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

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ABSTRACT

Reaction of two new phosphorus ylides $Ph_3PCHCOC_{10}H_7$ (Y^1) and $Ph_3PCHCOC_4H_3S$ (Y^2) with mercury(II) halides and a previously reported ylide (p-tolyl)$_3$PCHCOOCH$_2$Ph (Y^3) with $CdCl_2$ in equimolar ratios using methanol as solvent yielded binuclear complexes of the type $[(Y).HgX_2]_2$ ($Y = Y^1$ and Y^2, X = Cl, Br and I) and a complex of $[(Y^3).HgCl_2]_2$. The latter ylide reacts with $Hg(NO_3)_2.H_2O$ in the same solvent with equimolar ratios to give a polynuclear complex $[Hg(Y^3)(NO_3)(\mu\text{-}NO_3)]_n$. Also, the reaction between ylides and $AgNO_3$ 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 carbanion 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 $R_3P{=}C(R')COR''$ (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 $[Pd(C_6F_5)L_2)(APPY)](ClO_4)$[8] [APPY = $Ph_3PCHCOMe$; L = PPh_3 and PBu_3; L_2 = 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.

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2. Results and Discussion

Reaction of the ligands with HgX_2 (X = Cl, Br and I) and $CdCl_2$ in methanol (1:1) yielded the binuclear complexes (see Scheme 1).[7,14–16]

On the other hand, the reaction of ylides with $AgNO_3$ in a 1:2

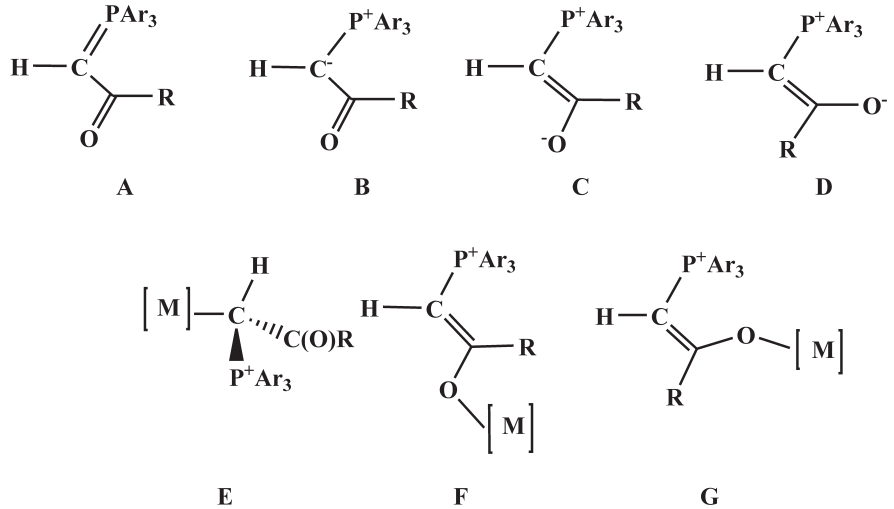
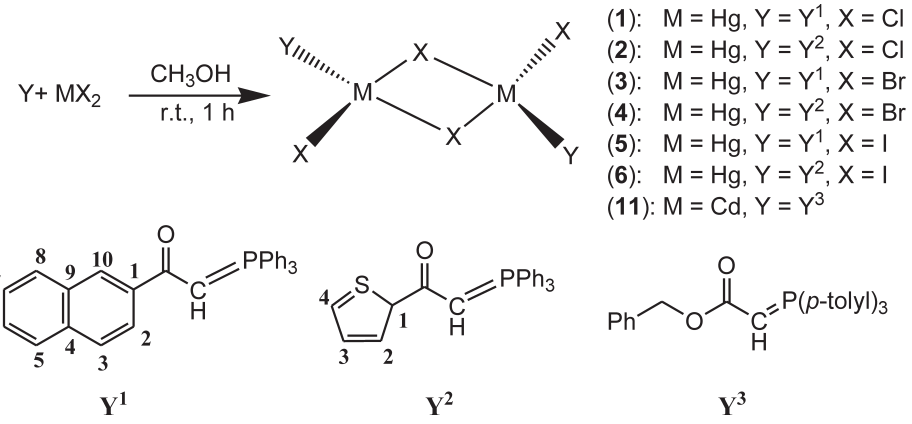


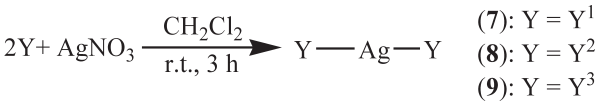
Figure 1 Structures of phosphorus ylides and their complexes.



Scheme 1

molar ratio in dichloromethane as solvent gave mononuclear complexes (see Scheme 2).[17]

According to our previous work[18] the compounds derived from phosphorus ylides and $Hg(NO_3)_2.H_2O$ form polynuclear structures with nitrate anions in the bridges (see Scheme 3).



Scheme 2

2.1. IR Spectra

The IR data of the ligands as well as those of the corresponding metal complexes are listed in Table 1.

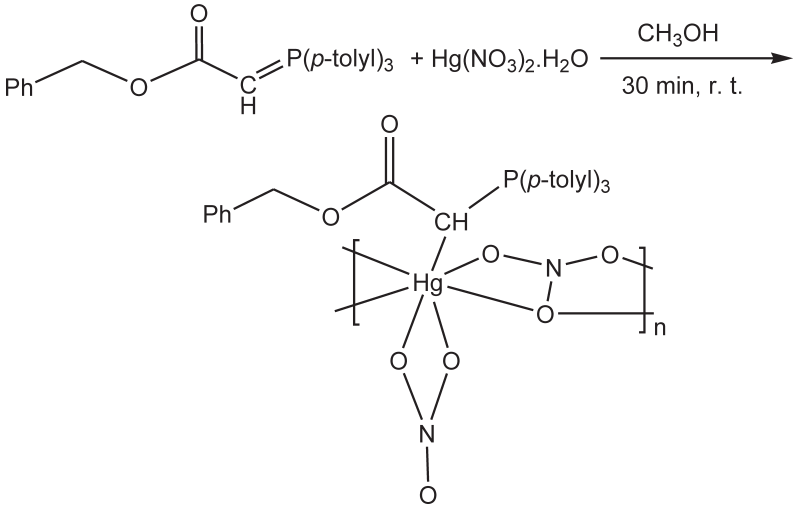
The ν(CO) absorption, which is sensitive to complexation, occurs at 1523, 1527 and 1615 cm^{-1} for Y^1, Y^2 and Y^3, respectively, as in the case of other resonance-stabilized ylides.[19] Coordination of the ylides through the carbon atom causes an increase in ν(CO), while for O-coordination a lowering of ν(CO) is expected. The infrared spectra of complexes in the solid state show ν(CO) in the range of 1588–1735 cm^{-1}, at higher wavenumbers with respect to the free ylide. The $\nu(P^+\text{-}C^-_y)$ mode, which is also diagnostic for the coordination modes, occurs at 873 and 874 cm^{-1} for Y^1 and Y^2. In the present study, the $\nu(P^+\text{-}C^-_y)$) values for Hg(II) complexes were shifted to lower wavenumbers and were observed in the range of 811–818 cm^{-1}, suggesting some removal of electron density from the P–C bond.[14,15,18]

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

The signals due to methinic protons, when recorded in $CDCl_3$ or DMSO-d_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^1, Y^2 and Y^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,[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).[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 $PdCl(\eta^3\text{-}2\text{-}XC_3H_4)(C_6H_5)_3PCHCOR$ (X = H, CH_3; R = CH_3, C_6H_5), and was attributed to a change in hybridization of the ylidic carbon.[23] Similar low field shifts of δ 3–7 ppm with reference to the parent ylide



Scheme 3

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

Compound [a]	ν(CO)/cm^{-1}	Ref.
$Ph_3PCHCON(CH_3)_2$	1530	19
APPY	1530	20
BPPY	1525	21
$Ph_3PCHCOC_{10}H_7$ (Y^1)	1523	This work
$Ph_3PCHCOC_4H_3O$ (Y^2)	1527	This work
$(C_6H_4CH_3)_3PCHCOOCH_2C_6H_5$ (Y^3)	1615	14
C-coordination		
$[(Y^1).HgCl_2]_2$	1631	This work
$[(Y^2).HgCl_2]_2$	1613	This work
$[(Y^1).HgBr_2]_2$	1626	This work
$[(Y^2).HgBr_2]_2$	1611	This work
$[(Y^1).HgI_2]_2$	1620	This work
$[(Y^2).HgI_2]_2$	1605	This work
$[(Y^1)_2.Ag]NO_3$	1603	This work
$[(Y^2)_2.Ag]NO_3$	1588	This work
$[(Y^3)_2.Ag]NO_3$	1670	This work
$[Hg(Y^3)(NO_3)(\mu\text{-}NO_3)]_n$	1703	This work
$[(Y^3).CdCl_2]_2$	1735	This work
O-coordination		
$[(Sn(CH_3)_3.BPPY]Cl$	1480	22
$[(SnPh_3).BPPY]Cl$	1470	22
$[Pd(C_6F_5)(PPh_3)_2(APPY)]ClO_4$	1513	12

[a] APPY = acetylmethylenetriphenylphosphorane; BPPY = benzoylmethylenephenylphosphorane.

were also observed in the case of $[(C_6H_5)_3PC_5H_4HgI_2]_2$,[17] and in our synthesized mercury complexes.[14,15,18] The ^{13}C 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 carbon of the CO group in these complexes. No coupling to metal ions was observed at room temperature in the ^{1}H, ^{31}P and ^{13}C NMR spectra. Failure to observe satellites in the above spectra was previously noted in the ylide complexes of Hg(II)[10] and Ag(I),[17] which had been assigned to fast exchange of the ligand with the metal complex.

3. Experimental

Methylnaphthyl ketone, methyl-2-thienyl ketone and triphenylphosphine were purchased from Merck (Tehran, Iran). The ligands **Y^1** and **Y^2** were synthesized by the reaction of triphenylphosphine with a chloroform solution of 2-bromomethylnaphthyl ketone and 2-bromomethyl-2-thienyl ketone and then deprotonated by NaOH. The ligand **Y^3** was prepared and characterized according to the published procedure.[14] All solvents were dried by reported methods.[24]

Solution-state ^{1}H, ^{31}P and ^{13}C NMR spectra at ambient temperature were obtained in DMSO-d_6 or $CDCl_3$ as solvents using a Jeol FX 90 Q FT-NMR spectrometer (Jeol, Ltd., Tokyo, Japan). Melting points were measured on a Stuart SMP3 apparatus (Bibby Scientific, Ltd., Stone, UK). Elemental analyses for C, H and N were performed using a PE 2400 series analyzer (Perkin-Elmer, Shelton, CT, USA). IR spectra were recorded on KBr pellets using a Shimadzu 435-U-04 spectrophotometer (Columbia, MD, USA) in the region of 4000–550 cm^{-1}. All the above equipment is located at Bu-Ali Sina University, Hamedan, Iran.

3.1. Synthesis of Y^1 (general procedure)

To a chloroform solution (25 mL) of triphenylphosphine (0.131 g, 0.5 mmol) was added 2-bromomethylnaphthyl ketone (0.123 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 Y^1. Yield: 84 %. M.p. 193–194 °C. % Anal. calcd. (found) for $C_{30}H_{23}OP$: C, 83.70 (83.46); H, 5.39 (5.31). IR (KBr disk): ν 1577 (CO) and 873 (P-C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.58 (d, $^2J_{PH}$ = 25.26 Hz, 1H, CH) and 7.23–8.49 ppm (m, 22H, arom.). ^{31}P NMR ($CDCl_3$): δ 14.1 ppm. ^{13}C NMR ($CDCl_3$): δ 50.77 (d, $^1J_{PC}$ = 108.92 Hz, CH), 126.76 (d, $^1J_{PC}$ = 92.27 Hz, PPh_3 (*i*)), 128.72 (d, $^3J_{PC}$ = 12.39 Hz, PPh_3 (*m*)), 131.97 (d, $^4J_{PC}$ = 2.32 Hz, PPh_3 (*p*)), 134.32 (d, $^2J_{PC}$ = 10.29 Hz, PPh_3 (*o*)), 138.20 (d, $^3J_{PC}$ = 14.10 Hz, (C1)), 125.58, 126.12, 126.58, 127.01, 128.81, 132.89, 133.96 (C_2–C_{10}) and 184.62 ppm (s, CO).

3.2. Data for Y^2

Yield: 79 %. M.p. 219–221 °C. % Anal. calcd. (found) for $C_{24}H_{19}OPS$: C, 74.59 (75.14); H, 4.96 (4.90). IR (KBr disk): ν 1527 (CO) and 874 (P-C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.32 (d, $^2J_{PH}$ = 23.11 Hz, 1H, CH) and 7.27–7.70 ppm (m, 18H, arom). ^{31}P NMR ($CDCl_3$): δ 13.8 ppm. ^{13}C NMR ($CDCl_3$): δ 49.82 (d, $^1J_{PC}$ = 112.77 Hz, CH), 125.63 (s, (C3)), 126.74 (s, (C2)), 126.42 (d, $^1J_{PC}$ = 91.23 Hz, PPh_3 (*i*)), 126.72 (s, (C4)), 128.53 (d, $^3J_{PC}$ = 18.63 Hz, PPh_3 (*m*)), 131.80 (d, $^4J_{PC}$ = 2.74 Hz, PPh_3 (*p*)), 132.70 (d, $^2J_{PC}$ = 10.36 Hz, PPh_3 (*o*)), 148.32 (d, $^3J_{PC}$ = 18.06 Hz, (C1)) and 177.81 ppm (d, $^2J_{PC}$ = 3.71 Hz, CO).

3.3. Data[14] for Y^3

IR (KBr disk): ν 1615 (CO) and 811 (P-C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.88 (d, $^2J_{PH}$ = 15.59 Hz, 1H, CH) and 7.16–7.88 ppm (m, 17H, arom.). ^{31}P NMR ($CDCl_3$): δ 13.9 ppm. ^{13}C NMR ($CDCl_3$): δ 30.5 (d, $^1J_{PC}$ = 125.03 Hz, CH) and 170.39 ppm (s, CO).

3.4. Synthesis of $[(Y^1).HgCl_2]_2$ (1) (general procedure for Hg(II) halide complexes)

To $HgCl_2$ (0.67 g, 0.25 mmol) dissolved in 5 mL of dried methanol was added Y^1 (0.107 g, 0.25 mmol) at room temperature. The mixture was stirred for 1 h. The white solid product was filtered, washed with diethyl ether and dried under reduced pressure. Yield: 87 %. M.p. 241–243 °C. % Anal. calcd. (found) for $C_{60}H_{46}Cl_4Hg_2O_2P_2$: C, 51.33 (51.68); H, 3.30 (3.26). IR (KBr disk): ν 1631 (CO) and 821 (P-C) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 5.73 (br, 1H, CH), 7.70–7.97 and 8.82 ppm (m, 22H, arom.). ^{31}P NMR (DMSO-d_6): δ 24.1 ppm. ^{13}C NMR (DMSO-d_6): δ 126.57 (d, $^1J_{PC}$ = 100.94 Hz, PPh_3 (*i*)), 130.33 (d, $^3J_{PC}$ = 2.18 Hz, PPh_3 (*m*)), 133.09 (s, PPh_3 (*p*)), 133.22 (d, $^2J_{PC}$ = 1.77 Hz, PPh_3 (*o*)), 135.47 (d, $^3J_{PC}$ = 6.89 Hz, (C1)) and 191.12 ppm (s, CO).

3.5. Data for $[(Y^2).HgCl_2]_2$ (2)

Yield: 62.5 %. M.p. 242–243 °C. % Anal. calcd. (found) for $C_{48}H_{38}Cl_4Hg_2O_2P_2S_2$: C, 43.81 (43.98); H, 2.91 (2.15). IR (KBr disk): ν 1613 (CO) and 818 (P-C) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 5.32 (br, 1H, CH) and 7.18–8.02 ppm (m, 18H, arom.). ^{31}P NMR (DMSO-d_6): δ 22.9 ppm. ^{13}C NMR (DMSO-d_6): δ 123.07 (d, $^1J_{PC}$ = 90.36 Hz, PPh_3 (*i*)), 128.09 (s, (C2)), 128.09 (s, (C3)), 129.35 (d, $^3J_{PC}$ =12.39 Hz, PPh_3 (*m*)), 132.99 (s, PPh_3 (*p*)), 133.22 (d, $^2J_{PC}$ = 10.27 Hz, PPh_3 (*o*)), 133.45 (s, (C4)), 144.34 (d, $^3J_{PC}$ = 8.24 Hz, (C1)) and 183.97 ppm (s, CO).

3.6. Data for $[(Y^1).HgBr_2]_2$ (3)

Yield: 80 %. M.p. 218–220 °C. % Anal. calcd. (found) for $C_{60}H_{46}Br_4Hg_2O_2P_2$: C, 45.56 (45.13); H, 2.93 (2.65). IR (KBr disk): ν 1626 (CO) and 816 cm^{-1} (P-C). ^{1}H NMR (DMSO-d_6): δ 5.66 (d, $^2J_{PH}$ =5.02 Hz, 1H, CH), 7.70–7.96 and 8.81 ppm (m, 22H, arom.). ^{31}P NMR (DMSO-d_6): δ 23.6 ppm. ^{13}C NMR (DMSO-d_6):

δ 126.63 (d, $^1J_{PC}$ = 92.70 Hz, PPh_3 (*i*)), 121.39, 125.33, 126.41, 127.35 and 129.49 (C2–C10), 130.30 (d, $^3J_{PC}$ = 2.20 Hz, PPh_3 (*m*)), 133.11 (s, PPh_3 (*p*)), 134.268 (d, $^2J_{PC}$ = 1.75 Hz, PPh_3 (*o*)), 156.23 (d, $^3J_{PC}$ = 9.69 Hz (C1)) and 190.42 ppm (s, CO).

3.7. Data for $[(Y^2).HgBr_2]_2$ (4)

Yield: 71 %. M.p. 202–204 °C; % Anal. calcd. (found) for $C_{48}H_{38}Br_4Hg_2O_2P_2S_2$: C, 38.60 (39.65); H, 2.56 (2.51); IR (KBr disk): ν 1611 (CO) and 814 cm^{-1} (P-C). ^1H NMR (DMSO-d_6): δ 5.29 (d, $^2J_{PH}$ = 7.07 Hz, 1H, CH) and 7.17–7.97 ppm (m, 18H, arom.). ^{31}P NMR (DMSO-d_6): δ 22.3 ppm. ^{13}C NMR (DMSO-d_6): δ 47.13 (s, CH), 123.11 (d, $^1J_{PC}$ = 89.05 Hz, PPh_3 (*i*)), 127.96 (s, (C3)), 127.96 (s, (C2)), 129.24 (d, $^3J_{PC}$ = 12.25 Hz, PPh_3 (*m*)), 131.71 (s, PPh_3 (*p*)), 133.18 (d, $^2J_{PC}$ = 10.18 Hz, PPh_3 (*o*)), 133.34 (s, (C4)), 144.66 (d, $^3J_{PC}$ = 12.25 Hz, (C1)) and 183.54 ppm (s, CO).

3.8. Data for $[(Y^1).HgI_2]_2$ (5)

Yield: 74 %. M.p. 198–199 °C; % Anal. calcd. (found) for $C_{60}H_{46}Hg_2I_4O_2P_2$: C, 40.72 (42.22); H, 2.62 (2.61). IR (KBr disk): ν 1620 (CO) and 813 cm^{-1} (P-C). ^1H NMR (DMSO-d_6): δ 5.39 (d, $^2J_{PH}$ = 10.30 Hz, 1H, CH) and 7.66–8.68 ppm (m, 22H, arom.). ^{31}P NMR (DMSO-d_6): δ 21.6 ppm. ^{13}C NMR (DMSO-d_6): δ 123.25 (d, $^1J_{PC}$ = 89.68 Hz, PPh_3 (*i*)), 124.34, 127.36, 133.1, 133.32 and 134.22 (C1–C10), 129.16 (d, $^3J_{PC}$ = 12.14 Hz, PPh_3 (*m*)), 132.03 (s, PPh_3 (*p*)), 133.11 (d, $^2J_{PC}$ = 9.30 Hz, PPh_3 (*o*)) and 188.83 ppm (s, CO).

3.9. Data for $[(Y^2).HgI_2]_2$ (6)

Yield: 66 %. M.p. 197–198 °C; % Anal. calcd. (found) for $C_{48}H_{38}I_4Hg_2O_2P_2S_2$: C, 34.28 (35.57); H, 2.28 (2.55). IR (KBr disk): ν 1605 (CO) and 811 cm^{-1} (P-C). ^1H NMR (DMSO-d_6): δ 5.08 (d, $^2J_{PH}$ = 10.39 Hz, 1H, CH) and 7.15–7.82 ppm (m, 18H, arom.). ^{31}P NMR (DMSO-d_6): δ 20.7 ppm. ^{13}C NMR (DMSO-d_6): δ 123.25 (d, $^1J_{PC}$ = 89.68 Hz, PPh_3 (*i*)), 128.05 (s, (C3)), 128.05 (s, (C2)), 129.36 (d, $^3J_{PC}$ = 12.45 Hz, PPh_3 (*m*)), 131.78 (s, PPh_3 (*p*)), 133.22 (d, $^2J_{PC}$ = 10.25 Hz, PPh_3 (*o*)), 133.45 (s, (C4)), 144.98 (d, $^3J_{PC}$ = 11.74 Hz, (C1)) and 183.43 ppm (s, CO).

3.10. Synthesis of $[(Y^1)_2.Ag]NO_3$ (7) (general procedure for Ag(I) complexes)

To a dichloromethane solution (5 mL) of $AgNO_3$ (1 mmol, 0.17 g) was added Y^1 (0.86 g, 2 mmol). The reaction mixture was stirred in the dark. After 3 h, the solvent was evaporated. The residues were extracted with dichloromethane. The solution was concentrated and diethyl ether or n-hexane was added to complete precipitation as a white solid. Yield: 69 %. M.p. 163–165 °C. % Anal. calcd. (found) for $C_{60}H_{46}AgNO_5P_2$: C, 69.91 (71.40); H, 4.50 (4.39); N, 1.36 (1.71). IR (KBr disk): ν 1603 (CO) and 873 cm^{-1} (P-C). ^1H NMR (DMSO-d_6): δ 5.26 (d, $^2J_{PH}$ = 10.66 Hz, 1H, CH) and 7.52–8.61 ppm (m, 22H, arom.). ^{31}P NMR (DMSO-d_6): δ 22.8 ppm. ^{13}C NMR (DMSO-d_6): δ 37.80 (d, $^1J_{PC}$ = 76.16 Hz, CH), 123.64, 127.10 and 127.44 (C1–C10), 124.51 (d, $^1J_{PC}$ = 89.21 Hz, PPh_3 (*i*)), 134.77 128.96 (d, $^3J_{PC}$ = 12.09 Hz, PPh_3 (*m*)), 130.08 (s, PPh_3 (*p*)), 132.68 (d, $^2J_{PC}$ = 9.21 Hz, PPh_3 (*o*)) and 190.50 ppm (s, CO).

3.11. Data for $[(Y^2)_2.Ag]NO_3$ (8)

To a dichloromethane solution (5 mL) of $AgNO_3$ (0.17 g, 1 mmol) was added Y^2 (0.77 g, 2 mmol). The reaction mixture was stirred in the dark. After 3 h, the solvent was evaporated and the residues were extracted with dichloromethane. The solution was concentrated and diethyl ether or n-hexane was added to complete precipitation as a white solid. Yield: 66 %. M.p. 182–184 °C; % Anal. calcd. (found) for $C_{48}H_{38}AgNO_5P_2S_2$: 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-d_6): δ 5.09 (br, 1H, CH) and 6.89–7.94 ppm (m, 18H, arom). ^{31}P NMR (DMSO-d_6): δ 24.0 ppm. ^{13}C NMR (DMSO-d_6): δ 36.33 (d, $^1J_{PC}$ = 70.08 Hz, CH), 124.34 (d, $^1J_{PC}$ = 90.02 Hz, PPh_3 (*i*)), 127.94, 132.93 and 133.88 (C2, C3 and C4), 129.11 (d, $^3J_{PC}$ = 12.57 Hz, PPh_3 (*m*)), 130.29 (d, $^4J_{PC}$ = 4.75 Hz, PPh_3 (*p*)), 132.71 (d, $^2J_{PC}$ = 9.68 Hz, PPh_3 (*o*)), 144.81(d, $^3J_{PC}$ = 13.83 Hz, (C1)) and 184.67 ppm (CO).

3.12. Data for $[(Y^3)_2.Ag]NO_3$ (9)

A solution of $AgNO_3$ (0.09 g, 0.5 mmol) in dichloromethane (10 mL) was added to a solution of Y^3 (0.45 g, 1 mmol) in dichloromethane (10 mL) and stirred for 12 h; the solution was protected from light with aluminium 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. calcd. (found) for $C_{60}H_{58}AgNO_7P_2.2H_2O$: C, 64.87 (64.64); H, 5.63 (5.35); N, 1.26 (1.38). IR (KBr disk): ν 1670 (CO) and 806 cm^{-1} (P-C). ^1H NMR ($CDCl_3$): δ 2.41 (s, 9H, CH_3), 3.37 (br, 1H, CH), 4.88 (s, 2H, CH_2) and 7.27–7.43 ppm (m, 17H, arom.). ^{31}P NMR ($CDCl_3$): δ 24.5 ppm. ^{13}C NMR ($CDCl_3$): δ 21.57 (s, CH_3), 24.46 (d, $^1J_{PC}$ = 68.03 Hz, CH), 65.90 (s, CH_2), 121.28–144.56 (arom.) and 171.81 ppm (s, CO).

3.13. Synthesis of $[Hg(Y^3)(NO_3)(\mu\text{-}NO_3)]_n$ (10)

A solution of $Hg(NO_3)_2.H_2O$ (0.106 g, 0.3 mmol) in methanol (15 mL) was added to a solution of Y^3 (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. calcd. (found) for $C_{30}H_{29}HgN_2O_8P$: C, 46.37 (46.49); H, 3.76 (3.72); N, 3.60 (3.11). IR (KBr disk): ν 1703 (CO) and 807 cm^{-1} (P-C). ^1H NMR ($CDCl_3$): δ 2.42 (s, 9H, CH_3), 4.65 (d, $^2J_{PH}$ = 4.48 Hz, 1H, CH), 5.12 (s, 2H, CH_2) and 7.26–7.57 ppm (m, 17H, arom.). ^{31}P NMR ($CDCl_3$): δ 22.8 ppm. ^{13}C NMR ($CDCl_3$): δ 21.59 (s, CH_3), 68.27 (s, CH_2), 128.24–145.72 (arom.) and 167.52 ppm (s, CO).

3.14. Synthesis of $[(Y^3).Cd_2]_2$ (11)

A solution of $CdCl_2.H_2O$ (0.058 g, 0.3 mmol) in acetonitrile (15 mL) was added to a solution of Y^3 (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. calcd. (found) for $C_{60}H_{58}Cd_2Cl_4O_4P_2$: C, 56.67 (56.72); H, 4.60 (4.62). IR (KBr disk): ν 1735 (CO) and 805 cm^{-1} (P-C). ^1H NMR (DMSO-d_6): δ 2.36 (s, 9H, CH_3), 3.35 (s, 2H, CH_2), 4.07 (br, 1H, CH) and 7.35–7.47 ppm (m, 17H, arom.). ^{31}P NMR (DMSO-d_6): δ 16.4 ppm. ^{13}C NMR (DMSO-d_6): δ 20.65 (s, CH_3), 48.76(s, CH_2), 117.25–145.77 (arom.) and 170.16 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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