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Structural, theoretical and multinuclear NMR study of mercury(II) and silver(I) complexes with two new ambidentate phosphorus ylides

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ABSTRACT

Reactions of new α -ketostabilized phosphorus ylides of the type Ph₃P = CHC(O)R (R = 2,4-dichlorophenyl (**L**¹) and 4-isopropylphenyl (**L**²)) with AgNO₃ and Hg(NO₃)₂.H₂O, using methanol as a solvent, are reported. The crystal structures of **L**² and [Ag(L²)₂(NO₃)] (**2**) have been determined. Characterization of the obtained compounds was also performed by elemental analysis, IR, ¹H, ³¹P and ¹³C NMR. Theoretical studies were carried out on the silver(I) complexes. It was shown that the nitrate ion shows a bonding interaction with the silver ion.

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1. Introduction

The utility of metallated phosphorus ylides in synthetic chemistry has been well documented [1,2]. The synthesis of complexes derived from ylides and Ag(I) began in 1975 by Yamamoto et al. [3]. Other types of ylide complexes of silver(I) have been reported [4–9]. In 1987 and 1983, Vicente et al. [10,11] reported the crystal structures of Ag(I) complexes of phosphorus ylides. The synthesis of complexes derived from phosphorus ylides and Hg(II) salts was limited to Hg(II) halides and was started in 1965 by Nesmeyanov et al. [12]. Weleski et al. [13] in 1975 proposed a symmetric halide-bridged dimeric structure for Hg(II) halide complexes, while Kalyanasundari et al. [14] in 1995 reported an asymmetric halidebridged structure. In 2007 we reported the first Hg(II) nitrate polymeric complexes with these ylides [15], wherein the nitrate anions are bridging, confirming the general belief that seven-coordinated complexes would be formed. In this study, we describe the preparation and spectroscopic characterization of Ag(I) and Hg(II) complexes with the title ylides. The single crystal X-ray diffraction study of L^2 and 2 demonstrates the C-coordination of the ylides to the metals (Scheme 1).

2. Experimental

2.1. Physical measurements and materials

All reactions were performed in air. Methanol was distilled over magnesium powder and diethyl ether over a mixture of sodium and benzophenone just before use. All other solvents were reagent grade and were used without further purification. The ligands were synthesized by the reaction of triphenylphosphine with 2- chloro and 2-bromoactophenones to produce the related phosphonium salts. Further treatment with aqueous NaOH solution led to elimination of HCl and HBr, giving the free ligands [16]. Melting points were measured on a Stuart SMP3 apparatus. Elemental analysis for C, H and N were performed using a Perkin-Elmer 2400 series analyzer. Fourier transform IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. ¹H, ³¹P and ¹³C NMR spectra were recorded on 90 MHz Jeol and 300 MHz Bruker spectrometers in CDCl₃ or DMSO-d₆ as the solvent at 25 °C. Chemical shifts (ppm) are reported according to internal TMS and external 85% phosphoric acid.

2.2. X-ray crystallography

The single crystal X-ray diffraction data of suitable crystals of L^2 and **2** were collected on a STOE IPDS-II diffractometer at 298 K, using graphite monochromated Mo K α radiation (λ = 0.71073 Å).



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Scheme 1. Schematic illustration of the complexes under study.

The data collection was performed using the ω -scan technique and using the STOE X-AREA software package [17], while data reduction was carried out using the program X-RED [17]. The crystal structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the programs SHELX and SHELXL, respectively [18], and using the X-STEP32 crystallographic software package [19]. The H atoms were included in calculated positions and treated as riding atoms using SHELXL [18] default parameters. Numerical absorption corrections were applied for both L^2 and **2**.

2.3. Computational methods

The geometries of the compounds have been optimized without symmetry constraints at the BP86 [20]/def2-SVP [21] level of theory using the Gaussian 03 [22] optimizer [23] in conjunction with



Fig. 1. X-ray crystal structure of L².

Table 1			
IR (cm ⁻¹), ¹ H and ³¹ P NMR	t [δ (ppm), J (Hz)]	spectral	data.

	v(C=0)	$\delta_{\rm PCH}$	² Ј _{РН} (у)	$^{2}J_{\rm PH}(\rm Ps)$	$\delta_{\rm PPh3}^{\rm a}$	$^{2}J_{\rm HgP}$
L ^{1, b}	1576	4.0(d)	23.66	12.36	12.40(s)	-
L ² , ^b	1579	4.38(d)	24.37	11.92	14.05(s)	-
1 ^b	1609	4.42 (d)	14.06	-	19.96(s)	-
2 ^c	1600	4.92(d)	9.67	-	23.11(s)	-
3 ^c	1667	6.28(d)	12.09	-	27.13(s)	285.31
4 ^c	1652	6.45(d)	5.55	-	28.48(s)	287.19

y, ylide; Ps, phosphonium salt; s, singlet; d, doublet; br, broad.

 $^{\rm a}$ T = 298 K; TMS δ = 0.00 ppm; shifts relative to internal TMS and external 85% phosphoric acid.

^b Recorded in CDCl₃.

^c Recorded in DMSO-d₆.

Turbomole 5 [24] energies and gradients. Single-point energies of both $[Ag(Ylide)_2]^+$ and NO_3^- fragments in the complexes at the BP86/SVP optimized geometries were calculated with BP86 and the def 2-SVP[21] basis set. The geometry of the metal complex **2**, as determined by the X-ray crystal structure analysis (see Fig. 1), was fully optimized at above mentioned level of theory. The observed geometry of compound **2** was used as a basis for the DFT calculations of compound **1**.

2.4. Sample preparation

2.4.1. Synthesis of $[2,4-Cl_2C_6H_3C(0)CHPPh_3]$ (L¹)

To an acetone solution (10 mL) of triphenylphosphine (0.262 g, 1 mmol) was added 2,2',4'-trichloroacetophenone (0.223 g, 1 mmol), and the mixture was stirred for 24 h. The solid product (phosphonium salt) was filtered off, washed with Et₂O and dried. Further treatment with aqueous NaOH solution led to elimination of HCl, giving the free ligand. Yield: 84%, M.p. 114–116 °C. *Anal.* Calc. for C₂₆H₁₉OPCl₂: C, 69.50; H, 4.26. Found: C, 69.61; H, 4.34%. IR (KBr disk, cm⁻¹) v: 1576 (CO), 878 (P⁺-C⁻). ¹H NMR (CDCl₃, ppm) δ_{H} : 3.98 (d, ²J_{PH} = 23.21 Hz, 1H, CHP), 7.12–7.34 (m, 18H, arom.). ³¹P NMR (CDCl₃, ppm) δ_{P} : 12.43. ¹³C{¹H} NMR (CDCl₃, ppm) δ_{C} : 53.44 (d, ¹J_{PC} = 94.05 Hz, CHP), [122.72 (d), 125.43 (s), 127.68 (d), 129.26 (s), 130.71 (s), 131.70 (d), 139.98 (s), 140.61 (d) (Ph)], 182.31 (s, CO).

2.4.2. Synthesis of $[4-(CH_3)_2CHC_6H_4C(0)CHPPh_3]$ (**L**²)

To a chloroform solution (10 mL) of triphenylphosphine (0.262 g, 1 mmol) was added 2-bromo-4-isopropylacetophenone (0.241 g, 1 mmol), and the mixture was stirred for 24 h. The solid product (phosphonium salt) was filtered off, washed with Et₂O and dried under reduced pressure. Further treatment with aqueous NaOH solution led to elimination of HBr, giving the free ligand. Yield: 81%, M.p. 217–219 °C. *Anal.* Calc. for C₂₉H₂₇OP: C, 82.44; H, 6.44. Found: C, 82.71; H, 6.57%. IR (KBr disk, cm⁻¹) v: 1579 (CO), 887 (P⁺-C⁻). ¹H NMR (CDCl₃, ppm) δ_{H} : 1.23 (d, ³J_{HH} = 6.76 Hz, 6H, CH₃), 2.90 (m, 1H, CH(CH₃)₂), 4.38 (d, ²J_{PH} = 24.37, 1H, CHP), 7.23–7.92 (m, 19H, arom.). ³¹P NMR (CDCl₃, ppm) δ_{P} : 14.05. ¹³C{¹H} NMR (CDCl₃, ppm) δ_{C} : 23.23 (s, CH₃), 33.15 (s, CH(CH₃)₂), 47.03 (d, ¹J_{PC} = 112.39 Hz, CHP), [124.62 (d), 125.03 (s), 126.38 (s), 127.89 (d), 131.31 (s), 132.18 (d), 138.18 (d), 149.44 (s) (Ph)], 184.13 (s, CO).

2.4.3. Synthesis of the Ag(I) complexes

2.4.3.1. General procedure. To $AgNO_3$ (0.5 mmol) dissolved in 10 mL of dried methanol was added the ylide L^1 (0.450 g, 1 mmol). The mixture was stirred for ~4 h, during which time it was protected from light. The white solid product was filtered, washed with Et₂O and dried under reduced pressure.

Table 2	
Crystal data	and refinement details for L² and 2 .

Empirical formula	$C_{29}H_{27}O_1P_1$	$C_{58}H_{54}Ag_1N_1O_5P_2$
Formula weight	422.48	1014.83
T (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
space group	P21/n	ΡĪ
Unit cell dimensions		
a (Å)	12.2435(15)	10.8914(5)
b (Å)	14.4144(14)	13.5866(7)
c (Å)	14.3923(18)	17.7670(8)
α (°)	90.00	79.417(4)
β (°)	107.280(10)	79.940(4)
γ (°)	90.00	81.634(4)
V (Å ³)	2425.3(5)	2527.1(2)
Ζ	4	2
Calculated density (mg/ m ³)	1.157	1.334
Absorption coefficient	0.131	0.511
F(000)	896	1052
Crystal size (mm)	$0.45\times0.38\times0.32$	$0.45 \times 0.30 \times 0.23$
θ Range for data	2.05-29.20	2.08-29.19
collection (°)		
Limiting indices	$-16 \leq h \leq 16$,	$-14 \leqslant h \leqslant 14$,
-	$-19 \leqslant k \leqslant 17$,	$-18 \leqslant k \leqslant 18$,
	$-19 \leqslant l \leqslant 17$	$-21 \leqslant l \leqslant 24$
Reflections collected/	16705/6510 (0.0805)	2889/13559 (0.0777)
unique (R _{int})		
Completeness (%)	99.3	99.1
Absorption correction	Numerical	Numerical
Maximum and	0.960 and 0.940	0.890 and 0.830
minimum		
transmission		
Refinement method	Full-matrix least-	Full-matrix least-
	squares on F^2	squares on F ²
Data/restraints/ parameters	6510/0/280	13559/0/604
Goodness-of-fit (GOF) on F^2	1.065	1.103
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0700$,	$R_1 = 0.0794$,
	$wR_2 = 0.1793$	$wR_2 = 0.1250$
R indices (all data)	$R_1 = 0.1076$,	$R_1 = 0.1487$
. ,	$wR_2 = 0.2107$	$wR_2 = 0.1446$
Largest difference in	0.688 and -0.323	0.534 and -0.394
peak and hole (e Å ⁻³)		

Table 3

Selected bond lengths (Å) and bond angles (°) for L^2 .

Bonds		Angles	
C7-C10	1.501(3)	01-C10-C7	118.1(2)
C10-C11	1.399(3)	O1-C10-C11	121.3(2)
C10-01	1.257(3)	C10-C11-P1	117.84(18)
C11-P1	1.715(2)	C11-P1-C12	106.41(11)
C12-P1	1.808(3)	C11-P1-C18	113.80(12)
C18-P1	1.803(2)	C11-P1-C24	115.53(12)
C24-P1	1.814(2)		

2.4.3.2. Data for $[Ag(2,4-Cl_2C_6H_3C(0)CHPPh_3)_2]NO_3$ (1). Yield: 77%, M.p. 204–206 °C. Anal. Calc. for $C_{52}H_{38}NO_5P_2Cl_4Ag$: C, 58.45; H, 3.58; N, 1.31. Found: C, 58.74; H, 3.69; N, 1.47%. IR (KBr disk, cm⁻¹) v: 1609 (CO), 861 (P⁺-C⁻). ¹H NMR (CDCl₃, ppm) δ_{H} : 4.42 (d, ² J_{PH} = 14.06 Hz, 1H, CH), 7.15–7.34 (m, 18H, arom.). ³¹P NMR (CDCl₃, ppm) δ_p : 19.96. ¹³C{¹H} NMR (CDCl₃, ppm) δ_c : 45.33 (d, ¹ J_{PC} = 80.67 Hz, CHP), [122.09 (d), 126.12 (s), 128.65 (d), 130.09 (s), 130.79 (s), 132.48 (d), 138.50 (s), 138.75 (d) (Ph)], 188.37 (s, CO).

2.4.3.3. Data for [Ag(4-(CH₃)₂CHC₆H₄C(0)CHPPh₃)₂]NO₃ (**2**). Yield: 68%, M.p. 185–187 °C. Anal. Calc. for C₅₈H₅₄AgNO₅P₂: C, 68.64; H,



Fig. 2. X-ray crystal structure of 2. Hydrogen atoms are omitted for clarity.



Fig. 3. A representation of part of the unit cell contents of L^2 showing the head-to-tail dimeric C-H··· π_{phen} interactions and non-classical C-H_{methyl}···O=C hydrogen bonds.

Table 4
Selected bond lengths (Å) and bond angles (°) for 2 .

Bonds		Angles	
Ag1-C11	2.207(4)	Ag1-C11-P1	109.2(2)
Ag1-C40	2.199(4)	Ag1-C11-C10	100.6(3)
P1-C11	1.757(4)	Ag1-C40-P2	111.7(2)
P2-C40	1.742(4)	Ag1-C40-C39	100.2(3)
01-C10	1.235(7)	C11-P1-C12	114.4(2)
O2-C39	1.299(6)	C11-Ag1-C40	171.3(1)
P1-C12	1.808(5)	C7-C10-C11	118.9(4)
C10-C11	1.4.57(6)	C36-C39-C40	118.3(3)
P2-C41	1.814(4)	P1-C11-C10	114.8(3)
C7-C10	1.505(6)	P2-C40-C39	117.2(3)
C36-C39	1.515(6)	C40-P2-C41	113.5(2)
C39-C40	1.466(6)	C41-P2-C53	108.3(2)

5.36; N, 1.38. Found: C, 68.93; H, 5.42; N, 1.47%. IR (KBr disk, cm⁻¹) v: 1600 (CO), 860 (P⁺-C⁻). ¹H NMR (DMSO-d₆, ppm) $\delta_{\rm H}$: 1.15 (d, ³*J*_{HH} = 6.72 Hz, 6H, CH₃), 2.89 (m, 1H, CH), 4.92 (d,



Fig. 4. A representation of complex **2** packing showing the association of the adjacent molecules through C-H_{phenyl}··· π_{phenyl} , C-H_{methyl}··· π , C-H_{phenyl}···O_{nitrate} and C-H_{methyl}···O_{nitrate} interactions. Different colours show different adjacent molecules.

 ${}^{2}J_{\text{PH}}$ = 9.67, 1H, CH), 7.14–7.60 (m, 19H, arom.). ${}^{31}\text{P}$ NMR (DMSO-d₆, ppm) δ_{P} : 23.11. ${}^{13}\text{C}{}^{1}\text{H}$ NMR (DMSO-d₆, ppm) δ_{C} : 23.35 (s, CH₃), 33.31 (s, CH(CH₃)₂), 35.48 (d, ${}^{1}J_{\text{PC}}$ = 69.38 Hz, CHP), [122.67 (d), 125.83 (s), 127.17 (s), 128.67 (d), 131.55 (s), 132.54 (d), 135.15 (d), 152.03(s) (Ph)], 189.82 (s, CO).

2.4.4. Synthesis of the Hg(II) complexes

2.4.4.1. General procedure. To a magnetically stirred solution of $Hg(NO_3)_2.H_2O(0.344 \text{ g}, 1 \text{ mmol})$ in methanol (10 mL), was added a methanolic solution (5 mL) of ylide L^1 (0.450 g, 1 mmol). After 30 min the solvent was removed under reduced pressure to 3 mL. Addition of diethylether (30 mL) gave the white solid product that was separated by filtration.

Table 6

A comparison between the selected calculated bond lengths (Å) and bond angles (°) for compounds **1** and **2**, and the corresponding experimental values for complex **2**.

	2 calculated	1 calculated	2 X-ray
Bond lengths			
Ag-C(40)	2.21866	2.22160	2.19932
Ag-C(11)	2.20279	2.20762	2.20655
Ag-O(3)	2.55419	2.55928	2.72571
Bond angles			
P(2)-C(40)-Ag	109.795	108.823	111.730
P(1)-C(11)-Ag	111.881	111.483	109.242
C(40)-Ag- $O(3)$	81.057	81.302	84.780
C(40)-Ag- $O(3)$	99.635	99.796	102.766
C(39)-C(40)-Ag	106.871	107.871	100.151
C(10)-C(11)-Ag	103.765	103.188	100.618
C(11)-Ag-C(40)	178.759	178.017	171.293

2.4.4.2. Data for $[2,4-Cl_2C_6H_3C(0)CHPPh_3.Hg(NO_3)_2]$ (**3**). Yield: 74%, M.p. 162–164 °C. Anal. Calc. for $C_{26}H_{19}Cl_2HgN_2O_7P$: C, 40.35; H, 2.47; N, 3.62. Found: C, 40.78; H, 2.56; N, 3.73%. IR (KBr disk, cm⁻¹) v: 1667 (CO), 818 (P⁺-C⁻). ¹H NMR (DMSO-d₆, ppm) δ_{H} : 6.28 (d, 1H, ²J_{PH} = 5.12 Hz, CH), 7.13–8.42 (m, 18H, arom.). ³¹P NMR (DMSO-d₆, ppm) δ_{p} : 27.13 (s with satellites, ²J_{HgP} = 285.31 Hz). ¹³C{¹H} NMR (DMSO-d₆, ppm) δ_{C} : 43.64 (d, ¹J_{PC} = 52.63 Hz, CHP), [119.06 (d), 127.29 (s), 129.52 (d), 132.18 (s), 132.57 (s), 133.52 (s), 133.97 (s), 137.24 (s) (Ph)], 192.89 (s, CO).

2.4.4.3. Data for $[4-(CH_3)_2CHC_6H_4C(O)CHPPh_3.Hg(NO_3)_2](4)$. Yield: 71%, M.p. 160–162 °C. Anal. Calc. for $C_{29}H_{27}HgN_2O_7P$: C, 46.62; H, 3.64; N, 3.75. Found: C, 46.95; H, 3.72; N, 3.81%. IR (KBr disk, cm⁻¹) v: 1652 (CO), 819 (P⁺–C⁻). ¹H NMR (DMSO-d₆, ppm) $\delta_{\rm H}$: 1.15 (d, ³*J*_{HH} = 6.04 Hz, 6H, CH₃), 2.96 (m, 1H, CH), 5.45 (d, 1H, ²*J*_{PH} = 4.57 Hz, CH), 7.44–8.15 (m, 19H, arom.). ³¹P NMR (DMSO-

Table 5

Significant C-H...O non-classical hydrogen bonds (interatomic distance (Å) and bond angles (°)) found in the structures of L² and complex 2.

D–H···A	D-H	H···A	D····A	D–H···A	Symmetry code
L^2					
C5-H5···01	0.9300	2.4400	3.358(3)	169.00	1/2 + x, $1/2 - y$, $1/2 + z$
Complex 2					
C6-H6···O1	0.9300	2.4400	2.768(6)	100.00	-
C8-H8····O4	0.9300	2.5500	3.464(7)	169.00	-
C15-H15···O4	0.9300	2.5900	3.338(8)	138.00	2 - x, 2 - y, 1 - z
C29-H29···O1	0.9300	2.3000	3.038(6)	135.00	-
C32-H32C···O5	0.9600	2.4700	3.430(13)	174.00	1 - x, $2 - y$, $2 - z$
C54-H5402	0.9300	2.5200	3.269(7)	138.00	-







Fig. 6. Shape of the energetically highest-lying orbitals HOMO-1, HOMO-4, HOMO-11 and HOMO-12 for complex 2.

d₆, ppm) δ_p : 28.48 (s with satellites, ²*J*_{HgP} = 287.19 Hz). ¹³C{¹H} NMR (DMSO-d₆, ppm) δ_C : 23.45 (s, CH₃), 33.97 (s, CH(CH₃)₂), 40.44 (d, ¹*J*_{PC} = 62.74 Hz, CHP), [119.62 (d), 128.29 (s), 129.50 (d), 131.56 (s), 133.45 (d), 138.71 (d), 155.30 (s) (Ph)], 193.15 (s, CO).

3. Results and discussion

3.1. Spectroscopy

The v(CO) values, which are sensitive to complexation, occur at 1576 and 1579 cm⁻¹ in the parent ylides, and these values increase for all complexes (Table 1), indicative of coordination of the ylide through carbon. The $v(P^+-C^-)$, which is also diagnostic for coordination, occurs at 878 and 887 cm⁻¹ in L¹ and L², respectively, and these values are shifted to lower frequencies for the complexes, suggesting removal of electron density in the P–C bond [25].

The ¹H NMR data for the complexes and the parent ylides are listed in Table 1. The methine proton was a doublet in all cases. Compounds wherein the ylide is C-coordinated exhibit a ${}^{2}I_{PH}$ value of 10 Hz or less [11]. The ³¹P NMR resonances of the complexes occur at a lower field with respect to the free ylide. The expected downfield shifts of the ¹H and ³¹P signals for the PCH group upon complexation were observed. The appearance of single signals for the PCH group in both the ³¹P and ¹H spectra at ambient temperature indicates the presence of only one molecule for all the complexes, as expected for C-coordination; O-coordination of the ylide sometimes leads to formation of cis- and trans-isomers, giving rise to two different signals in the ³¹P and ¹H NMR spectra [26]. Although two diastereoisomers (RR/SS and RS) are possible for the silver complexes (because the methane carbons are chiral), NMR spectroscopy does not distinguish them at room temperature. Methine resonances are intermediate between those in the free ylides and phosphonium salts (Table 1), and ${}^{2}J_{PH}$ values are smaller, as observed for other C-coordinated carbonyl-stabilized phosphorus ylide complexes, due to the hybridization change in the ylidic carbon (sp²-sp³) upon C coordination [6,11,26]. Much larger values of ${}^{2}J_{PH}$ (ca 20 Hz) have been observed in complexes where coordination is through the oxygen [27]. Neither H–Ag nor P–Ag coupling was observed at room temperature in the spectra; possibly a fast equilibrium between the complexes and the free ylides is responsible for the failure to observe NMR coupling or two diastereoisoThe most interesting aspect of the ¹³C NMR spectra of the complexes is the upfield shift of the signals due to the ylidic carbon. Such an upfield shift observed in PdCl(η^3 -2-XC₃H₄) (C₆H₅)₃PCH-COR (X = H, CH₃; R = CH₃, C₆H₅) was attributed to the change in hybridization of the ylidic carbon [28]. Similar upfield shifts of δ 2–3 ppm with reference to the parent ylide were also observed in the case of [(C₆H₅)₃PC₅H₄Hgl₂]₂ [29] and our synthesized complexes [15]. The ¹³C shifts of the CO group in the complexes are around 190 ppm, relative to 182 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of the carbon of the CO group in these complexes.

3.2. X-ray crystallography

Crystals of L² were obtained by slow evaporation of a CHCl₃ solution at room temperature. Significant bond distances and angles are collected in Table 3 and crystallographic details in Table 2. An ORTEP plot (Fig. 1) shows that in the molecule of L^2 , the geometry around the P atom is nearly tetrahedral, and the O atom is oriented cis to the P atom. The aromatic ring of the benzoyl group is twisted with respect to the plane of the carbonyl group through an angle of $-8.3(4)^{\circ}$. The P-C(11) (1.715 (2)Å) and C(11)-C(10, sp²) (1.399(4) Å) bond lengths are shorter than the P⁺–C(sp³) and C–C normal values, 1.800 and 1.511 Å, respectively. This is due to the ylidic resonance and the values are intermediate between common values for single and double bonds (for example P-C = 1.80 and P = C = 1.66 Å). The CO bond also is longer (1.256(3) Å) than the normal value (1.210 Å). This bond distance suggests resonance delocalization in these molecules [30]. In L², there are head-to-tail C- H_{phenyl} ... π_{phenyl} (2.694 Å) interactions between adjacent molecules, forming dimeric rings. These dimeric rings are further linked to adjacent molecules by C-H_{phenyl}···O=C non-classical hydrogen bonds to generate three dimensional packing (Fig. 3, Table 5).

Crystals of **2** were obtained by slow diffusion of *n*-hexane into a CHCl₃ solution at room temperature. The complex is shown in Fig. 2, crystallographic details in Table 2 and significant bond distances and angles are collected in Table 4. The Ag(I) atom is located in a slightly distorted linear environment, surrounded by C atoms of the methine of the ylide.

The relative configuration at the chiral carbon atoms are RR. The configuration about the molecular axis C(11)...C(40) is almost eclipsed (Fig. 2). The coordination geometry at silver is essentially linear, although the bond lengths and angles at silver are slightly distorted (C(11)-Ag-C(40), 171.3(1)°). The P(1)-C(11) (methine) distance is 1.757(4) Å, shorter than the average P-C (Ph) single bond distance (1.807 Å), indicating some multiple bond character [33]. For comparison, the P-C bond distance in Ph₃PCH₂ is 1.66 Å, which corresponds to a bond order of 1.33 [31-33]. The C(10)-C(11) distance is 1.457(6) Å, indicating single bond character. The C(10)-O(1) distance is 1.235(7) Å, similar to C-O bond distances found in C-bonded ylides [13,34,35]. Complex 2 is an example of an ylide C-bonded to a soft metal center. In complex 2, a combination of several weak and medium intermolecular interactions, including C-H_{phenyl}··· π_{phenyl} (3.332 Å), C-H_{methyl}··· π_{phenyl} (3.548 Å), C-H_{phenyl}···O_{nitrate} and C-H_{methyl}···O_{nitrate}, determine the structural assembly in this compound (Fig 4, Table 5).

3.3. Theoretical studies

We carried out DFT calculations at the BP86 [20]/def2-SVP [21] level of theory using the GAUSSIAN 03 [22] optimizer [23] in

conjunction with Turbomole 5 [24] energies and gradients. The geometry of the metal complex 2, as determined by X-ray crystal structure analysis (see Fig. 2), was fully optimized at above mentioned level of theory. The observed geometry of compound 2 was used as a basis for DFT calculations of compound 1. Fig. 5 shows the optimized geometries of both complexes 1 and 2. The calculated bond lengths and bond angles of 2 are in good agreement with the experimental values (see Table 6). The computed Ag–C distances are 0.2–0.3 Å longer than the X-ray values. The computed values for the Ag–O distance are about 0.17 Å shorter than the X-ray value. The calculated bond lengths of these compounds are also gathered in Table 6. As it can be seen in this Table, there is good agreement between the calculated bond lengths for this compound with those derived from the X-ray crystal structure. Fig. 6 shows the shape of the energetically highest-lying orbitals, HOMO-1. HOMO-4. HOMO-11 and HOMO-12. HOMO-1 and HOMO-4 are localized at the Ag-C(Ylide). The shape of HOMO-11 can be associated with the Ylide \rightarrow Ag σ donation. Also the shape of HOMO-12 can be associated with the interaction of $[Ag(Ylide)_2]^+$ with the oxygen atom of the NO_3^- group. We were interested in studying the interaction between the nitrate anion and the [Ag(Y- $[lide)_2]^+$ cation. The interaction energies of $[Ag(Ylide)_2]^+$ with the NO_3^- group in compounds **1** and **2** were calculated according to the breakdown of $[Ag(Ylide)_2]NO_3$ to $[Ag(Ylide)_2]^+$ and NO_3^- . The bonding energy of Ag^+ ... NO_3^- in compounds **1** and **2** is about 93.6 and 99.9 K cal mol⁻¹, respectively, at the BP86 [20]/def2-SVP level of theory. Thus both the theoretical and experimental data show that the nitrate ion in compound **2** has a bonding interaction with Ag(I), and the $[Ag(Ylide)_2(NO_3)]$ formulation for this complex is more correct than $[Ag(Ylide)_2](NO_3)$, in which the nitrate ion is only a counter ion.

4. Conclusions

The present study describes the synthesis and characterization of mononuclear Ag(I) and polymeric Hg(II) complexes of two new phosphorus ylides. On the basis of the physico-chemical and spectroscopic data, we propose monodentate C-coordination to the metal, which is further confirmed by the X-ray crystal structures of L^2 and 2. There is good agreement between the theoretical calculated bond lengths and angles for the Ag(I) complexes with those derived from the X-ray crystal structure. A bonding interaction between the Ag(I) centre and the nitrate ion in compound 2 was confirmed with the theoretical data.

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Appendix A. Supplementary data

CCDC 837049 and 837048 contain the supplementary crystallographic data for compounds L^2 and 2, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.02.034.

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