. A white product formed by slow evaporation of the solvent. The product was washed several times with petroleum ether and dried in vacuo. Yield: 0.296 g (73 %). M.p. 165–168 °C. % Anal. calc'd. (found) for C48H38AgNO5P2S2: C, 61.15 (60.20); H, 4.06 (3.74); N, 1.49 (1.68). IR (KBr disk): ν 1588 (CO) and 861 cm –1 (P-C). 1H NMR (DMSO-d6): δ 5.09 (br, 1H, CH) and 6.89–7.94 ppm (s, H1, CH3, arom.). 31P NMR (DMSO-d6): δ 24.0 ppm (s, CH2). C60H38I4Hg2O2P2: C, 34.28 (35.57); H, 2.28 (2.55). IR (KBr disk): ν 1620 (CO) and 813 cm –1 (P-C). 1H NMR (DMSO-d6): δ 19.69 Hz (C1) and 190.42 ppm (s, CO).

3.11. Synthesis of [(Y2)2.AgNO3]11 (8)
A solution of AgNO3 (0.09 g, 0.5 mmol) in dichloromethane (10 mL) was added to a solution of Y (0.45 g, 1 mmol) in dichloromethane (10 mL) and stirred for 12 h; the solution was protected from light with aluminum foil. A white product formed by slow evaporation of the solvent. The product was washed several times with petroleum ether and dried in vacuo. Yield: 0.296 g (73 %). M.p. 165–168 °C. % Anal. calc'd. (found) for C48H38AgNO5P2S2: C, 61.15 (60.20); H, 4.06 (3.74); N, 1.49 (1.68). IR (KBr disk): ν 1588 (CO) and 861 cm –1 (P-C). 1H NMR (DMSO-d6): δ 5.09 (br, 1H, CH) and 6.89–7.94 ppm (s, H1, CH3, arom.). 31P NMR (DMSO-d6): δ 24.0 ppm (s, CH2). C60H38I4Hg2O2P2: C, 34.28 (35.57); H, 2.28 (2.55). IR (KBr disk): ν 1620 (CO) and 813 cm –1 (P-C). 1H NMR (DMSO-d6): δ 19.69 Hz (C1) and 190.42 ppm (s, CO).

3.12. Data for [(Y1)2.AgNO3]9 (9)
A solution of AgNO3 (0.09 g, 0.5 mmol) in dichloromethane (10 mL) was added to a solution of Y (0.45 g, 1 mmol) in dichloromethane (10 mL) and stirred for 12 h; the solution was protected from light with aluminum foil. A white product formed by slow evaporation of the solvent. The product was washed several times with petroleum ether and dried in vacuo. Yield: 0.296 g (73 %). M.p. 165–168 °C. % Anal. calc'd. (found) for C48H38AgNO5P2S2: C, 61.15 (60.20); H, 4.06 (3.74); N, 1.49 (1.68). IR (KBr disk): ν 1588 (CO) and 861 cm –1 (P-C). 1H NMR (DMSO-d6): δ 5.09 (br, 1H, CH) and 6.89–7.94 ppm (s, H1, CH3, arom.). 31P NMR (DMSO-d6): δ 24.0 ppm (s, CH2). C60H38I4Hg2O2P2: C, 34.28 (35.57); H, 2.28 (2.55). IR (KBr disk): ν 1620 (CO) and 813 cm –1 (P-C). 1H NMR (DMSO-d6): δ 19.69 Hz (C1) and 190.42 ppm (s, CO).

3.13. Synthesis of [(HgY)2(NO3)6(c-NO3)]10 (10)
A solution of Hg(NO3)2.H2O (0.016 g, 0.3 mmol) in methanol (15 mL) was added to a solution of Y (0.14 g, 0.3 mmol) in dry methanol (15 mL) and stirred for 14 h. A white product formed by slow evaporation of the solvent. The product was washed several times with dry diethyl ether and dried in vacuo. Yield: 0.214 g (73 %). M.p. 165–168 °C. % Anal. calc'd. (found) for C48H38AgNO5P2S2: C, 61.15 (60.20); H, 4.06 (3.74); N, 1.49 (1.68). IR (KBr disk): ν 1620 (CO) and 813 cm –1 (P-C). 1H NMR (DMSO-d6): δ 19.69 Hz (C1) and 190.42 ppm (s, CO).

A solution of C2CdCl2.H2O (0.058 g, 0.3 mmol) in acetonitrile (15 mL) was added to a solution of Y (0.13 g, 0.3 mmol) in dry methanol (15 mL) and stirred for 3 h. A white product formed by slow evaporation of the solvent. The product was washed several times with dry diethyl ether and dried in vacuo. Yield: 0.138 g (73 %). M.p. 158–161 °C. % Anal. calc'd. (found) for C48H38AgNO5P2S2: C, 61.15 (60.20); H, 4.06 (3.74); N, 1.49 (1.68). IR (KBr disk): ν 1735 (CO) and 805 cm –1 (P-C). 1H NMR (DMSO-d6): δ 2.36 (s, 9H, CH3), 3.35 (s, 2H, CH2), 4.07 (br, 1H, CH) and 7.35–7.47 ppm (m, 17H, arom.). 31P NMR (DMSO-d6): δ 22.8 ppm. 13C NMR (DMSO-d6): δ 21.59 (s, CH3), 68.27 (s, CH2), 124.28–145.72 (arom.) and 167.52 ppm (s, CO).

4. Conclusion
The present study describes the synthesis and characterization of some binuclear Hg(II) and Cd(II), mononuclear Ag(I) and one polynuclear Hg(II) complexes of phosphorus ylides. On the basis of the physicochemical and spectroscopic data we propose that the ligands herein exhibit monodentate C-coordination to the metal centres.

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References