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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 $Ph_3P=CHC(O)R$ (R = 2,4-dichlorophenyl (**L¹**) and 4-isopropylphenyl (**L²**)) with $AgNO_3$and $Hg(NO_3)_2.H_2O$, using methanol as a solvent, are reported. The crystal structures of **L²** and $[Ag(L^2)_2(NO_3)]$ (**2**) have been determined. Characterization of the obtained compounds was also performed by elemental analysis, IR, ^1H, ^{31}P and ^{13}C 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 halide-bridged 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 **L²** 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, ^{31}P and ^{13}C NMR spectra were recorded on 90 MHz Jeol and 300 MHz Bruker spectrometers in $CDCl_3$ or DMSO-d_6 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 **L²** and **2** were collected on a STOE IPDS-II diffractometer at 298 K, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å).

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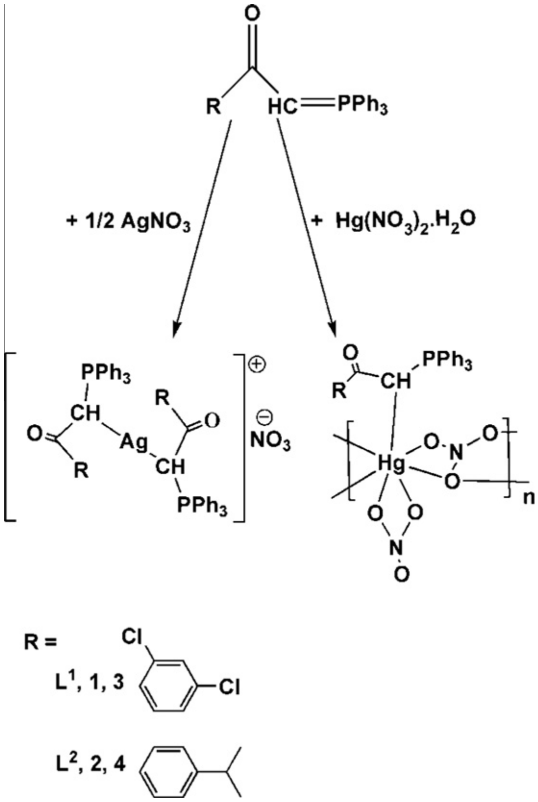

Scheme 1. Schematic illustration of the complexes under study.

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 $\mathbf{L^2}$ 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 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**.

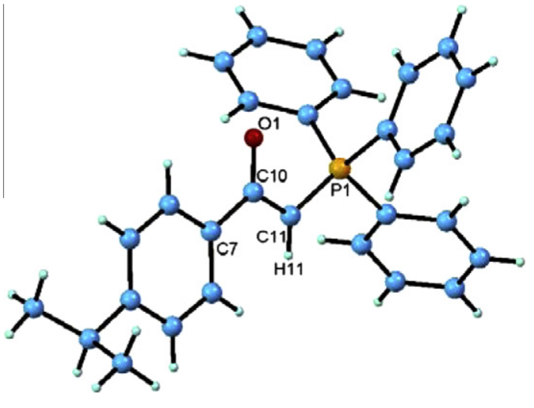

Fig. 1. X-ray crystal structure of $\mathbf{L^2}$.

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

	ν(C=O)	δ_{PCH}	$^2J_{PH}$(y)	$^2J_{PH}$(Ps)	δ $_{PPh3}$[a]	$^2J_{HgP}$
$\mathbf{L^1}$,[b]	1576	4.0(d)	23.66	12.36	12.40(s)	–
$\mathbf{L^2}$,[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.
[a] T = 298 K; TMS δ = 0.00 ppm; shifts relative to internal TMS and external 85% phosphoric acid.
[b] Recorded in $CDCl_3$.
[c] Recorded in DMSO-d_6.

2.4. Sample preparation

2.4.1. Synthesis of [2,4-$Cl_2C_6H_3C(O)CHPPh_3$] ($\mathbf{L^1}$)

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 Et_2O 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 $C_{26}H_{19}OPCl_2$: C, 69.50; H, 4.26. Found: C, 69.61; H, 4.34%. IR (KBr disk, cm^{-1}) ν: 1576 (CO), 878 (P^+-C^-). ^1H NMR ($CDCl_3$, ppm) δ_H: 3.98 (d, $^2J_{PH}$ = 23.21 Hz, 1H, CHP), 7.12–7.34 (m, 18H, arom.). ^{31}P NMR ($CDCl_3$, ppm) δ_P: 12.43. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 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-$(CH_3)_2CHC_6H_4C(O)CHPPh_3$] ($\mathbf{L^2}$)

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 Et_2O 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 $C_{29}H_{27}OP$: C, 82.44; H, 6.44. Found: C, 82.71; H, 6.57%. IR (KBr disk, cm^{-1}) ν: 1579 (CO), 887 (P^+–C^-). ^1H NMR ($CDCl_3$, ppm) δ_H: 1.23 (d, $^3J_{HH}$ = 6.76 Hz, 6H, CH_3), 2.90 (m, 1H, $CH(CH_3)_2$), 4.38 (d, $^2J_{PH}$ = 24.37, 1H, CHP), 7.23–7.92 (m, 19H, arom.). ^{31}P NMR ($CDCl_3$, ppm) δ_P: 14.05. $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) δ_C: 23.23 (s, CH_3), 33.15 (s, $CH(CH_3)_2$), 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 $\mathbf{L^1}$ (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 Et_2O and dried under reduced pressure.

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