Synthesis, spectroscopic and structural characterization of new linear mononuclear silver(I) complexes containing α -keto phosphorus ylides as ambidentate ligands

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Abstract. The reaction of 2 equiv. phosphorus ylides, $(\text{C}_6\text{H}_5)_3\text{PCHC}(\text{O})\text{C}_6\text{H}_4\text{R}$ ($\text{R} = \text{CH}_3$ (**L1**), Br (**L2**), Cl (**L3**), NO_2 (**L4**) and OCH_3 (**L5**)) with 1 equiv. AgNO_3 using methanol as solvent leads to formation of linear mononuclear Ag–CH complexes, $[\{\text{RC}_6\text{H}_4\text{CO}\{(\text{C}_6\text{H}_5)_3\text{P}\}\text{CH}\}_2\text{Ag}(\text{NO}_3)]$, ($\text{R} = \text{CH}_3$ (**C1**), Br (**C2**), Cl (**C3**), NO_2 (**C4**) and OCH_3 (**C5**)), which contain one NO_3 and two phosphorus ylides coordinated via the ylidic carbon atom. The silver complexes were synthesized and investigated by elemental analysis, Fourier transform infrared spectroscopy (FTIR), multinuclear (^1H , ^{31}P and ^{13}C) Nuclear magnetic resonance (NMR). In addition, the identities of complexes **C1** and **C3** were unequivocally determined by single crystal X-diffraction techniques. X-ray single crystal diffraction studies show that both complexes **C1** and **C3** belong to the triclinic crystal system and $P\bar{1}$ space group. This crystal packing of structures shows a close association between the nitrate anion and the metal centre. The Ag(I) atom is located in a slightly distorted linear environment, surrounded by C atoms of the methine of the ylide.

Keywords. Phosphorus ylide; coordination mode; ambidentate ligand; mononuclear silver(I) complexes.

1. Introduction

The utility of metalated phosphorus ylides in synthetic chemistry has been well-documented.^{1,2} 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 also been reported.^{4–9} In 1987 and 1993, Vicente *et al.*^{10,11} reported crystal structures of Ag(I)

complexes of phosphorus ylides. The α -keto-stabilized phosphorus ylides $\text{R}_3\text{E}=\text{C}(\text{R}')\text{COR}''$ ($\text{E} = \text{P}, \text{As}$; $\text{R}, \text{R}', \text{R}'' = \text{H}$, alkyl or aryl groups) show high stability (which allow them to be easily handled in air) and ambidentate character as ligands (C- versus O-coordination). This ambidentate character can be rationalized in terms of resonance forms **a–c** (where **c** is represented by the *cis* and *trans* geometrical isomers).

Forms **b** and **c** account for the metal C-coordination **A** and O-coordination **B** (in *cis* and *trans* forms), respectively.

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Although many coordination modes are possible for keto ylides,¹² coordination through carbon is dominant in soft metal ions, e.g., Pd(II), Pt(II), Ag(I), Hg(II), Au(I) and Au(III)^{13–16} and very few examples of O-coordinated ylides, e.g., Sn(IV), Ti(IV) and Hf(IV)¹⁷ are known. In this study, we describe the preparation, structural and spectroscopic characterization of Ag(I) complexes with the title ylides. The single crystal X-ray diffraction of **C1** and **C3** demonstrates C-coordination of ylides with metals.

2. Experimental

All reactions were performed in nitrogen atmosphere. Methanol was distilled over magnesium powder and diethyl ether was distilled over a mixture of sodium and benzophenone just before use. All other solvents were reagent grade and 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 of the salts with aqueous NaOH solution led to elimination of H₂O and NaBr, giving free ligands.^{18–20} Melting points were measured on a Stuart SMP3 apparatus. Elemental analysis 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.

2.1 X-ray crystallography

The single crystal X-ray diffraction analysis of suitable crystals of **C1** and **C3** were performed on a STOE IPDS-II diffractometer at 298 K, using graphite monochromated Mo K α radiation (λ = 0.71073 Å). Data collection was performed using ω -scan technique and the STOE X-AREA software package.²¹ The crystal structures were solved by direct methods and refined by full-matrix least-squares on F^2 by SHELX 97²² and using the X-STEP32 crystallographic software package.²³

2.2 Syntheses of Ag(I) complexes

2.2a Syntheses of [(L1)₂Ag]NO₃ (C1): General procedure: To a solution of AgNO₃ (0.06 g, 0.38 mmol) in methanol (20 ml) was added **L1** (0.3 g, 0.76 mmol) and stirred for 10 h. The solution was protected from light with aluminium foil. A colourless product formed by slow evaporation of the solvent and concentration

to 3 ml. The product was washed several times with petroleum ether (3 $\times$ 10 ml). Yield: 0.266 g (74%). Anal. Calc. for C₅₄H₄₆AgNO₅P₂: C 67.64; H 4.83; N 1.46%. found: C 67.32; H 5.13; N 1.28%. Melting point: 186–187°C. FT-IR (KBr, cm⁻¹): 1598 (CO), 863 (P-C). ¹H NMR (CDCl₃, δ ppm): 2.27 (s, 3H, CH₃), 5.19 (d, 1H, CH, ²J = 8.69 Hz), 6.98–7.91 (m, 19H, arom.). ³¹P NMR (CDCl₃, δ ppm): 21.72. ¹³C NMR (CDCl₃, δ ppm): 20.74 (s, CH₃), 36.65 (d, CH, ¹J_{PC} = 71.39 Hz), 124.23 (d, ¹J_{PC} = 89.86 Hz, PPh₃ (i)); 132.25 (d, ²J_{PC} = 8.83 Hz, PPh₃ (o)); 128.61 (d, ³J_{PC} = 12.57 Hz, PPh₃ (m)); 134.38 (d, ⁴J_{PC} = 10.31 Hz, PPh₃ (p)); 141.23 (s, CPh(i)); 132.05 (s, CPh(o)); 126.89 (s, CPh(m)); 128.33 (s, CPh(p)); 190.30 (s, CO).

2.2b Data for [(L2)₂Ag]NO₃ (C2): Yield: 0.216 g (65%). Anal. Calc. for C₅₂H₄₀AgBr₂NO₅P₂: C 57.38; H 3.70; N 1.29%. found: C 57.31; H 3.42; N 1.21%. Melting point: 202–204°C. FT-IR (KBr, cm⁻¹): 1613 (CO), 855 (P-C). ¹H NMR (CDCl₃, δ ppm): 5.25 (br, 1H, CH), 7.04–7.86 (m, 19H, arom.). ³¹P NMR (CDCl₃, δ ppm): 21.45. ¹³C NMR (CDCl₃, δ ppm): 36.54 (d, CH, ¹J_{PC} = 72.10 Hz), 123.89 (d, ¹J_{PC} = 89.24 Hz, PPh₃ (i)); 133.16 (d, ²J_{PC} = 8.54 Hz, PPh₃ (o)); 128.14 (d, ³J_{PC} = 13.72 Hz, PPh₃ (m)); 135.46 (d, ⁴J_{PC} = 11.30 Hz, PPh₃ (p)); 137.42 (s, CPh(i)); 131.54 (s, CPh(o)); 127.16 (s, CPh(m)); 129.0 (s, CPh(p)); 191.17 (s, CO).

2.2c Data for [(L3)₂Ag]NO₃ (C3): Yield: 0.231 g (77%). Anal. Calc. for C₅₂H₄₀AgCl₂NO₅P₂: C 62.47; H 4.03; N 1.40%. found: C 62.12; H 4.41; N 1.62%. Melting point: 196–199°C. FT-IR (KBr, cm⁻¹): 1609 (CO), 861 (P-C). ¹H NMR (CDCl₃, δ ppm): 5.19 (br, 1H, CH), 7.14–8.00 (m, 19H, arom.). ³¹P NMR (CDCl₃, δ ppm): 21.15. ¹³C NMR (CDCl₃, δ ppm): 37.68 (d, CH, ¹J_{PC} = 74.07 Hz), 124.49 (d, ¹J_{PC} = 89.90 Hz, PPh₃ (i)); 132.52 (d, ²J_{PC} = 9.16 Hz, PPh₃ (o)); 128.88 (d, ³J_{PC} = 12.32 Hz, PPh₃ (m)); 135.96 (d, ⁴J_{PC} = 10.92 Hz, PPh₃ (p)); 137.00 (s, CPh(i)); 132.31 (s, CPh(o)); 127.91 (s, CPh(m)); 128.60 (s, CPh(p)); 189.05 (s, CO).

2.2d Data for [(L4)₂Ag]NO₃ (C4): Yield: 0.213 g (71%). Anal. Calc. for C₅₂H₄₀AgN₃O₉P₂: C 61.18; H 3.95; N 4.11%; found: C 61.49; H 4.35; N 4.31%. Melting point: 196–199°C. FT-IR (KBr, cm⁻¹): 1618 (CO), 872 (P-C). ¹H NMR (CDCl₃, δ ppm): 5.15 (d, 1H, CH, ²J = 8.24 Hz), 7.24–8.09 (m, 19H, arom.). ³¹P NMR (CDCl₃, δ ppm): 20.75. ¹³C NMR (CDCl₃, δ ppm): 40.33 (d, CH, ¹J_{PC} = 80.65 Hz), 124.48 (d, ¹J_{PC} =

90.08 Hz, PPh₃ (i)); 132.82 (d, $^2J_{\text{PC}} = 9.88$ Hz, PPh₃ (o)); 129.22 (d, $^3J_{\text{PC}} = 12.66$ Hz, PPh₃ (m)); 128.33 (s, PPh₃ (p)); 143.23 (d, $^3J_{\text{PC}} = 11.60$ Hz, CPh(i)); 133.04 (s, CPh(o)); 123.12 (s, CPh(m)); 149.15 (s, CPh(p)); 187.73 (s, CO).

2.2e Data for $[(L_5)_2\text{Ag}]\text{NO}_3$ (C5): Yield: 0.242 g (68%). Anal. Calc. for C₅₄H₄₆AgNO₇P₂: C 66.54; H 4.76; N 1.44%. found: C 66.32; H 4.86; N 1.31%. Melting point: 192–194°C. FT-IR (KBr, cm⁻¹): 1583 (CO), 852 (P-C). ¹H NMR (CDCl₃, δ ppm): 3.89 (s, 3H, CH₃), 5.33 (d, 1H, CH, $^2J = 9.25$ Hz) and 6.93–7.72 (m, 19H, arom.). ³¹P NMR (CDCl₃, δ ppm): 22.13. ¹³C NMR (CDCl₃, δ ppm): 29.62 (s, CH₃), 46.28 (d, CH, $^1J_{\text{PC}} = 68.65$ Hz), 123.98 (d, $^1J_{\text{PC}} = 90.65$ Hz, PPh₃ (i)); 132.93 (d, $^2J_{\text{PC}} = 9.32$ Hz, PPh₃ (o)); 127.98 (d, $^3J_{\text{PC}} = 13.52$ Hz, PPh₃ (m)); 135.15 (d, $^4J_{\text{PC}} = 11.84$ Hz, PPh₃ (p)); 140.57 (s, CPh(i)); 131.66 (s, CPh(o)); 127.25 (s, CPh(m)); 128.89 (s, CPh(p)); 188.48 ppm (s, CO).

3. Results and discussion

The reaction of ylides with AgNO₃ in 2:1 molar ratios in methanol as solvent yielded mononuclear complexes **C1–C5** (scheme 1).

3.1 Spectral studies

The $\nu(\text{CO})$ values, which are sensitive to complexation, occur in the range of 1565–1580 cm⁻¹ in the parent ylides, increase for all complexes (table 1), indicative of coordination of the ylide through carbon. The $\nu(\text{P}^+ - \text{C}^-)$, which is also diagnostic for coordination, occur in the range of 870–900 cm⁻¹ in **L1–L5**, shifted to lower frequencies for complexes suggesting removal of electron density in the P–C bond.²⁴

The IR and ¹H NMR data for all complexes are listed in table 1. The methine proton was broad for **C2** and **C3**. Compounds wherein the ylide is C-coordinated exhibit a $^2J_{\text{PH}}$ value of 10 Hz or less.¹¹ The ³¹P NMR

Scheme 1. Synthetic route for preparation of Ag(I) complexes. In order to ease the visualization of the reactions, letter R refers to the substituent on para positions of the phenyl. Reagents and conditions: (i) in acetone, using dry nitrogen atmosphere, 4 h at room temperature (RT); (ii) in NaOH in water, 2 h in 40°C; (iii) in methanol, using aluminium foil to protect from light, 10 h at RT.

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

Complexes	$\nu(\text{C}=\text{O})$	$\nu(\text{P}-\text{C})$	δ_{PCH}	$^2J_{\text{PH}}$	δ_{PPh_3}
C1	1598	863	5.19(d)	8.69	21.72(s)
C2	1613	855	5.25(br)	—	21.45(s)
C3	1609	861	5.19(br)	—	21.15(s)
C4	1678	872	5.15(d)	8.24	20.75(s)
C5	1583	852	5.33(d)	9.25	22.13(s)

s, singlet; d, doublet; br, broad

$T = 298$ K; Tetramethylsilane (TMS) $\delta = 0.00$ ppm; shifts relative to internal TMS and external 85% phosphoric acid

resonances occur at lower field with respect to free ylide. The expected downfield shifts of ^1H and ^{31}P signals for the PCH group upon complexation were observed. The appearance of single signals for the PCH group in both the ^{31}P and ^1H spectra at ambient temperature indicates the presence of only one resonance 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 ^{31}P and ^1H NMR.¹³ Although two diastereoisomers (RR/SS and RS) are possible for silver complexes (because the methine carbons are chiral), NMR spectroscopy does not distinguish them at room temperature. Methine resonances are intermediate between, and $^2J_{\text{PH}}$ values smaller than, those in the free ylides and phosphonium salts^{19,20} as observed for other C-coordinated carbonyl-stabilized phosphorus ylide complexes, due to hybridization change in

the ylidic carbon ($\text{sp}^2\text{--sp}^3$) with C-coordination.^{6,11,13} Much larger values of $^2J_{\text{PH}}$ (ca. 20 Hz) have been observed in complexes where coordination is through the oxygen.²⁵ Neither H–Ag nor P–Ag coupling was observed at room temperature in the spectra, possibly a fast equilibrium between complexes and free ylides is responsible for the failure to observe NMR coupling or two diastereoisomers.

The most interesting aspect of the ^{13}C NMR spectra of the complexes is the upfield shift of the signals due to the ylidic carbon. Such an upfield shift observed in $\text{PdCl}(\eta^3\text{--}2\text{-XC}_3\text{H}_4)(\text{C}_6\text{H}_5)_3\text{PCHCOR}$ ($\text{X} = \text{H}, \text{CH}_3$; $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) was attributed to the change in hybridization of the ylidic carbon.²⁶ The ^{13}C shifts of the CO group in the complexes are around 190 ppm, relative to ~ 180 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of the carbon of the CO group in these complexes.

Table 2. Crystal and experimental data.

Compound	C1	C3
Chemical formula	$\text{C}_{54}\text{H}_{46}\text{Ag}_1\text{N}_1\text{O}_5\text{P}_2$	$\text{C}_{52}\text{H}_{40}\text{Ag}_1\text{Cl}_2\text{N}_1\text{O}_5\text{P}_2$
Formula weight	958.73	999.56
Temperature (K)	120(2) K	120(2) K
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> –1	<i>P</i> –1
<i>a</i> (Å)	10.6372(3)	10.5500(4)
<i>b</i> (Å)	13.2466(4)	13.1609(4)
<i>c</i> (Å)	18.3250(5)	17.7761(6)
α (°)	80.536(2)	79.041(3)
β (°)	77.079(2)	77.216(3)
γ (°)	79.418(3)	77.474(3)
Volume (Å ³)	2453.34(12)	2323.36(14)
<i>Z</i>	2	2
<i>D_x</i> (Mg/m ³)	1.298	1.429
Wavelength (Å)	0.71073	0.71073
μ (Mo <i>Kα</i>) (mm ^{–1})	0.523	0.666
<i>F</i> (000)	988	1020
Crystal size (mm ³)	$0.31 \times 0.30 \times 0.25$	$0.36 \times 0.35 \times 0.25$
Absorption correction	numerical	numerical
Maximum and minimum transmission	0.880 and 0.850	0.8607 and 0.7837
No. of reflections collected	13159	26044
No. of independent reflections	13159	12488
θ range for data collection (°)	2.30 to 29.17	2.13 to 29.21
Data/Restraints/Parameters	13159/0/585	12488/0/568
Goodness-of-fit on <i>F</i> ²	1.083	1.086
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	$R_1 = 0.0556, wR_2 = 0.1229$	$R_1 = 0.1010, wR_2 = 0.2466$
<i>R</i> indices (all data)	$R_1 = 0.0716, wR_2 = 0.1290$	$R_1 = 0.1319, wR_2 = 0.2700$
(Δ/ρ) _{max} (eÅ ^{–3})	0.753	2.033
(Δ/ρ) _{min} (eÅ ^{–3})	–0.789	–1.588
Measurement	STOE IPDS II diffractometer	STOE IPDS II diffractometer
Programs system	SHELXLS-97 and SHELXL-97	SHELXLS-97 and SHELXL-97
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Cambridge Crystallographic Data	865649	811867
Centre (CCDC) deposition number		

Table 3. Selected key bond lengths (Å) and angles (°).

C1		C3	
Bond lengths (Å)		Bond lengths (Å)	
Ag1–C9	2.206(3)	Ag1–C1	2.197(6)
Ag1–C36	2.194(3)	Ag1–C27	2.189(6)
C35–C36	1.463(4)	C1–C2	1.466(9)
C8–C9	1.454(4)	C27–C28	1.472(9)
C8–O1	1.238(4)	C2–O1	1.247(8)
C35–O2	1.242(4)	C28–O2	1.225(8)
P1–C9	1.761(3)	P1–C1	1.749(7)
P2–C36	1.754(3)	P2–C27	1.748(7)
Bond angles (°)		Bond angles (°)	
Ag1–C9–C8	100.4(2)	Ag1–C27–C28	100.0(4)
Ag1–C9–P1	108.7(1)	Ag1–C1–P1	108.0(3)
Ag1–C36–C35	102.9(2)	Ag1–C1–C2	101.7(4)
Ag1–C36–P2	108.7(1)	Ag1–C27–P2	108.8(3)
C9–Ag1–C36	174.5(1)	C1–Ag1–C27	174.2(2)
P1–C9–C8	116.3(2)	P1–C1–C2	115.5(5)
P2–C36–C35	113.6(2)	P2–C27–C28	117.5(5)
C9–C8–O1	121.8(3)	C1–C2–O1	119.9(6)
C36–C35–O2	113(3)	C27–C28–O2	122.2(6)
C7–C8–C9	119.1(3)	C1–C2–C3	119.8(6)
C34–C35–C36	119.7(3)	C27–C28–C29	118.1(5)

Figure 1. Molecular structure drawing of **C1** with the selected atom-numbering scheme. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at 50% probability level. For the molecular structure of **C1**, one nitrate oxygen atom is highly disordered and it is split into two positions with 50% occupancy (O5A–O5B).

Figure 2. Molecular structure drawing of **C3** with the selected atom-numbering scheme. Displacement ellipsoids are drawn at 30% probability level.

3.2 Description of the crystal structures

All crystallographic details of **C1** and **C3** are in table 2 and significant bond distances and angles are collected

Figure 3. A packing representation of complex **C1** showing the association of the adjacent molecules through C-Hphenyl... π -phenyl, C-Hphenyl...O-carbonyl, C-Hphenyl...Onitrate, C-Hmethine...Onitrate, Onitrate...Ag, and C-Hphenyl...Onitrate interactions. Dotted lines represent the short contacts.

in table 3. Molecular structures of **C1** and **C3** are shown in figures 1 and 2, respectively. Crystals of **C1** were obtained by slow diffusion of *n*-hexane into CHCl_3 solution at room temperature. Also, crystals of **C3** were obtained by slow diffusion of EtO_2 into CHCl_3 solution at room temperature.

The relative configuration at the chiral carbon atoms is RR. The Ag(I) atom is located in a slightly distorted linear environment, surrounded by C atoms of the methine of the ylide. The configuration about the molecular axis {C(9)...C(36) and (C(1)...C(27))} is almost eclipsed (figures 1 and 2). The coordination geometry at silver is essentially linear, although bond lengths and angles at silver are slightly distorted {C(9)–Ag–C(36)=171.3(1)° and C(1)–Ag–C(27)=174.2(2)°}. The P(1)–C(9) (methine) distance in **C1** and the P(1)–C(1) distance in **C3** are 1.761(3) and 1.749(7) Å, respectively, shorter than the average P–C (Ph) single bond distance (1.807 Å), indicating some multiple bond character.^{3,27} For comparison, the P–C bond distance in Ph_3PCH_2 is 1.66 Å, which corresponds to a bond order of 1.33.^{27–29} The C(8)–C(9) distance in **C1** and the C(1)–C(2) distance in **C3** are 1.454(4) and 1.466(9) Å, respectively, indicating single bond character. The C(8)–O(1) distance in **C1** and the C(2)–O(1) distance in **C3** are 1.238(4) and 1.247(8) Å, respectively, similar to C–O bond distances found in C-bond ylides.^{30–33} All complexes are examples of an ylide C-bond to a soft metal centre.

Figure 4. A packing representation of complex **C3** showing the association of adjacent molecules through C-Hphenyl... π phenyl, C-Hphenyl...Ocarbonyl, C-Hphenyl...Onitrate, C-Hmethine...Onitrate, and Onitrate...Ag interactions. Dotted lines represent the short contacts. Different colours show different adjacent molecules.

Table 4. Significant C–H...O non-classical hydrogen bonds (interatomic distance (Å) and bond angles (°)) found in the structures of **C1** and **C3**.

D–H...A	D–H	H...A	D...A	D–H...A	Symmetry code
Complex C1					
C6–H6...O3	0.930	2.600	3.476(6)	158	–
C27–H27...O1	0.930	2.500	3.326(5)	148	–
C28–H28...O4	0.930	2.540	3.461(5)	173	–
C28–H28...O5A	0.930	2.570	3.176(8)	123	–
C36–H36...O4	1.02(6)	2.55(5)	3.484(4)	151(4)	–
C40–H40...O4	0.93	2.50	3.326(5)	148	2 – x, 2 – y, 1 – z
Complex C3					
C1–H1...O5	0.980	2.590	3.420(9)	143	–
C4–H4...O5	0.930	2.510	3.428(8)	170	–
C8–H8...O1	0.930	2.440	3.223(9)	141	2 – x, 2 – y, 1 – z
C26–H26...O1	0.930	2.290	3.071(9)	141	–
C36–H36...O2	0.930	2.930	3.132(9)	144	–
C50–H50...O4	0.930	2.930	3.463(12)	158	1 – x, 1 – y, 2 – z

3.3 Intermolecular interactions

In complexes **C1** and **C3**, a combination of several weak and medium intermolecular interactions, determine the structural assembly in this compound (figures 3 and 4, table 4).

The Ag(1).....O(3) distances in **C1** and **C3** are 2.760 and 2.748 Å, respectively (figures 2 and 3). In fact, the crystal structure of the complexes show a close association between the nitrate anion and the metal centre, with Ag.....O distances of 2.76 and 2.75 Å.¹¹ For the structure of **C1**, nitrate oxygen atom is highly disordered and is split into two positions with 50% occupancy (O5A–O5B).

4. Conclusions

The present study describes very simple and efficient synthesis and characterization of two linear Ag(I) complexes. On the basis of the physicochemical and spectroscopic data, we have proposed that ligands employed here exhibit a linear coordination behaviour to the metal centre. The metal centre is coordinated by two phosphorus ylides via ylidic carbon atom and one NO₃ ion. For two of them, **C1** and **C3**, the crystal structures had the expected typical structure for linear silver(I) complexes.

Supplementary data

CCDC 865649 and 811867 contain supplementary crystallographic data for the compounds **C1** and **C3**, respectively. These data can be obtained free of charge

via <http://www.ccdc.cam.ac.uk/contents/retrieving.html> or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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