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Exploring the reactivity of an *N*-pyrazole, *P*-phosphine hybrid ligand with Cu(I), Ag(I) and Au(I) precursors

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ABSTRACT

The reactivity of (3,5-dimethyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphine (**L**) hybrid ligand against Cu(I), Ag(I) and Au(I) has been assayed and compounds $[Cu(L)_2](PF_6)$ (**1**), $[Ag(L)]_2(PF_6)_2 \cdot 2C_2H_4Cl_2 \cdot 2C_4H_{10}O$ (**2**) and $[AuCl(L)]_2$ (**3**) have been isolated and fully characterised. A fully characterisation by analytical and spectroscopic methods of **1**–**3** are presented and X-ray crystal structures of **1** and **2** are also reported. The similar data obtained between **2** and **3** permits to do a serious purpose of the structure of **3** in solid and solution.

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1. Introduction

The interest in coordination chemistry has increased impressively in the last decades. The synthesis, characterisation and the study of the specific properties of a great variety of complexes composed by organic molecules called ligands connected to metals have focused interesting studies in many laboratories for its potential applicability in a large quantity of fields [1–8]. One of the extended lines in progressively expansion is the family of the complexes that contain *N*-pyrazole ligands [9–13].

In the last thirteen years, our group has realised great efforts to synthesise and characterise complexes that contain simple and hybrid *N*-pyrazole ligands. Hybrid ligands are composed by an *N*-pyrazole group and another functional group (with different electronic and steric properties in comparison with *N*-pyrazole group) capable to connect to the metallic centre and build metallocycles or macrometallocycles. One of our research lines is the synthesis and characterisation of *N*-pyrazole, *P*-phosphine ligands. In particular, previously we synthesised the ligand (3,5-dimethyl-1*H*-pyrazol-1-

yl)ethyldiphenylphosphine (**L**) and we have studied the reactivity against Rh(I) and Ru(II) [14,15]. All the complexes obtained were mononuclear structures where **L** was coordinated to the metal via k^2 -*N*,*P* generating six-membered rings. The different nature of the metallic centres generates distorted square planar geometries for Rh(I) and distorted octahedral geometry or an intermediate geometry between square pyramidal and trigonal-bipyramid for Ru(II).

As our knowledge, there are approximately three hundred papers and more than seven-hundred and fifty crystalline structures of compounds where the metallic centre is coordinated to *N*-pyrazole ligands and *P*-phosphine ligands [16]. However, only fourteen crystalline structures with *N*-pyrazole, *P*-phosphine hybrid ligands with the elements of Group 11 with oxidation state +1 are reported: twelve structures of Cu(I) and three structures of Ag(I) (no structure with Au(I) has been published). The majority of these structures have been reported by Mak and coworkers [17–24]. In particular, these authors shows the 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine and assay the reactivity with Cu(II) [22–24] and Ag(I) [21]. In all complexes the ligand act as tridentate (*P*,*N*,*N*).

Metals of Group 11 are extensively investigated for their presence in biological systems and for their importance in the medical science. Also, the literature presents studies of copper(I)/(II) for its potential applicability in catalytic systems, of silver for its historical



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photographic applications (less used nowadays for the increase of new technologies) and finally of gold for its organometallic applications [25].

In order to enlarge the few quantity of structures of Cu(I) and Ag(I) published and to increase knowledge of the coordination behaviour of metals of Group 11 with oxidation state +1 against *N*-pyrazole, *P*-phosphine ligands, in this paper we present the synthesis and characterisation of complexes of Cu(I), Ag(I) and Au(I) with the ligand (3,5-dimethyl-1*H*-pyrazol-1-yl)ethyldiphenyl-phosphine (**L**) [14].

2. Experimental

2.1. General details

All reactions were performed with the use of vacuum line and Schlenk techniques. All reagents were commercial grade and were used without further purification. All solvents were dried and distilled by standard methods when it was necessary. The elemental analyses (C, H, N) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona, or in the University of Leeds microanalytical service, using a Carlo Erba CHNS EA-1108 instrument separated by chromatographic column and thermoconductivity detector. Conductivity measurements were performed at room temperature in 10^{-3} M acetonitrile solutions employing a CyberScan CON 500 (Eutech instrument) conductimeter. Infrared spectra were run in a Perkin Elmer FT-2000 spectrophotometer as KBr pellets. The ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra and bidimensional NMR spectra were run on an NMR-FT Bruker AC-250 spectrometer. All NMR experiments were recorded on CDCl₃ or CD₃CN solvents under nitrogen. ¹H and ¹³C{¹H} NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. ³¹P{¹H} NMR chemical shifts (δ) were determined relative to external 85% H₃PO₄ and are given in ppm. Electrospray Mass spectra (ESI⁺) were carried out by the staff of the Chemical Analysis Service of the Universitat Autònoma de Barcelona in an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics. Mass experiments were done on CH₃CN solvent. Matrix assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry were carried out by the staff of the Institut de Biotecnologia i Medicina of the Universitat Autònoma de Barcelona on a positive ion mode on a Bruker-Daltonics Ultraflex time-offlight instrument. Ion acceleration was set to 25 kV. All mass spectra were externally calibrated using a standard peptide mixture. The sample was dissolved in CHCl₃ and mixed with 2,5-dihydroxybenzoic acid (DHB) solution matrix (0.5 µl sample:0.5 µl matrix). The mixed solution was applied on a ground steel plate $(1 \mu l)$.

The precursor complex $AgPF_6$ is commercially available, $[Cu(CH_3CN)_4](PF_6)$ [26] and $[AuCl(SC_4H_8)]$ [27] and the ligand 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphine (**L**) [14] were prepared as described in the literature.

2.2. Synthesis and characterisation of complexes 1-3

2.2.1. [Cu(L)₂](PF₆) (1)

A solution of **L** (0.325 mmol, 0.100 g) dissolved in dry CH_2Cl_2 (10 mL) was added to a solution of $[Cu(CH_3CN)_4](PF_6)$ (0.160 mmol, 0.060 g) in dry CH_2Cl_2 (15 mL). The mixture was stirred during 12 h, the solution was concentrated to 5 mL and precipitated with 5 mL of cold dry diethyl ether. Filtration of the powder leads a white solid that corresponds to **1**. The complex was then crystallised in an acetone/diethyl ether mixture (1:10).

Yield: 80%, 0.134 mmol, 0.106 g. Anal. Calc. for $C_{38}H_{42}N_4P_3F_6Cu$: C, 55.31; H, 5.13; N, 6.79. Found C, 55.20; H, 5.15; N, 6.65%. MS (MALDI-TOF): m/z (%) 679 (100%) [CuL₂]⁺. IR: (KBr, cm⁻¹) 3055 ν(C–H)_{ar}, 2922, ν(C–H)_{al}, 1550 ν(C=C/C=N)_{ar}, 1432 δ(C=C/C=N)_{ar}, 838 ν(P–F), 739, 698 δ(C–H)_{oop}. ¹H NMR (CDCl₃ at 298 K, 250 MHz): δ = 7.59–7.17 (m, 20H, C₆H₅), 5.77 (s, 2H, pz-CH), 4.43 (br, 4H, pz-CH₂CH₂–P), 2.77 (br, 4H, pz-CH₂CH₂–P), 2.34 (s, 6H, pz-CH₃), 1.39 (s, 6H, pz-CH₃) ppm. ¹³C{¹H} NMR (CDCl₃ at 298 K, 63 MHz) δ: 148.7, 140.9 (pzC–CH₃), 132.4–127.1 (C₆H₅), 105.1 (pz-CH), 42.4 (pz-CH₂CH₂–P), 26.9 (pz-CH₂CH₂–P), 12.3, 10.6 (pz-CH₃) ppm. ³¹P{¹H} NMR (CDCl₃ at 298 K, 81 MHz) δ: –14.2 (s, *P*(C₆H₅)₂), –146.8 (sp, ¹*J*_{FP} = 706 Hz, *P*F₆⁻) ppm.

2.2.2. $[Ag(L)]_2(PF_6)_2 \cdot 2C_2H_4Cl_2 \cdot 2C_4H_{10}O(\mathbf{2})$

A solution of **L** (0.325 mmol, 0.100 g) dissolved in dry CH₂Cl₂ (10 mL) was added to a solution of AgPF₆ (0.320 mmol, 0.081 g) in dry CH₂Cl₂ (15 mL) protected from light. The mixture was stirred during 12 h and the solution was concentrated to dryness and washed with cold dry diethyl ether. The white powder obtained corresponds to **2**. The complex was then crystallised in a 1,2-dichloroethane/diethyl ether mixture (1:10). Complex **2** decomposes slowly in solid or solution to $[Ag(L)]_2(PF_2O_2)_2$.

Yield: 30%, 0.096 mmol, 0.054 g. Anal. Calc. for $C_{38}H_{42}N_4P_4F_{12}Ag_2 \cdot 2C_2H_4Cl_2 \cdot 2C_4H_{10}O$: C, 40.89; H, 4.80; N, 3.82. Found C, 41.27; H, 4.42; N, 3.74%. Conductivity (1.05 × 10⁻³ M in acetonitrile): 211 Ω^{-1} cm² mol⁻¹. MS [ESI (+)]: *m/z* (%) 723 (100%) [AgL_2]⁺. IR: (KBr, cm⁻¹) 3055 ν (C–H)_{ar}, 2922 ν (C–H)_{al}, 1554 ν (C=C/C=N)_{ar}, 1437 δ (C=C/C=N)_{ar}, 841 ν (P–F), 743, 695 δ (C–H)_{oop}. ¹H NMR (CD₃CN at 298 K, 250 MHz): δ = 7.85–7.17 (m, 20H, C₆H₅), 5.74 (s, 2H, pz-CH), 4.22 (m, 4H, pz-CH₂CH₂–P), 2.70 (m, 4H, pz-CH₂CH₂–P), 2.10 (s, 6H, pz-CH₃), 2.01 (s, 6H, pz-CH₃) ppm. ¹³C{¹H} NMR (CD₃CN at 298 K, 63 MHz) δ : 148.9, 141.9 (pzC–CH₃), 133.7–128.7 (C₆H₅), 106.4 (pz-CH), 45.2 (d, ²*J*_{PC} = 9.9 Hz, pz-CH₂CH₂–P), 28.2 (d, ¹*J*_{PC} = 17.3 Hz, pz-CH₂CH₂–P), 13.2, 10.6 (pz-CH₃) ppm. ³¹P{¹H} NMR (CD₃CN at 298 K, 81 MHz) δ : -1.4 (s, *P*(C₆H₅)₂), -17.2 (t, ¹*J*_{FP} = 952, *P*F₂O₂⁻), -146.8 (sp, ¹*J*_{FP} = 706 Hz, *P*F₆⁻) ppm.

2.2.3. $[AuCl(L)]_2$ (3)

A solution of **L** (0.325 mmol, 0.100 g) dissolved in dry CH_2Cl_2 (10 mL) was added to a solution of [AuCl(SC₄H₈)] (0.320 mmol, 0.103 g) in dry CH_2Cl_2 (15 mL). The mixture was stirred during 12 h and the solution was concentrated to dryness and washed with cold dry diethyl ether. The white powder obtained corresponds to **3**.

Yield: 90%, 0.288 mmol, 0.156 g. Anal Calc. for $C_{38}H_{42}N_4P_2Cl_2Au_2$: C, 42.20; H, 3.91; N, 5.18. Found C, 41.95; H, 3.72; N, 4.88%. Conductivity (1.09 × 10⁻³ M in acetonitrile): 14 Ω^{-1} cm² mol⁻¹. MS [ESI (+)]: m/z (%) 1045 (100%) [Au₂ClL₂]⁺, 813 (35%) [AuL₂]⁺. IR: (KBr, cm⁻¹) 3047 ν (C–H)_{ar}, 2959 ν (C–H)_{al}, 1552 ν (C=C/C=N)_{an} 1435 δ (C=C/C=N)_{an} 800 ν (P–C), 742, 690 δ (C–H)_{oop}. ¹H NMR (CDCl₃ at 298 K, 250 MHz): δ = 7.92–7.04 (m, 20H, C₆H₅), 5.61 (s, 2H, pz-CH), 4.27 (m, 4H, pz-CH₂CH₂–P), 3.01 (m, 4H, pz-CH₂CH₂–P), 2.12 (s, 6H, pz-CH₃), 2.08 (s, 6H, pz-CH₃) ppm. ¹³C{¹H} NMR (CDCl₃ at 298 K, 63 MHz) δ : 148.5, 140.0 (pzC–CH₃), 134.3–127.9 (C₆H₅), 106.1 (pz-CH), 44.6 (d, ²J_{PC} = 7.9 Hz, pz-CH₂CH₂–P), 29.6 (d, ¹J_{PC} = 36.8 Hz, pz-CH₂CH₂–P), 13.7, 11.8 (pz-CH₃) ppm. ³¹P{¹H} NMR (CDCl₃ at 298 K, 81 MHz) δ : +22.9 (*P*(C₆H₅)₂) ppm.

2.3. X-ray crystal structures of 1 and 2

Suitable colourless crystals for X-ray diffraction of **1** and **2** were obtained from solutions of **1** in acetone and **2** in 1,2-dichloroethane by slow diffusion of diethyl ether vapour (1:10). Diffraction data for **1** were measured using a Bruker X8 Apex diffractometer, with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) generated by a rotating anode. Diffraction data for **2** were carried out on a Nonius KappaCCD area detector diffractometer, using graphite-

monochromated Mo- K_{α} radiation from a sealed tube source. Both diffractometers were fitted with an Oxford Cryostream low temperature device.

Unit-cell parameters were determined from 28382 reflections for **1** (1.90 < θ < 30.32°) and 27532 reflections for **2** (1.65 < θ < 27.49°) and refined by least-squares methods. Semiempirical absorption corrections were applied. Intensities were collected with graphite monochromatized Mo- K_{α} radiation. 28382 reflections were measured in the range 1.90 < θ < 30.32° for **1** which 5779 were non-equivalent by symmetry (R_{int} (on I) = 0.0351). 4671 reflections were assumed as observed applying the condition $I > 2\sigma$ (I). 27532 reflections were measured in the range 1.65 $\leq \theta \leq$ 27.49 for **2** which 6379 were non-equivalent by symmetry (R_{int} (on I) = 0.0817). 3751 reflections were assumed as observed applying the condition $I > 2\sigma$ (I).

Both structures were solved by Direct Methods using SHELXS-97, and refined by full-matrix least-squares method with SHELXL-97 [28] using 28382 reflections for **1** and 27532 for **2**. The function minimised was $\Sigma w ||F_0|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0417P)^2 + 2.7662P]^{-1}$ and $P = (|F_0|^2 + 2|F_c|^2)/3$ for **1** and $w = [\sigma^2(I) + (0.1532P)^2]^{-1}$ and $P = (|F_0|^2 + 2|F_c|^2)/3$ for **2**.

The unit cell of **2** contained a large amount of badly disordered solvent, which could not be modelled satisfactorily. This disordered region corresponds to channels in the lattice running parallel to the unit cell *c* direction, of approximate dimensions 4.2×6.3 Å². This solvent was treated using the PLATON SQUEEZE routine [29]. The void area located by this procedure was 1423.4 Å³ or 25.5% of the total volume of the unit cell. This region contained 728 electrons, or 182 per complex molecule. This is equivalent to 2.0 disordered molecules of 1,2-dichloroethane plus 2.0 disordered molecules of diethyl ether per formula unit, which would give 184 electrons per formula unit. Therefore, this formulation was used for the density and *F*(000) calculations in the final refinement.

The phenyl group C18–C23 in **2** is disordered over two sites, labelled "A" (occupancy 0.70) and "B" (0.30). These two residues

were refined as rigid hexagonal groups, with the P2-C18A/B bonds restrained to 1.80 (1) Å. Although the thermal ellipsoids on the other phenyl ring C12-C17 are a little large, attempts to refine a disorder model for this group as well proved unsuccessful. The unique anion is also disordered, over two sites with occupancy 0.60 and 0.40. The disordered P—F bonds were restrained to 1.60 (2) Å, and cis-F…F distances in each partial anion to 2.26 (2) Å. All wholly occupied non-H atoms, the major phenyl disorder site C18A–C23A and both partial P sites in the disordered anions, were refined anisotropically. All H atoms in both structures were placed in calculated positions and refined using a riding model. The parameters refined and other details concerning the refinement of the crystal structures are gathered in Table 1.

3. Results and discussion

3.1. Synthesis and characterisation of 1-3

The reaction of $[Cu(CH_3CN)_4](PF_6)$ [26], AgPF₆ or $[AuCl(SC_4H_8)]$ [27] with **L** in dry CH₂Cl₂ using a 1:1 or 1:2 metal:ligand ratio led to the compounds $[Cu(L)_2](PF_6)$ (1), $[Ag(L)]_2(PF_6)_2 \cdot 2C_2H_4Cl_2 \cdot 2C_4H_{10}O$ (2) and $[AuCl(L)]_2$ (3) (Scheme 1). The synthesis of **2** has been done protected from light, and this complex decomposes slowly in the solid or solution to $[Ag(L)]_2(PF_2O_2)_2$. Compounds **1–3** have been characterised by elemental analysis, mass spectrometry, conductivity measurements, IR and NMR spectroscopies and single crystal X-ray diffraction.

Elemental analyses of **1–3** are consistent with the formulae $[Cu(L)_2](PF_6)$, $[Ag(L)]_2(PF_6)_2 \cdot 2C_2H_4Cl_2 \cdot 2C_4H_{10}O$ and $[AuCl(L)]_2$, respectively. It is important to observe that elemental analysis of **2** also contains four molecules of solvent, two molecules of 1,2-dichloroethane and two molecules of diethyl ether. Probably, these molecules have been occluded in the crystalline structure during the formation of the single crystals used for the analysis. MS-MALDI-TOF of **1** gives peaks with m/z values of 679 (100%)

Table	1
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Crystallographic data for 1 and 2.

	1	2	
Formula	C ₃₈ H ₄₂ N ₄ P ₃ F ₆ Cu	C ₅₀ H ₇₀ N ₄ O ₂ Cl ₄ P ₄ F ₁₂ Ag ₂	
Formula weight	825.22	1468.54	
Temperature (K)	150 (2)	150 (2)	
Wavelength (Å)	0.71073	0.71073	
System, space group	Monoclinic, C 2/c Monoclinic, C 2/c		
Unit cell dimensions			
a (Å)	15.4242 (11)	26.4901 (5)	
$b(\mathbf{A})$	16.4533 (13)	14.9457 (4)	
c (Å)	16.6223 (12)	17.1480 (4)	
$\beta(\circ)$	113.740 (3)	124.732 (2)	
$U(Å^3)$	3861.4 (5)	5579.5 (2)	
Ζ	4	4	
D_{calc} (g cm ⁻³)	1.419	1.748	
$\mu (\mathrm{mm}^{-1})$	0.752	1.093	
F (000)	1704	2976	
Crystal size (mm ³)	$0.25 \times 0.19 \times 0.10$	$0.26\times0.23\times0.18$	
hkl ranges	$-21 \le h \le 20, -21 \le k \le 23, -22 \le l \le 23$	$-33 \le h \le 34, -18 \le k \le 19, -22 \le l \le 22$	
2θ Range (°)	1.90 to 30.32	1.65 to 27.49	
Reflections collected/unique/ [R _{int}]	28382/5779 [R(int) = 0.0351]	27532/6379 [R(int) = 0.0817]	
Completeness to θ (%)	99.9	99.5	
Absorption correction	Multi-scan	Multi-scan	
Data/restrains/parameters	5779/0/239	6379/38/278	
Goodness-of-fit on F^2	1.033	0.964	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0340, wR_2 = 0.0813$	$R_1 = 0.0727$, w $R_2 = 0.2076$	
R indices (all data)	$R_1 = 0.0471$, w $R_2 = 0.0879$	$R_1 = 0.1071$, w $R_2 = 0.2277$	
Largest diff. peak and	+0.57, -0.38	+1.14, -1.12	
hole (e Å ⁻³)			





corresponding to $[Cu(L)_2]^+$. The MS-ESI (+) of **2** shows one peak at 723 (100%) attributable to $[Ag(L)_2]^+$ and **3** at 1045 (100%) and 813 (35%), corresponding to $[Au_2Cl(L)_2]^+$ and $[Au(L)_2]^+$, respectively. The molar conductivity of 10^{-3} M solutions of compounds **2** and **3** in acetonitrile shows values of 211 and $14 \Omega^{-1} \text{cm}^2 \text{ mol}^{-1}$, respectively. The value of **2** is attributable to a 2:1 electrolyte (probably **2** is present in solution as the dimmer $[(AgL)_2]^{+2}[PF_6]_2^{-1}$. The value of **3** implies that the compound is a non-electrolyte with a formula [AuLCl]₂, so probably the chlorine atoms are connected to gold [30]. The molar conductivity of **1** was not measured because of its low solubility in typical solvents. The IR spectra of these complexes, in the range 4000–400 cm⁻¹, support that **L** is coordinated to the metallic centre. Complexes **1** and **2** show signals at 838 and 841, respectively, attributable to $\nu(P-F)$ [31]. The signals in the ³¹P{¹H</sup>

NMR spectra for all complexes appear at slightly high fields than for the free ligand and permit to know that phosphorus atom is connected to metallic centre [-14.9 ppm (1), -1.4 (2), +22.9 (3) and -20.9 (**L**) ppm [14]. Also, the signal corresponding to the anion PF_6^- of **1** and **2** appears as a septet at $\delta = -146.8$ ppm with a ${}^{1}J_{PF} = 706$ ppm for the two compounds. Also, in the ${}^{31}P{}^{1}H$ NMR spectrum of **2** the tendency to decompose of the complex produces with respect to 2 a new band at $\delta = -17.2$ ppm as a triplet with a ${}^{1}J_{PF} = 952$ ppm. This signal corresponds to $PF_2O_2^-$ anion, produced by the oxidation of PF_6^- . This peak is well explained in the literature [32,33]. The ${}^{1}H$ NMR signals N- CH_2CH_2 -P and N- CH_2CH_2 -P appear at low fields respect to free ligand [N- CH_2CH_2 -P: 4.43 (1), 4.22 (2), 4.27 (3) and 4.05 ppm (L); N- CH_2CH_2 -P: 2.77 (1), 2.70 (2), 3.01 (3) and 2.57 (L) ppm [14]. Finally, the signals in the ${}^{13}C{}^{1}H$ NMR spectra of **1-3**, appear at lower fields than for the free ligand $[C_{DZ}: 105.1 (1), 106.4 (2), 106.1$ (3) and 104.8 (L) ppm]. It is important to highlight that the NMR spectra of **2** and **3** is very similar, so probably the ligands of the complexes are disposed in a similar distribution around the metallic centre. Also, PFG-NMR of 2 and 3 in a CD₃CN solution at 298 K has been assayed. Compound 2 (MW: 1122.38 g mol⁻¹) shows a diffusion coefficient (D) of $1.12 \pm 0.09 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ that corresponds to a hydrodynamic radius ($R_{\rm H}$) of 6.4 \pm 0.09 \times 10⁻¹⁰ m. according to the Stokes–Einstein equation [34]. The value of $R_{\rm H}$ is in concordance with its crystal structure (6.6×10^{-10} m). Also, **3** (MW: 1081.55 g mol⁻¹) has a value of diffusion coefficient D $1.17 \pm 0.09 \times 10^{-9}$ m² s⁻¹ and a $R_{\rm H}$ of 6.1 $\pm 0.09 \times 10^{-10}$ m, similar to the radius of 2. The PFG-NMR study and the rest of the data obtained in the characterisation indicates that probably **3** has the same nuclearity and metal:ligand ratio as **2**, and that the ligand is coordinated and disposed around metallic centre similar to 2.

3.2. Crystal and molecular structure of 1 and 2

The structures of **1** and **2** complexes were confirmed by single crystal X-ray diffraction. ORTEP pictures and selected bond lengths (Å) and angle values (°) are shown in Figs. 1 and 2 and Table 2.

Colourless crystals of 1 have been obtained by slow evaporation of an acetone:diethyl ether solution (1:10). Complex 1 (Fig. 1, Table 2) consists of cationic and anionic units: $[CuL_2]^+$ and $[PF_6]^-$. The cation $[CuL_2]^+$ displays a distorted tetrahedral geometry around Cu(I). The metallic centre is coordinated to two **L** via κ^2 -*N*,*P* generating two metallocycle rings of six members. The values of the angles N6–Cu1–P2 [99.02 (4)°] and N6–Cu1–P2ⁱ [110.81 (4)°], and the values of the distances Cu1-N6 [2.0710 (12) Å] and Cu1-P2 [2.2700 (4) Å] are in agreement with the values described in the literature: N-Cu-P [99.191-119.77°], Cu-N [2.045-2.087 Å] and Cu–P [2.248–2.359 Å] [35,36]. Otherwise, the values of the angles N6-Cu1-N6ⁱ [114.91 (7)°] and P2-Cu1-P2ⁱ [123.16 (2)°] are higher than the values presented in the literature for similar structures: N-*Cu*-N [90.469–92.596°] and P-*Cu*-P [115.481–119.829°] [35,36]. As our knowledge, around two-hundred and forty structures of Cu(I) with a [Cu, 2N, 2P] core [16] are described in the literature. However, only two monomeric complexes with [Cu,







Fig. 2. ORTEP drawing of $[Ag(L)]_2^{2+}$ cation showing all non-hydrogen atoms and numbering scheme; 50% probability amplitude displacement ellipsoid shown.

2N_{pz}, 2P] *core* are presented in the literature [35,36]. In these structures the metallic centre is coordinated to bispyrazolylborate and triphenylphosphine ligands.

Colourless crystals of 2 have been obtained by slow evaporation of a 1,2-dichloroethane:diethyl ether solution (1:10) (Fig. 2, Table 2). The structure consists of ionic units: $[AgL]_2^{2+}$ and $[PF_6]^-$. The crystalline structure of 2 also contains four molecules of solvent: two of 1,2-dichloroethane and two of diethyl ether with a high disorder (see Experimental section). The structure consists of a bimetallic Ag(I) complex where metallic centres are connected via k^2 -*N*,*P* to two ligands in a head-to-face arrangement generating an homobimetallic macrocycle of 12 members. The Ag(I) centres have a distorted linear geometry observed by the value of the angle $N6^{ii}$ -Ag1-P2 [166.92 (12)°]. The value of the distances Ag1···Ag1 [2.9691 (9) Å] and Ag1-P2 [2.3497 (14) Å] are comparable to similar structures presented in the literature: Ag...Ag [2.798-5.078 Å] and Ag-P [2.351-2.398 Å] [21.37-45]. Otherwise the values of the distances Ag1–N6ⁱⁱ [2.120 (4) Å] is slightly lower than the values described in the literature: Ag-N [2.148-2.358 Å] [21,37-45].

In the literature, around one-hundred and eighty crystalline structures with a similar disposition of the ligands to the metallic centre and [2Ag, 2N, 2P] *core* are described [16]. Twelve of these structures are bimetallic Ag(I) complexes where the ligands are coordinated vía k^2 -N,P generating metallocycle rings of eight, ten

Table 2

Selected bond lengths (Å) and angles (°) of **1** and **2**. Symmetry codes: (i) 1-x, *y*, ${}^{3}/2-z$; (ii) ${}^{1}/2-x$, ${}^{3}/2-y$, 1-z.

1		2	
Cu(1)-N(6)	2.0710 (12)	Ag(1)–N(6 ⁱⁱ)	2.120 (4)
Cu(1) - P(2)	2.2700 (4)	Ag(1)-P(2)	2.3497 (14)
$N(6)-Cu(1)-N(6^{i})$	114.91 (7)	$N(6^{ii})-Ag(1)-P(2)$	166.92 (12)
N(6)-Cu(1)-P(2)	99.02 (4)		
$N(6)-Cu(1)-P(2^{i})$	110.81 (4)		
$P(2)-Cu(1)-P(2^{i})$	123.16 (2)		

and twelve members and finishing its coordination by different molecules [21,37–45].

3.3. Predicted structure of 3

In the literature is not reported any crystalline structure of Au(I) with the core proposed [Au, 2P, Cl] for **3** [16]. In this work we have tried to obtain good monocrystals for X-ray diffraction of **3** without success. However, with the information compiled in the characterisation of 2 and 3 we have observed a lot of similarities that permit to do a serious purpose of the structure of 3 in solid and solution. The values described previously indicates that **3** probably presents a [AuClL]₂ molecular formula. The specie depicted in MS- $ESI(+)([Au_2Cl(L)_2]^+, 100\%)$ and the elemental analysis corroborates this stoichiometry. The conductivity value of 14 $\Omega^{-1} \text{cm}^2 \ \text{mol}^{-1}$ implies the **3** is a non-electrolyte compound and that the chlorine atoms are connected to Au(I). Also, the high similarity in 1 H and 13 C ¹H} NMR spectra and the similar hydrodynamic radii, elucidate that the two compounds (2 and 3) present a similar disposition of L around the metallic centre. Finally, the general knowledge indicates complexes of Au(I) have linear, trigonal planar or tetrahedral geometries [25]. In this case, the tendency of the L ligand to coordinate to the metallic centre by the two active sites and the presence of two chlorine atoms, indicates that the two L ligands are bridging the two Au(I) atoms to give 12-membered ring with a transannular double-bridging of the Au(I) atoms by the chlorine atoms. In summary, the Au(I) atoms have a coordination number four, so the most probable geometry should be tetrahedral [46] (Scheme 1).

4. Conclusions

Three new complexes with metals of group eleven and oxidation state +1 containing **L** as ligand are reported. The particular hybrid characteristics of **L** and the different geometric preferences of the metallic centres lead to three different complexes: $[Cu(L)_2](PF_6)$ (**1**), $[Ag(L)]_2(PF_6)_2$ (**2**) and $[AuCl(L)]_2$ (**3**). Compound **1** is the first X-ray crystal structure of a monomeric compound with a *N*-pyrazole, *P*-phosphine ligand. Also, it has been contributed with another X-ray crystalline structure of Ag(I) and finally it has been reported a deep characterisation of **1**–**3**. With all the data obtained it has been suggested the structure of **3**.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 806715 for compound **1** and 806716 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: +44 1223336033; e-mail: diposit@ccdc.cam.acuk or www.htpp://ccdc.cam.ac.uk.

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