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Synthesis and characterization of new nitrate-bridged polymeric complexes of mercury(II) with phosphorus ylides

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Abstract

Reaction of phosphorus ylides of the type $X–C_6H_4–COCH=PAr_3$ (X = Cl and NO_2; Ar = phenyl and *p*-tolyl) with $Hg(NO_3)_2 \cdot H_2O$ in equimolar ratios using methanol as solvent are reported. X-ray crystal structure analysis of $[Hg(ClC_6H_4C(O)CHPPh_3)(NO_3)-(\mu-NO_3)]_n \cdot (DMSO)_n$ shows that the 1:1 complex adopts the noncentrosymmetric polymeric structure in the solid state with NO_3^- anion bridges. Variation of temperature or concentration in a ^{31}P NMR study indicates that the disappearance of satellites, due to coupling to ^{199}Hg, occurs at increasing temperature or decreasing concentration.
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1. Introduction

The utility of metalated phosphorus ylides in synthetic chemistry has been well documented [1,2]. 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. [3] Weleski et al. [4] in 1975 proposed a symmetric halide-bridged dimeric structure for Hg(II) halides complexes while Kalianasundari et al. [5] in 1995 reported an asymmetric halide-bridged structure. As far as we are aware, no Hg(II) nitrate polymeric complexes with these ylides have been reported to date. This paper reports the first examples of polymeric Hg(II)–phosphorus ylide complexes wherein the nitrate anions are bridging, confirming the general belief that the seven-coordinated complexes would be formed. The aims of our present work are (i) to correctly determine and compare the molecular structure of the products formed by the $Hg(NO_3)_2 \cdot H_2O$ with title ylides and (ii) to characterize all the products by IR, ^1H, ^{31}P, ^{13}C NMR spectra and elemental analyses.

Juxtaposition of the keto group and carbanion in the phosphorus ylides allows for the resonance delocalization of the ylidic electron density providing additional stabilization to the ylide species (Scheme 1). This so-called α-stabilization provides ylides with the potential to act as an ambidentate ligand and thus bond to an Hg(II) centre through the either carbon (B) or oxygen (A_1 and A_2) (Scheme 1).

Although many bonding 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), [5,7–10] whereas, O-coordination dominates when the metals involved are hard, e.g., Ti(IV), Zr(IV), and Hf(IV) [11].

2. Experimental

2.1. Physical measurements and materials

Solvents were reagent grade and used without further purification. Melting points were measured on a SMPI apparatus. Solution state NMR spectra were recorded on 300 and 90 MHz Bruker and Jeol spectrometer, respec-

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O-co-ordination, cisoid   O-co-ordination, transoid   C-co-ordination
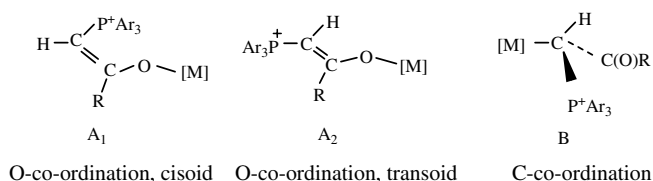
Scheme 1.

tively, using $CDCl_3$ or DMSO-d_6 as solvent. IR spectra were recorded on a Shimadzu-U-04 FT-IR instrument from KBr pellets. X-ray analysis was made on a STOE IPDS-II diffractometer.

2.2. X-ray crystallography

A colorless needle crystal with a dimension of $0.50 \times 0.03 \times 0.02$ mm^3 was mounted on a glass fiber and used for data collection. All measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 6660 unique reflections. Data were collected at a temperature of 293(2) K to a maximum 2θ value of 53.58 and in a series of ω scans in 1° oscillations and integrated using the STOE X-AREA software package [12]. A numerical absorption correction was applied using X-RED [13] and X-SHAPE [15] software's. The data were corrected for Lorentz and Polarizing effects. The structure was solved by direct methods [14] and subsequent difference Fourier map and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [15]. All of hydrogen atoms were located in a difference Fourier map and thereafter refined isotropically. Subsequent refinements then converged with R factors and parameters errors significantly better than for all attempts to model the solvent disorder.

2.3. Sample preparation

2.3.1. Preparation of [Ph₃PCHC(O)C₆H₄Cl] (1a)

General procedure [16]: A solution of triphenylphosphine (0.131 g, 0.5 mmol) and 2-bromo-4′-chloroacetophenone (0.117 g, 0.5 mmol) in acetone (15 mL) was stirred at room temperature for 4 h. The resulting white precipitate was filtered off, washed with diethylether and dried. Further treatment with aqueous solution of NaOH (0.5 M, 50 mL) led to elimination of HBr, giving the free ligand **1a**. Yield 0.372 g (90%), mp, 196–198 °C. Anal. Calc. for $C_{26}H_{20}ClOP$: C, 75.27; H, 4.86. Found: C, 75.42; H, 4.88%. IR (KBr, cm^{-1}) v: 1579 (C=O), 1522, 1480, 1435, 1404, 1383, 1188, 1175, 1104, 1085, 1009, 882 (P–C), 848, 747, 716, 693. ^{1}H NMR (CDCl$_3$) δ_H: 4.38 (d, 1H, $^2J_{PH} = 23.75$ Hz, CH); 7.25–7.94 (m, 19H, arom.). ^{31}P NMR (CDCl$_3$) δ_P: 14.19. ^{13}C NMR (CDCl$_3$) δ_c: 50.65 (d, $^1J_{PC} = 110.3$ Hz, CH); 126.0 (d, $^1J_{PC} = 91.40$ Hz, PPh$_3$ (i)); 127.31 (COPh (m)); 128.03 (PPh$_3$ (p)); 128.48 (d, $^3J_{PC} = 12.41$ Hz, PPh$_3$ (m)); 131.80 (d, $^4J_{PC} = 2.73$ Hz,

COPh (O)); 132.60 (d, $^2J_{PC} = 10.25$ Hz, PPh$_3$ (o)); 134.71 (COPh (p)); 139.15 (d, $^2J_{PC} = 14.69$ Hz, COPh (i)); 182.84 (d, $^2J_{PC} = 3.1$ Hz, CO).

2.3.2. [(p-tolyl)₃PCHC(O)C₆H₄Cl] (1b) [17]

Yield 0.406 g (89%), mp, 160–162 °C. Anal. Calc. for $C_{29}H_{26}ClOP$: C, 76.23; H, 5.74. Found: C, 76.29; H, 5.96. IR (KBr, cm^{-1}) v: 1581 (C=O), 1522, 1497, 1485, 1402, 1382, 1186, 1103, 1087, 1077, 1011, 882 (P–C), 845, 813, 750, 718, 681, 649. ^{1}H NMR (CDCl$_3$) δ_H: 4.34 (d, 1H, $^2J_{PH} = 23.12$ Hz, CH); 7.31–8.34 (m, 16H, arom.). ^{31}P NMR (CDCl$_3$) δ_P: 13.15. ^{13}C NMR (CDCl$_3$) δ_C: 20.95 (CH$_3$); 51.19 (d, $^1J_{PC} = 112.1$ Hz, CH); 123.33 (d, $^1J_{PC} = 93.56$ Hz, p-tolyl (i)); 127.12 (COPh (m)); 127.88 (p-tolyl (p)); 129.10 (d, $^3J_{PC} = 12.66$ Hz, p-tolyl (m)); 132.53 (d, $^2J_{PC} = 10.50$ Hz, p-tolyl (o)); 134.27 (COPh (p)); 139.71 (d, $^2J_{PC} = 14.91$ Hz COPh (i)); 142.00 (d, $^4J_{PC} = 2.84$ Hz COPh (o)); 182.31 (d, $^2J_{PC} = 3.58$ Hz, CO).

2.3.3. [Ph₃PCHC(O)C₆H₄NO₂] (1c) [18]

Yield 0.374 g (88%), mp 182–184 °C (lit. [18] 160–162 °C). Anal. Calc. for $C_{26}H_{20}NO_3P$: C, 73.41; H, 4.74; N, 3.29. Found: C, 73.12; H, 4.81; N, 3.53%. IR (KBr, cm^{-1}) v: 1529 (C=O), 1481, 1437, 1408, 1390, 1341, 1318, 1180, 1104, 1083, 884 (P–C), 863, 750, 720, 693. ^{1}H NMR (CDCl$_3$) δ_H: 4.51 (d, 1H, $^2J_{PH} = 22.85$ Hz, CH); 7.34–7.94 (m, 19H, arom.). ^{31}P NMR (CDCl$_3$) δ_P: 14.19. ^{13}C NMR (CDCl$_3$) δ_C: 53.40 (d, $^1J_{PC} = 110.2$ Hz, CH) 122.90 (COPh (m)); 126.05 (d, $^1J_{PC} = 91.28$ Hz, PPh$_3$ (i)); 127.69 (PPh$_3$ (p)); 128.91 (d, $^3J_{PC} = 12.46$ Hz, PPh$_3$ (m)); 132.98 (d, $^2J_{PC} = 10.21$ Hz, PPh$_3$ (o)); 132.27 (COPh (o)); 147.19 (d, $^2J_{PC} = 15.45$ Hz, COPh (i)); 148.11 (COPh (p)); 181.79 (s, CO).

2.3.4. [(p-tolyl)₃PCHC(O)C₆H₄NO₂] (1d) [17]

Yield 0.374 g (80%), mp, 156–158 °C. Anal. Calc. for $C_{29}H_{26}NO_3P$: C, 74.51; H, 5.61; N, 3.00. Found: C, 74.21; H, 6.03; N, 3.33%. IR (KBr, cm^{-1}) v: 1600 (C=O), 1530, 1407, 1339, 1187, 1179, 1112, 886 (P–C), 862, 807, 718, 718, 665, 656. ^{1}H NMR (CDCl$_3$) δ_H: 4.47 (d, 1H, $^2J_{PH} = 22.67$ Hz, CH); 7.26–8.14 (m, 16H, arom.). ^{31}P NMR (CDCl$_3$) δ_P: 13.13. ^{13}C NMR (CDCl$_3$) δ_C: 21.33 (CH$_3$); 54.13 (d, $^1J_{PC} = 113.5$ Hz, CH); 122.72 (COPh (m)); 122.98 (d, $^1J_{PC} = 93.63$ Hz, p-tolyl (i)); 127.55 (p-tolyl (p)); 129.52 (d, $^3J_{PC} = 12.64$ Hz, p-tolyl (m)); 132.84 (d, $^2J_{PC} = 10.52$ Hz, p-tolyl (o)); 142.66 (d, $^4J_{PC} = 2.57$ Hz COPh (o)); 147.21 (d, $^2J_{PC} = 1.58$ Hz COPh (i)); 147.87 (COPh (p)); 181.14 (s, CO).

2.3.5. Synthesis of [Ph₃PCHC(O)C₆H₄Cl · Hg(NO₃)₂] (2a)

General procedure: To a magnetically stirred solution of Hg(NO$_3$)$_2$ · H$_2$O (0.344 g, 1 mmol) in methanol (10 mL), was added a methanolic solution (5 mL) of ylide **1a** (0.414 g, 1 mmol). After 30 min the solvent was removed under reduced pressure to 3 mL. After addition of diethylether (30 mL) the white solid product was separated by filtration.

Crystals can be obtained from dimethylsulfoxide by diethyl ether diffusion method. Yield 0.554 g (75%). Anal. Calc. for $C_{26}H_{20}ClHgN_2O_7P$: C, 42.23; H, 2.73; N, 3.79. Found: C, 42.28; H, 2.89; N, 4.16%. mp. 154–155 °C. IR (KBr, cm^{-1}) v: 1662 (C=O), 1588, 1502, 1438, 1401, 1382, 1309, 1288, 1266, 1195, 1108, 1007, 997, 824 (P–C), 749, 722, 690. ^{1}H NMR (DMSO-d_6) δ_H: 6.52 (d, 1H, $^2J_{PH} = 5.74$ Hz, CH); 7.58–8.21 (m, 19H, arom.). ^{31}P NMR (DMSO-d_6) δ_P: 28.38 (s with satellites, $^2J_{HgP} = 295.2$ Hz). ^{13}C NMR (DMSO-d_6) δ_C: 121.50 (d, $^1J_{PC} = 89.08$ Hz, PPh$_3$ (i)); 128.63 (COPh (m)); 129.85 (d, $^3J_{PC} = 12.89$ Hz, PPh$_3$ (m)); 130.72 (PPh$_3$ (p)); 133.81 (d, $^2J_{PC} = 10.27$ Hz, PPh$_3$ (o)); 134.26 (COPh (p)); 134.34 (COPh (o)); 138.99 (COPh (i)); 192.66 (s, CO).

2.3.6. Synthesis of [(p-tolyl)₃PCHC(O)C₆H₄Cl · Hg-(NO₃)₂] (2b)

Yield 0.603 g (77.2%). Anal. Calc. for $C_{29}H_{26}ClHgN_2O_7P$: C, 44.57; H, 3.35; N, 3.58. Found: C, 44.73; H, 3.42; N, 3.80%. mp. 155–156 °C. IR (KBr, cm^{-1}) v: 1655 (C=O), 1598, 1589, 1499, 1438, 1399, 1384, 1268, 1193, 1107, 1006, 830 (P–C), 805, 659. ^{1}H NMR (DMSO-d_6) δ_H: 2.32 (s, 9H, 3CH$_3$); 6.27 (br d, 1H, $^2J_{PH} = 5.65$ Hz, CH); 7.48–8.21 (m, 16H, arom.). ^{31}P NMR (CDCl$_3$) δ_P: 27.23 (s with satellites, $^2J_{HgP} = 289.2$ Hz). ^{13}C NMR (DMSO-d_6) δ_C: 20.99 (3CH$_3$); 118.1 (d, $^1J_{PC} = 90.97$ Hz, p-tolyl (i)); 128.41 (COPh (m)); 130.22 (d, $^3J_{PC} = 12.71$ Hz, p-tolyl (m)); 130.50 (p-tolyl (p)); 133.49 (d, $^2J_{PC} = 10.52$ Hz, p-tolyl (o)); 137.72 (COPh (p)); 138.67 (COPh (o)); 144.91 (COPh (i)); 192.06 (d, $^2J_{PC} = 15.77$ Hz, CO).

2.3.7. Synthesis of [Ph₃PCHC(O)C₆H₄NO₂ · Hg(NO₃)₂] (2c)

Yield 0.552 g (73.6%). Anal. Calc. for $C_{26}H_{20}HgN_3O_9P$: C, 41.64; H, 2.69; N, 5.60. Found: C, 42.00; H, 2.73; N, 5.71. mp. decomp. at 132 °C. IR (KBr, cm^{-1}) v: 1659 (C=O), 1524, 1497, 1486, 1437, 1382, 1346, 1311, 1270, 1108, 1008, 997, 832 (P–C), 747, 719, 691. ^{1}H NMR (DMSO-d_6) δ_H: 6.57 (br d, 1H, $^2J_{PH} = 4.57$ Hz, CH); 7.74–8.36 (m, 16H, arom.). ^{31}P NMR (DMSO-d_6) δ_P: 28.31 (s with satellites, $^2J_{HgP} = 290.6$ Hz). ^{13}C NMR (DMSO-d_6) δ_C: 118.86 (d, $^1J_{PC} = 89.4$ Hz, PPh$_3$ (i)); 127.76 (COPh (m)); 130.39 (d, $^3J_{PC} = 12.62$ Hz, PPh$_3$ (m)); 134.33 (d, $^2J_{PC} = 10.21$ Hz, PPh$_3$ (o)); 135.14 (PPh$_3$ (p)); 145.91 (COPh (o)); 146.72 (COPh (i)); 150.60 (COPh (p)); 192.32, (s, CO).

2.3.8. Synthesis of [(p-tolyl)₃PCHC(O)C₆H₄NO₂ · Hg(NO₃)₂] (2d)

Yield 0.626 g (79.1%). Anal. Calc. for $C_{29}H_{26}HgN_3O_9P$: C, 43.97; H, 3.31; N, 5.30. Found: C, 44.32; H, 3.34; N, 5.44. mp. decomp. at 152 °C. IR (KBr, cm^{-1}) v: 1663 (C=O), 1599, 1525, 1500, 1384, 1347, 1266, 1192, 1007, 857, 833 (P–C), 805, 718, 654. ^{1}H NMR (DMSO-d_6) δ_H: 2.5 (9H, s, 3CH$_3$); 6.55 (d, 1H, $^2J_{PH} = 5.02$ Hz, CH); 7.55–8.42 (m, 16H, arom.). ^{31}P NMR (DMSO-d_6) δ_P:

27.34 (s with satellites, $^2J_{HgP} = 297.7$ Hz). ^{13}C NMR (DMSO-d_6) δ_C: 21.78 (CH$_3$); 43.57 (d, $^1J_{PC} = 58.11$ Hz, CH); 117.6 (d, $^1J_{PC} = 92.15$ Hz, p-tolyl (i)); 123.97 (COPh (m)); 129.69 (p-tolyl (p)); 130.91 (d, $^3J_{PC} = 12.60$ Hz, p-tolyl (m)); 133.48 (d, $^2J_{PC} = 9.66$ Hz, p-tolyl (o)); 140.07 (COPh (i)); 145.93 (COPh (o)); 150.48 (COPh (p)); 192.47 (s, CO).

3. Results and discussion

The polymeric structure of the titled complexes may be obtained from the reaction of Hg(NO$_3$)$_2$ · H$_2$O and related ylide in equimolar ratios using methanol as solvent (Scheme 2).

3.1. Spectroscopy

The v(CO) which is sensitive to complexation occurs at higher frequencies comparing to parent ylides, indicating coordination of the ylide thorough carbon. C-coordination causes an increase in v(CO) and decrease in v(P$^+$–C$^-$) while, for O-coordination, a lowering for both frequencies is expected. The v(P$^+$–C$^-$) which is also diagnostic for the coordination occurs at lower frequencies for the complexes, suggesting some removal of electron density in the P–C bond [19,20].

In the ^{1}H NMR spectra, methinic protons exhibit doublet or broad doublet signals. This broadening might be due to coupling to ^{199}Hg and forming satellites. Similar behavior was observed earlier in the case of ylide complexes of platinum(II) chloride [21]. The expected downfield shifts of ^{31}P and ^{1}H signals for the PCH group upon complexation in the case of C-coordination were observed in their corresponding spectra. It must be noted that O-coordination of the ylide generally leads to the formation of cisoid and transoid isomers giving rise to two different signals in ^{31}P and ^{1}H NMR (Scheme 1) [7]. The ^{31}P NMR spectra at room temperature clearly exhibit the previously mentioned satellites (8% intensity each, $^2J_{PHg}$ ~295 Hz) while these satellites for ylidic complexes of Hg(II) halides are only observed at low temperature [5,19,20,22] or by solid state ^{31}P NMR [22]. Variable temperature ^{31}P NMR study on **2d**, using DMSO-d_6 as solvent showed that disappearance of satellites occurs when the

a: X = Cl, Ar = C₆H₅
b: X = Cl, Ar = C₆H₄-CH₃
c: X = NO₂, Ar = C₆H₅
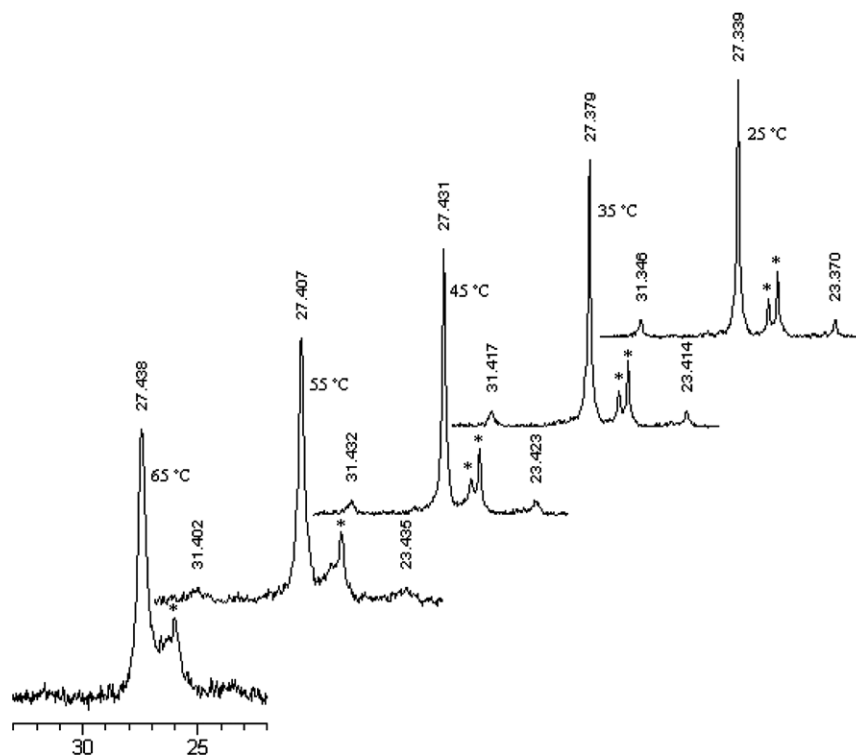d: X = NO₂, Ar = C₆H₄-CH₃
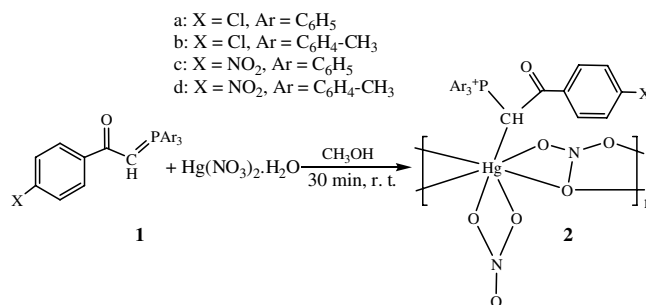
Scheme 2.

Fig. 1. Variable temperature ^{31}P NMR study for **2d** (*, impurity).

temperature is increased to 65 °C (Fig. 1). This also occurs when the concentration is decreased (Fig. S2). Greater solvent strength caused by increasing temperature [22] or decreasing concentration, led to a faster exchange of the ylide with the metal [23], which caused exchange decoupling. Thus it seems that the solvent (DMSO) can affect directly on the nature of the polymeric structure in the solution state and probably it is cleaved to smaller species.

The most interesting aspect of the ^{13}C NMR spectra of the complexes is the up field shift of the signals due to ylidic carbon. Similar up field shifts of 2–3 ppm with reference to the parent ylide were also observed in the case of [Ph$_3$PC$_5$H$_4$HgI$_2$]$_2$ [23] and in our synthesized Hg(II) complexes [24,25]. High solubility of **2d** in CDCl$_3$ allowed us to record the spectrum in this solvent but, for the others, we had to use DMSO-d_6 and the presence of a solvent septet peak at 39.5 ppm in the CH resonance region prevented the observation of these signals. However one clear doublet for CH resonance at 43.57 ppm was obtained for **2d** that shows the previously mentioned up field shift compared to the same carbon in the parent ylide (54.13 ppm). The ^{13}C NMR shifts of the CO group in the complexes are around 192 ppm, lower field than around 182 ppm noted for the same carbon in the parent ylides, indicating much lower shielding of carbon of the CO group in these complexes.

3.2. X-ray crystallography

Table 1 provides the crystallographic results and refinement information for complex **2a**. The molecular structure

Table 1
Crystal data and structure refinement for [Hg(ClC$_6$H$_4$C(O)CHPPh$_3$)(NO$_3$)(μ-NO$_3$)]$_n$ · (DMSO)$_n$

|	
Empirical formula	C$_{28}$H$_{26}$Cl$_1$Hg$_1$N$_2$O$_8$P$_1$S$_1$
Formula weight	817.59
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	9.3582(8)
b (Å)	17.674(2)
c (Å)	18.8267(17)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	3113.9(5)
Z, Calculated density (Mg/m^3)	4, 1.744
Absorption coefficient (mm^{-1})	5.197
$F(000)$	1600
Crystal size (mm)	0.50 × 0.03 × 0.02
θ Range for data collection (°)	1.58–26.79
Limiting indices	−11 ⩽ h ⩽ 11, −22 ⩽ k ⩽ 22, −23 ⩽ l ⩽ 23
Reflections collected/unique (R_{int})	20768/6660 (0.0616)
Completeness to theta = 26.79	99.3%
Absorption correction	Numerical
Maximum and minimum transmission	0.901 and 0.829
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6660/0/381
Goodness-of-fit on F^2	1.172
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0384$, $wR_2 = 0.0677$
R indices (all data)	$R_1 = 0.0482$, $wR_2 = 0.0708$
Absolute structure parameter	−0.009(7)
Largest difference in peak and hole (e Å^{-3})	0.564 and −0.730
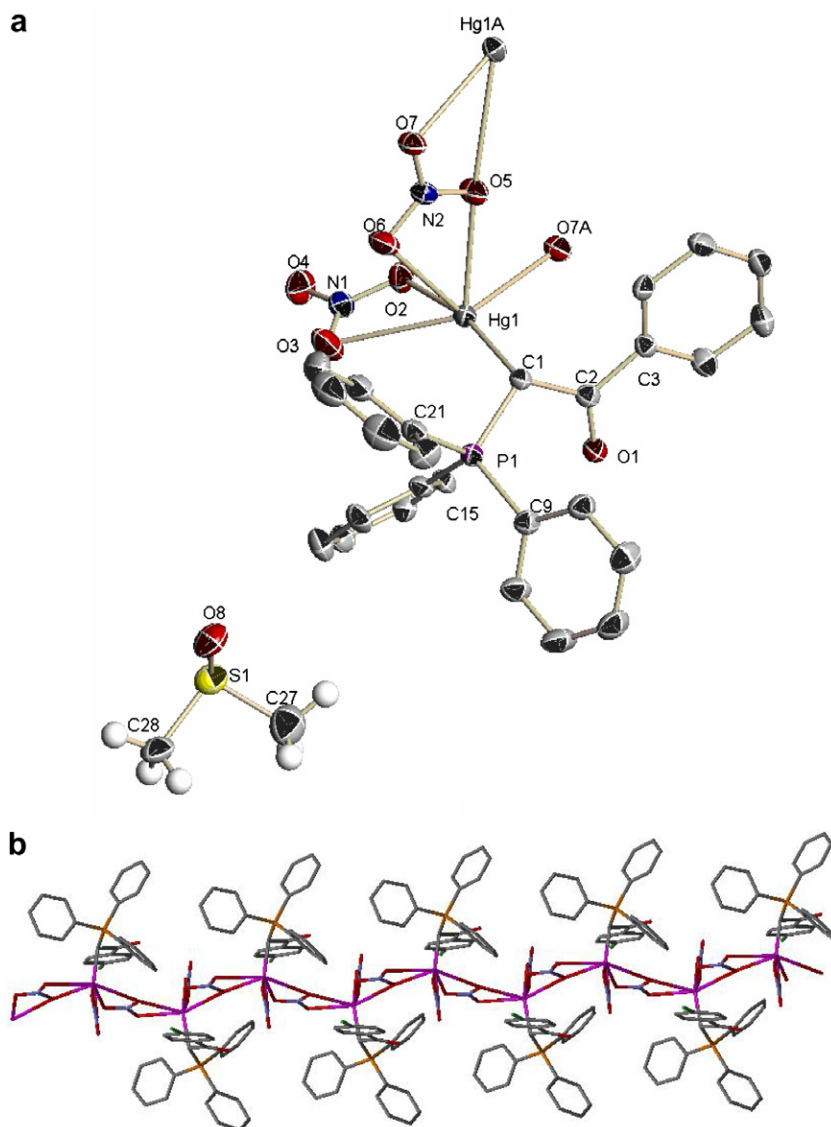
Fig. 2. X-ray crystal structure of **2a**. (a) Asymmetric unit and (b) polymeric chain. Hydrogen atoms are omitted for clarity.

of **2a** is shown in Fig. 2. Packing diagram, fractional atomic coordinates and equivalent isotropic displacement coefficients (U_{eq}) for the non-hydrogen atoms of complex **2a** are shown in Supplementary material. Table 2 lists key bond lengths and angles for complex **2a**.

X-ray crystal structure analysis shows that the 1:1 complex, $[Hg(ClC_6H_4C(O)CHPPh_3)(NO_3)(\mu-NO_3)]_n \cdot (DMSO)_n$ adopts the noncentrosymmetric polymeric structure in the solid state with NO_3^- anion bridges. The mercury atom is surrounded by one carbon atom of the ylide ligand with Hg–C distance of 2.133(6) Å and two oxygen atoms of the nitrate ligand with Hg–O distances of 2.143(5) and 2.815(4) Å and also four oxygen atoms of bridged nitrate anion with Hg–O distances of 2.744(4), 2.636(5), 2.545(5) and 2.927(4) Å. The coordination number in this complex is seven (one of ylide, two of one bidentate nitrate anion and four of two bridged nitrates). There are only a few inorganic examples of bridging

Table 2
Selected bond lengths (Å) and bond angles (°) for the compound **2a** with corresponding experimental values

Bond lengths	
Hg(1)–C	2.133(6)
Hg(1)–O(2)	2.143(5)
Hg(1)–O(7)#1	2.545(5)
Hg(1)–O(5)	2.636(5)
Hg(1)–O(3)	2.815(4)
Hg(1)–O(6)	2.744(4)
O(7)–Hg(1)#2	2.545(5)
Bond angles	
C(1)–Hg(1)–O(2)	164.6(2)
C(1)–Hg(1)–O(7)#1	103.72(19)
O(2)–Hg(1)–O(7)#1	83.12(18)
C(1)–Hg(1)–O(5)	105.1(2)
O(2)–Hg(1)–O(5)	90.1(2)
O(7)#1–Hg(1)–O(5)	70.13(14)

nitrates with different coordination modes: bidentate [26], tridentate [27] and tetradentate [28] but in **2a** there are two different nitrate anions: one of them acts as bidentate and the other one acts as both bidentate and bridging group (totally tetradentate).

The C-coordination of **1a** is in stark contrast to the O-coordination of the phosphorus ylide Ph$_3$PC(COMe)-(COPh) (ABPPY) to the Hg(II) centre [29]. The difference in coordination mode between ABPPY and **1a** to Hg(II) can be rationalized in terms of the electronic properties and steric requirements of the ylides.

The lower electronic density at the ylidic C atom in doubly stabilized ylides compared with simple stabilized ylides has been calculated by DFT (density functional theory) methods recently [30], but it has also been demonstrated in the same contribution that this above factors are not the solely responsible of the bonding properties of double stabilized ylides. On the other hand, and concerning "simple" stabilized ylides, the C- versus O-bonding is also a very delicate balance of steric and electronic properties [31]. In this balance not only the size and shape of the ligand in the final bonding mode must be considered, but also the electronic nature of the metal (Pd, Pt, Ru, Au, etc.) and the donor atoms (C, O, N, etc.) and even the coordination site (trans to a C atom, trans to a N atom, trans to an O atom, and so on). All these facts must be considered as a whole in order to discuss the final bonding mode of a given ylide. The nucleophilicity of the carbanion in ABPPY is less than **1a**; this is due to the additional delocalization of the ylide electron density in ABPPY which is facilitated by the second carbonyl group. This will reduce the ability of ABPPY to bind via the ylidic carbon. Belluco et al. have studied steric influences on the coordination modes of ylide molecules to Pt(II) systems [32]. These authors concluded that the preferred coordination mode is via the ylidic carbon, but that steric hindrance around the metal centre or the ylidic carbon will necessitate O-coordination.

Indeed, this trend is reflected here, both BPPY and **1a** are slightly less sterically demanding than ABPPY, and are both C-coordinated to Hg(II). The significance of the Hg–C bond length, 2.134(4) Å in **2a** compared to analogous distances in [BPPY · HgI$_2$]$_2$ [6] and in [(C$_6$H$_5$)$_3$-PC$_5$H$_4$ · HgI$_2$]$_2$ [31] (2.312(13) and 2.292(8) Å, respectively) must be attributed to the use of Hg(II) orbitals with high s character for bonding to ylidic carbon. As expected on the basis of the Bent rule, the Hg–C bonds in **2a** and [BPPY · HgCl$_2$]$_2$ [6] are much shorter than in [BPPY · HgI$_2$]$_2$ because of the very low difference in electronegativity between carbon and iodine.

4. Conclusion

New complexes of the type [Hg(XC$_6$H$_4$C(O)CHPAr$_3$)-(NO$_3$)(μ- NO$_3$)]$_n$ · (DMSO)$_n$ (X = Cl, NO$_2$; Ar = PPh$_3$, P(p-tolyl)$_3$) have been synthesized and characterized.

X-ray crystal structure analysis showed that polymeric complexes may be formed via the nitrate anion bridges. In this type of complex, in comparison to mercury halide complexes, satellites due to coupling to ^{199}Hg could be seen at room temperature or high concentrations but disappear at higher temperatures or lower concentrations.

Appendix A. Supplementary material

CCDC 617451 contains the supplementary crystallographic data for **2a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.044.

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