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Synthesis, reactivity and comparative structural studies on copper(I) and gold(I) halo complexes with tripodal polyphosphines in 1:1 metal to ligand ratio. The X-ray crystal structures of three mononuclear neutral compounds

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Abstract

Cu(I) and Au(I) halides interact with equimolecular amounts of tripodal polyphosphines as $CH_3C(CH_2PPh_2)_3(CP_3)$ in CH_2Cl_3 , $N(CH_2CH_2PPh_2)_3(NP_3)$ in CH_2Cl_2 or CH_2Cl_2-S (S = MeOH, Et₂O) and $P(CH_2CH_2PPh_2)_3$ (PP₃) in CH_2Cl_2 to form $Cu(CP_3)X$ [X = Br (1), I (2)], [Au₃(CP₃)_2Cl_2]Cl (3), [Au₃(CP₃)_3X]X_2 [X = Br (4), I (5)], Cu(NP₃)X [X = Cl (6), Br (7), I (8)], [Au₂(NP₃)_2]X_2 [X = Cl (9), Br (10)], Au(NP₃)I (11), [Cu₂(PP₃)_2X]X [X = Cl (12), Br (13)] and [Au₂(PP₃)_2]X_2 [X = Br (14), I (15)]. Complexes 1, 7 and 11 were shown by X-ray diffraction to consist of neutral monomers with distorted tetrahedral geometry around the metal and the phosphine acting as tridentate chelating ligand. The mass spectra, conductivity measurements and ³¹P{¹H} NMR studies for 9 and 10 are indicative of a coexistence with mononuclear forms. Complexes 3, 9 and 14 were also achieved in solution by addition of the appropriate polyphosphine to the compounds Au₃(CP₃)Cl₃ (3a), Au₃(NP₃)Cl₃ (9a) and Au₄(PP₃)Br₄ (14a), respectively, involving ring-closure reactions. Likewise, crystals of 1 were obtained both from solutions of this compound in CH₂Cl₂–EtOH and from solutions in CHCl₃ of (1a) $\cdot 2.5Et_2O$ (1a = Cu₃(CP₃)Br₃). Further additions of the appropriate polyphosphine to 9 and 14 give complexes with new "MP₄" environments and dangling phosphorus that for 14 involve ring-opening processes. By reaction of 3 with CP₃ the complex [Au₃(CP₃)₃Cl]Cl₂, isostructural with 4 and 5, is afforded in solution. The reaction of Cu(CP₃)Cl (1) with CP₃ followed by ³¹P{¹H} NMR seems to occur with retention in part of the starting CuP₃ core and formation of other species containing linear arrangements for Cu(I). No reaction was observed between 6 or 13 and NP₃ or PP₃, respectively.

Keywords: Copper(I) and gold(I); Tripodal polyphosphines; X-ray diffraction; ³¹P NMR spectroscopy; Ring-closure and opening reactions

1. Introduction

Polynuclear P- or N-donor ligands have been usually employed in the synthesis of a broad diversity of monoand polynuclear species that in the case of latter transition metals may present interesting applications [1-4]. The way in which a given polyphosphine or aminophosphine coordinates to Group 11 metal centres depends on the metal, the counter ions, the ligand arrangement and the other ligands surrounding the metal centre [3]. In recent years, manipulation of the metal-halide functionality has revealed that this can be used as a highly valuable method of tuning the reactivity of a given complex that can provide a way for the development of new catalytic systems [5]. The starting point for these findings was a work dealing with the study of the chemistry salt effects in inorganic and organometallic chemistry [6]. On the other hand, changes in the nature of the "non-coordinating" ligands of cationic complexes also influence the outcome of catalytic processes [7]. In a previous work we found that while the tripodal tetraphosphine tris[2-(diphenylpho-

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sphino)ethyl]phosphine (PP₃) reacted with AgNO₃ in 1:1 stoichiometric ratio to form the ionic dinuclear system $[Ag_2(PP_3)_2](NO_3)_2$ the triphosphines 1,1,1-tris(diphenyl-phosphinomethyl)ethane (CP₃) and tris[2-(diphenylphosphino)ethyl]amine (NP₃) afforded mononuclear complexes with AgX salts (X = nitrate or halide) there being not influence of the halogen in the nuclearity of the resultant compounds [8].

Balch and Fung reported in 1990 the crystal structure of the ionic dinuclear complex [Au₂(PP₃)₂]Cl₂ prepared in 1:1 metal to ligand ratio where the tripodal tetraphosphine is coordinating in a tridentate chelating and a monodentate bridging fashion [9]. Likewise, the crystal structure of Cu(CP₃)Cl was reported in 1993 by Fife et al. consisting of monomers with a distorted tetrahedral environment around the metal [10]. However, little work has been directed toward the analysis of how the effect of changing the nature of the metal, the halide or the tripodal polyphosphine influences the structure of the compounds and their reactivity. For that reason, this work is focussed on a comparative structural study of copper(I) and gold(I) halo complexes containing tripodal ligands as CP₃, NP₃ and PP₃ in 1:1 metal to ligand ratio. For gold(I) we also report the preparation in solution of 1:1 ionic compounds starting from neutral polynuclear systems, containing linear P-Au-X fragments, upon reaction with the appropriate polyphosphine via ring-closure reactions. The formation of mononuclear complexes for copper(I) starting from polynuclear systems and the reactivity of 1:1 compounds with tripodal polyphosphines are also described.

2. Experimental

2.1. General procedures and instrumentation

Dichloromethane and chloroform were redistilled under nitrogen over CaCl₂ and P₄O₁₀, respectively. 1,1,1-Tris(diphenylphosphinomethyl)ethane, copper(I) bromide and iodide and gold(I) iodide were purchased from Strem Chemicals, 2,2'-thiodiethanol and tris[2-(diphenylphosphino)ethyl]phosphine from Aldrich and gold metal from SEMPSA. Microanalyses were performed on a Fisons Instrument EA 1108 CHNS-O. Fast Atom Bombardment (FAB) or Liquid Secondary-Ion (LSI MS) mass spectra were obtained in a Micromass Autospec spectrometer using nitrobenzylic alcohol as the matrix. Positive electrospray ion mass spectra (ESI MS) were recorded on a Micromass VG-QUATTRO spectrometer from 0.5×10^{-4} M solutions of the complexes using CH₃CN-H₂O-formic acid 1% as mobile phase. Infrared spectra were recorded at ambient temperature as KBr pellets (4000–500 cm⁻¹) or Nujol mulls $(500-100 \text{ cm}^{-1})$ on a Nicolet IMPACT 400 with a DTGS detector and a Mattson Cygnus 100 spectrophotometer. The bands are reported as vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad. ³¹P{¹H} NMR spectra were recorded on a Bruker AMX500 NMR spectrometer at 202.46 MHz. Chemical shifts (δ) are reported in ppm relative to external 85% H₃PO₄; s, singlet; d, doublet; q, quartet; m, multiplet; bs, broad signal; *J*, coupling constant in Hz. Conductivities were measured at 25 °C using 10⁻³ M solutions in DMF or CH₃CN on a WTW model LF-3 instrument.

2.2. Syntheses

2.2.1. Au(tdg)X

Au(tdg)X (X = Cl, Br; tdg = 2,2'-thiodiethanol = thiodiglycol) were prepared following literature procedures [11–14].

2.2.2. Tris(2-diphenylphosphinoethyl)amine (NP₃)

Tris(2-diphenylphosphinoethyl)amine (NP₃) was prepared as previously described [15].

2.2.3. Synthesis of 1–15 and 1a, 3a, 9a and 14a

In the syntheses with copper halides and gold iodide dry CHCl₃ or CH₂Cl₂ were used to dissolve the phosphine. To a solution of L $[L = CP_3: 0.127 - 0.320]$ mmol; PP₃: 0.347-0.523 mmol; NP₃: 0.230 mmol) in a minimum volume of CHCl₃ or CH₂Cl₂, solutions of Au(tdg)X in MeOH (X = Cl) or in Et₂O (X = Br) or CuX (X = Cl, Br, I) and AuI as solids were added in the appropriate stoichiometric ratio. For copper halide and gold iodide complexes the mixture reaction was stirred under nitrogen until the metallic salt was completely dissolved (with AuI in an ice bath). Solvents were partially removed in vacuo and n-hexane (1, 5) or Et_2O (2, 6-8, 11-13, 15) was added to complete the precipitation of the complexes. For gold chloride or bromide complexes the resultant mixtures were stirred for 14–24 h at room temperature and after that solvents were removed in vacuo to leave precipitates which were filtered off and treated with H₂O. Some of the solids were recrystallised from CH₂Cl₂-Et₂O and in all cases the final solids were filtered off and dried in vacuo. Crystals of 1 and 7, used for X-ray diffraction studies, were obtained by recrystallisation from CH₂Cl₂-EtOH (2:1) and MeOH-CH₃CN (1:2), respectively, and of 11 by slow evaporation of a saturated solution in CD₂Cl₂-CD₃OD (1:1). 1: Yield: 87%. Colour: white, melting point (m.p.) > 250 °C. Found: C, 63.7; H, 4.9. Calc. for $C_{41}H_{39}P_3CuBr: C, 64.1; H, 5.1\%. IR v_{max} (cm^{-1}) (Cu-$ Br) 212s. MS (FAB): m/z 767 (M^+ , 10%); 687 (M^+ – Br, 100%). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): see Table 1. $\Lambda(DMF) = 2.1 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. (1a) $\cdot 2.5 \text{Et}_2 \text{O}$: Yield: 97%. Colour: white, m.p. > 250 °C. Found: C, 50.4; H, 5.0. Calc. for C₅₁H₆₄P₃Cu₃Br₃O_{2.5}: C, 49.4; H, 5.2%. IR v_{max} (cm⁻¹) (Cu-Br) 227w. MS (FAB): m/z 975 (M^+ – Br, 6%); 830 $(M^+ - 2Br - Cu, 51\%)$; 767 $(M^+ - 2Br -$

Table 1 ${}^{31}P{}^{1}H{}$ NMR data for complexes I, Ia, 1–15 and for titrations of I, 3a, 9a and 14a with the appropriate polyphosphine

Compound	$\delta_{\rm P} ({\rm ppm})^{\rm a}$	Solvent		
I ^a	-33.6s	CDCl ₃		
Ia ^a	-28.0bs (I), 27.4s, 26.8s, 24.4s, -	CDCl ₃		
	15.1bs, -21.5bs (Ia', Ia")			
I + 0.5 equiv.	-33.5bs (I), -11.5bs, -18.2bs, -	CDCl ₃		
CP ₃	27.6s, -29.8s (Ia ₁ , Ia ₂ , CP ₃)			
1	-35.4bs	CDCl ₃		
$1a \cdot 2.5Et_2O$	-25.3bs (1), 32.7s, 31.2s	CDCl ₃		
1a	-22.6bs (1), 31.0s, 28.0s	CDCl ₃		
$(2) \cdot CHCl_3 \cdot$	-15.2bs	DMSO-d ₆		
5H ₂ O				
$2a \cdot Et_2O$	-24.9s (2), 30.1s, 28.6s	DMSO-d ₆		
3	24.7s, 16.4bs, -5.4bs, -12.0bs	CDCl ₃		
3a	15.2s	CDCl ₃		
3a + 1.0 equiv.	15.6s, 15.0s, -4.8bs, -12.6bs (3)	CDCl ₃		
CP ₃				
3a + 2.0 equiv.	24.7s, -5.3bs, -12.8bs	CDCl ₃		
CP ₃				
$(4) \cdot 3H_2O$	24.9s, -5.4bs, -12.5bs	CDCl ₃		
5	25.0s, -5.2bs, -11.8bs	CDCl ₃		
6	-26.1bs	CDCl ₃		
7	-8.4s	CD_2Cl_2-		
		CD_3OD		
8	-29.4bs	CDCl ₃		
(9) · 8H ₂ O	29.0s, 26.5s, 23.8s	CDCl ₃		
9a	28.6s	DMSO-d ₆		
9a + 2.0 equiv.	35.9bs, 30.9s, 28.4s (9)	DMSO-d ₆ -		
NP ₃		CDCl ₃		
9a + 3.0 equiv.	30.9s, 22.4s, -12.2bs	DMSO-d ₆ -		
NP ₃		CDCl ₃		
$(10) \cdot 8H_2O$	33.5s, 27.0bs, 22.8s	CDCl ₃		
11	24.4s	CD_2Cl_2-		
		CD_3OD		
$12 \cdot CH_2Cl_2$	8.6bs, 3.2bs, -11.1bs	CDCl ₃		
$13 \cdot CH_2Cl_2$	8.8bs, 3.3bs, -9.4bs	CD_2Cl_2		
14 ^b	34.0m, 26.6m, 15.0m	CD_2Cl_2		
14a ^b	36.8q, 35.7d	DMSO-d ₆		
14a+2.0 equiv.	37.9m, 28.4m, 18.6m (14)	DMSO-d ₆ -		
PP ₃		CDCl ₃		
14a+3.0 equiv.	37.7m, 28.4m, 18.5m (14), 23.9m,	DMSO-d ₆ -		
PP ₃	0.0bs, -10.4m	CDCl ₃		
15 °	33.9m, 25.7m, 15.2m	CD_2Cl_2		

^a δ_P (CDCl₃): CP₃ (-27.6s), PP₃ (-14.7q, -18.9d), NP₃ (-22.7s); I, Cu(CP₃)Cl; Ia, Cu₃(CP₃)Cl₃.

^b $J({}^{31}P, {}^{31}P)$ (Hz): **14** (132, 72, 60), **14a**: (48), **15** (132, 71, 62).

2Cu, 22%); 687 $(M^+ - 3Br - 2Cu, 100\%)$. ³¹P{¹H} NMR (CDCl₃): see Table 1. Λ (DMF) = 67.1 Ohm⁻¹ cm² mol⁻¹. (**2**) · CHCl₃ · 5H₂O: Yield: 93%. Colour: white, m.p. > 250 °C. Found: C, 50.0; H, 5.0. Calc. for C₄₂H₅₀P₃CuICl₃O₅: C, 49.2; H, 4.9%. IR v_{max} (cm⁻¹) (Cu-I) 149sh. ³¹P{¹H} NMR (DMSO-d₆): see Table 1. **3**: Yield: 53%. Colour: white, m.p. 201 °C. Found: C, 51.7; H, 4.0. Calc. for C₈₂H₇₈P₆Au₃Cl₃: C, 50.6; H, 4.0%. IR v_{max} (cm⁻¹) (Au-Cl) 316sh, 308sh. ESI MS (+): m/z 937 ([Au₃(CP₃)₂Cl]²⁺, 14%). MS (FAB): m/z 1054 $(M^+ - 2Cl - Au - CP_3, 16\%)$; 821 $(M^+ - 2Cl - 2Au - CP_3, 20\%)$. ³¹P{¹H} NMR (CDCl₃): see Table 1.

 $\Lambda(DMF) = 19.7 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. (4)·3H₂O: Yield: 74%. Colour: white, m.p. 187 °C. Found: C, 53.0; H, 4.0. Calc. for C123H123P9Au3Br3O3: C, 53.5; H, 4.5%. IR v_{max} (cm⁻¹) (Au-Br) 233sh. ESI MS (+): *m*/*z* 1273 $([Au_3(CP_3)_3Br]^{2+}, 32\%)$. MS (FAB): m/z 1098 (M^+ – $2Br-Au-2CP_3$, 15%); 821 ($M^+-2Br-2Au-CP_3$, 53%). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): see Table 1. $\Lambda(DMF) = 19.0 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. 5: Yield: 43%. Colour: white, m.p. 182 °C. Found: C, 51.3; H, 4.3. Calc. for C₁₂₃H₁₁₇P₉Au₃I₃: C, 51.9; H, 4.1%. ESI MS (+): m/z 1296 ([Au₃(CP₃)₃I]²⁺, 35%). MS (FAB): m/z821 (M^+ -2I-2Au-CP₃, 53%). ³¹P{¹H} NMR (CDCl₃): see Table 1. Λ (DMF) = 19.5 Ohm⁻¹ cm² mol^{-1} . 6: Yield: 84%. Colour: white, m.p. > 250 °C. Found: C, 66.5; H, 6.0; N, 2.0. Calc. for $C_{42}H_{42}NP_3CuCl: C, 67.0; H, 5.6; N, 1.9\%$. IR v_{max} (cm^{-1}) (Cu-Cl) 244sh. MS (FAB): m/z 716 (M^+ -Cl, 100%). ${}^{31}P{}^{1}H$ NMR (CDCl₃): see Table 1. $\Lambda(CH_3CN) = 10.4 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. 7: Yield: 77%. Colour: white, m.p. > 250 °C. Found: C, 63.0; H, 5.7; N, 1.8. Calc. for C₄₂H₄₂NP₃CuBr: C, 63.3; H, 5.3; N, 1.8%. IR v_{max} (cm⁻¹) (Cu–Br) 223vs,br. MS (FAB): m/z 716 $(M^+ - Br, 100\%)$. ³¹P{¹H} NMR (CD₂Cl₂-CD₃OD): see Table 1. $\Lambda(CH_3CN) = 11.1 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. 8: Yield: 84%. Colour: beige, m.p. > 250 °C. Found: C, 59.1; H, 5.3; N, 1.7. Calc. for C₄₂H₄₂NP₃CuI: C, 59.8; H, 5.0; N, 1.7%. IR v_{max} (cm⁻¹) (Cu–I) 158vs,br. MS (FAB): m/z 716 (M^+ – I, 100%). ³¹P{¹H} NMR (CDCl₃): see Table 1. Λ (CH₃CN) = 12.7 Ohm⁻¹ cm² mol^{-1} . (9)·8H₂O: Yield: 80%. Colour: white, m.p. 171 °C. Found: C, 52.6; H, 5.1; N, 1.6. Calc. for $C_{84}H_{100}N_2P_6Au_2Cl_2O_8{:}$ C, 52.6; H, 5.3; N, 1.5%. MS (FAB): m/z 1082 (M^+ -Cl-NP₃, 2%); 850 (M^+ - 2Cl-NP₃-Au, 100%). ³¹P{¹H} NMR (CDCl₃): see Table 1. $\Lambda(CH_3CN) = 136.7 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. (10). 8H2O: Yield: 79%. Colour: white, m.p. 181 °C. Found: C, 50.5; H, 4.8; N, 1.5. Calc. for C₈₄H₁₀₀N₂P₆Au₂Br₂O₈: C, 50.3; H, 5.0; N, 1.4%. MS (FAB): m/z 1047 (M⁺ - $2Br-NP_3$, 1%); 850 ($M^+-2Br-NP_3-Au$, 100%). ³¹P{¹H} NMR (CDCl₃): see Table 1. Λ (CH₃CN) = 114.3 $Ohm^{-1} cm^2 mol^{-1}$. 11: Yield: 67%. Colour: white, m.p. 278 °C (dec.). Found: C, 50.9; H, 4.5; N, 1.4. Calc. for C₄₂H₄₂NP₃AuI: C, 51.6; H, 4.3; N, 1.4%. MS (FAB): m/z 850 (M^+ – I, 100%). ³¹P{¹H} NMR (CD₂Cl₂-CD₃OD): see Table 1. Λ (DMF) = 74.6 $Ohm^{-1} cm^2 mol^{-1}$. 12 · CH₂Cl₂: Yield: 59%. Colour: white, m.p. 162 °C. Found: C, 62.6; H, 5.5. Calc. for $C_{85}H_{86}P_8Cu_2Cl_4$: C, 62.8; H, 5.3%. IR v_{max} (cm⁻¹) (Cu-Cl) 240m,br. LSI MS: m/z 833 (M^+ -Cl-PP₃, 58%); 735 $(M^+ - 2Cl - PP_3 - Cu, 57\%)$. ³¹P{¹H} NMR (CDCl₃): (see Table 1). Λ (DMF) = 63.9 Ohm⁻¹ cm² mol^{-1} . 13 · CH₂Cl₂: Yield: 53%. Colour: white, m.p. 179 °C. Found: C, 60.0; H, 5.3. Calc. for $C_{85}H_{86}P_8Cu_2Br_2Cl_2$: C, 59.6; H, 5.1%. IR v_{max} (cm⁻¹) (Cu-Br) 200m,br. LSI MS: m/z 877 (M^+ – Br – PP₃, 16%); 735 $(M^+ - 2Br - PP_3 - Cu, 29\%)$. ³¹P{¹H} NMR

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 (CD_2Cl_2) : (see Table 1). $\Lambda(DMF) = 72.1 \text{ Ohm}^{-1} \text{ cm}^2$ mol^{-1} . 14: Yield: 60%. Colour: white, m.p. 160 °C. Found: C, 52.8; H, 4.5. Calc. for C₈₄H₈₄P₈Au₂Br₂: C, 53.2; H, 4.5%. LSI MS: m/z 1522 $(M^+ - 2Br C_2H_4PPh_2$, 12%); 1064 ($M^+ - 2Br - PP_3$, 6%); 867 $(M^+ - 2Br - PP_3 - Au,$ 100%). ${}^{31}P{}^{1}H{}$ NMR (CD_2Cl_2) : (see Table 1). $\Lambda(DMF) = 132.6 \text{ Ohm}^{-1} \text{ cm}^2$ mol^{-1} . 14a: Yield: 30%. Colour: white, m.p. 257 °C (dec). Found: C, 28.8; H, 2.7. Calc. for C₄₂H₄₂P₄Au₄Br₄: C, 28.4; H, 2.4%. IR v_{max} (cm⁻¹) (Au–Br) 232vs, 220s. ³¹P{¹H} NMR (DMSO-d₆): (see Table 1). Λ (DMF) = 4.2 Ohm⁻¹ cm² mol⁻¹. 15: Yield: 45%. Colour: white, m.p. 271 °C. Found: C, 50.3; H, 4.3. Calc. for C₈₄H₈₄P₈Au₂I₂: C, 50.7; H, 4.3%. LSI MS: m/z 1522 $(M^+ - 2I - C_2H_4PPh_2, 12\%); 867 (M^+ - 2I - PP_3 - Au,$ 100%). ${}^{31}P{}^{1}H{}$ NMR (CD₂Cl₂): (see Table 1). Characterisation of complexes 3a and 9a was previously reported [16,17].

2.3. Titrations of I, 3a, 9a and 14a

To a solution of complexes I (Cu₃(CP₃)Cl₃) and **3a** in CDCl₃ and of **9a** and **14a** in DMSO-d₆ solutions of the corresponding polyphosphine in CDCl₃ were added reaching the 1:1, 1:2 or 2:1 (I, Ia₁, Ia₂), 3:2 (**3**) and 1:1 (**9** and **14**) metal to ligand stoichiometric ratios. The ${}^{31}P{}^{1}H{}$ NMR spectra were recorded and the most significant signals are given in Table 1.

2.4. Crystal structure determination of 1, 7 and 11

Colourless plates of 1, colourless needles of 7 and yellow needles of 11 were mounted on glass fibres and used for data collection. Crystal data for 1 were collected at 220(2) K, using a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystem variabletemperature device [18]. Graphite monochromated Cu $K\alpha$ radiation was used throughout and a semi-empirical absorption correction was made. Crystal data for 7 and 11 were collected at 293(2) K, using a BRUKER SMART CCD 1000 diffractometer. Graphite monochromated Mo Ka radiation was used throughout. The data were processed with SAINT [19] and empirical absorption correction was made using SADABS [20]. The structures were solved by direct methods, 1 using the program SHELXS-97 [21] and 7 and 11 using the program siR-92 [22]. The structures were refined by fullmatrix least-squares techniques against F^2 using SHELXL-97 [21]. Positional and anisotropic atomic displacement parameters were refined for all nonhydrogen atoms. Hydrogen atoms were placed geometrically and positional parameters were refined using a riding model. Atomic scattering factors were obtained with the use of International Tables for X-ray Crystallography [23]. Molecular graphics were obtained from ORTEP-3 for WINDOWS [24].

3. Results and discussion

3.1. Syntheses

Scheme 1 shows the complexes prepared in this work. The tripodal ligand tris[2-(diphenylphosphino)ethyl]amine (NP₃) was synthesised following a variation of the method described in the literature [25].

Complexes 4, 9 and 10 gave satisfactory microanalyses for hydrates, while 12 and 13 were isolated as dichloromethane solvates. Analytical data for complex 2 were in agreement with the presence of water and chloroform molecules.

Compounds 1-15 were obtained as solids using a 1:1 metal to ligand ratio that for 3 resulted in a trinuclear ionic compound with a 3:2 stoichiometric ratio. To avoid the oxidation from Cu(I) to Cu(II), reactions with the copper salts were carried out under nitrogen.

Crystals suitable for X-ray diffraction of 1, 7 and 11 were obtained from solutions of the complexes in the appropriate solvent system. Crystals of 1 were also achieved from solutions of $(1a) \cdot 2.5 \text{Et}_2\text{O}$ $(1a = \text{Cu}_3(\text{CP}_3)\text{Br}_3)$ in CHCl₃.

3.2. Characterisation

Complexes 1-4, 6-8, 12 and 13 showed in the far IR spectra copper-halogen or gold-halogen vibrational frequencies assigned to terminal M–X stretches [26,27].

3.2.1. Complexes with CP_3

Conductivity measurements for complexes 1-5 are consistent with a non electrolyte behaviour in 10^{-3} M DMF solutions [28]. The FAB mass spectrum for 1 exhibits a peak at m/z 767 due to the molecular ion M^+ . The positive electrospray mass spectrum of 3 displays a peak at m/z 937 corresponding to $[Au_3(CP_3)_2Cl]^{2+}$, the spectra of 4 and 5 showing a peak due to $[Au_3(CP_3)_3X]^{2+}$ (m/z = 1273 and 1296, respectively). In accordance with these results, trinuclear ionic species seem to exist in solution for 3-5 and the non electrolyte behaviour observed in DMF is probably due to the formation of ion pairs or trios. The only broad signal at δ -35.4 and -15.2 present in the ³¹P{¹H} NMR spectrum of 1 and 2, respectively, is consistent with the formation of neutral tetrahedral complexes with the three phosphorus of the ligand and the halide coordinated to the copper. The broadening of the signal is indicative of a fluxional behaviour.

The ³¹P{¹H} NMR spectra for 3–5, recorded at room (Table 1) and low temperature [16], confirm in all three cases the coexistence of mixtures of species containing linear and tetrahedral environments for Au(I) and some phosphine oxide forms ($\delta \sim 25.0$). Scheme 2 shows the proposal for one of these structures of compounds 3–5.



Scheme 1. Copper(I) and gold(I) complexes prepared with CP_3 (1–5), NP_3 (6–11) and PP_3 (12–15) in 1:1 metal to ligand ratio. Reactions of 3a, 9a and 14a with CP_3 , NP_3 and PP_3 , respectively, and formation of 1 from 1a.

In case of **3** this proposal coincides with the structure found in solid state by X-ray diffraction [16].

3.2.2. Complexes with NP_3

Conductivity measurements for solutions in CH_3CN of $Cu(NP_3)X$ complexes (6–8) reflected a non electrolyte behaviour. However, solutions of 9 and 10 in CH_3CN and 11 in DMF resulted to be conductors (~1:1 electrolytes) [28]. The FAB mass spectra of complexes 6–8 showed a peak due to the $Cu(NP_3)$ fragment. On

the other hand, in the spectrum of complexes 9 and 10 peaks assigned to the dinuclear Au₂(NP₃)Cl (m/z 1082) and Au₂(NP₃) (m/z 1047) fragments, respectively, were observed. The presence of these peaks, absent in the iodo derivative, seems to be consistent with a dimeric structure for both compounds. The ³¹P{¹H} NMR spectra for complexes 6–8 exhibit only one resonance at δ –26.1, –8.4 and –29.4, respectively. This is in accordance with the formation of tetrahedral complexes, with the three phosphorus atoms of the ligand coordi-



Scheme 2. Structures proposed in solution for complexes 1-8 and 12-15.

nated to the copper in an equivalent arrangement (Scheme 2). However, due to the broadening of the signal observed for 6 and 8 a fluxional behaviour in solution involving the N of the aminophosphine in the coordination to Cu(I) should not be excluded.

The ³¹P{¹H} NMR spectrum of the complexes **9** and **10** exhibits three signals [δ 29.0, 26.5, 23.8 (**9**); 33.5, 27.0, 22.8 (**10**)] (Fig. 1(a, b)). The set of signals formed by the two resonances at down field can be assigned to the dinuclear compounds $[Au_2(NP_3)_2]X_2$ where each aminophosphine of the cation acts as bidentate chelating and bridging ligand, each metal centre being threecoordinate. The signal at higher field can be attributed to the monomers $Au(NP_3)X$ containing equivalent phosphorus atoms with gold(I) in a tetrahedral (AuP_3CI) environment. The coexistence of both structures allows to justify the low value of conductivities for 2:1 electrolytes.

The signal at δ 24.4 found in the ³¹P{¹H} NMR spectrum for **11** (Fig. 1(c)) points to the presence of only monomers. The high value of conductivity can be due to the replacement of iodide by DMF [8,16] or to the presence of Au(I) in a trigonal pyramidal geometry with a iodide as counter anion.

3.2.3. Complexes with PP_3

Complexes 12-15 are conductors in DMF solutions and behave as 1:1 (12, 13) and 1:2 (14, 15) electrolytes [28]. The FAB mass spectra of complexes 12 and 13 showed a peak at m/z 833 and 877, respectively, assigned to the dinuclear fragment Cu₂(PP₃)X. The ${}^{31}P{}^{1}H$ NMR spectra exhibit three broad signals around 8, 3 and -10 ppm (Table 1) with integration 2:4:2, the downfield resonance, assigned to the apical phosphorus, being splitted into two signals. The resonance at higher field is characteristic for uncoordinated phosphorus of the ligand, the width of the signal indicating the existence of exchange processes that could involve the dangling phosphorus and the halogen. According to these data, the conductivity values and the presence of dinuclear species in the mass spectra, a dinuclear ionic structure as that one shown in Scheme 2 was proposed. In the cation one phosphine acts as a tridentate chelating ligand with an uncoordinated dangling phosphorus and the other coordinates to the metal centres in both tridentate chelating and bridging fashions giving rise to CuP₄ and CuP₃X environments, there being one halide as counter ion.

The ³¹P{¹H} NMR spectra of complexes **14** and **15** showed three multiplets at δ 34.0, 26.6 and 15.0 (**14**) and δ 33.9, 25.7 and 15.2 (**15**). On the basis of the multiplicity and the integration ratio (1:1:2) these signals suggest the formation of the dinuclear species [Au₂(PP₃)₂]X₂ (X = Br (**14**), I (**15**)] as was previously observed for the chloro derivative [9]. The spectra can be analysed as AMX₂ systems and the resonances can be



Fig. 1. ${}^{31}P{}^{1}H$ NMR spectra for 9 (a) and 10 (b) in CDCl₃ and 11 (c) in CD₂Cl₂-CD₃OD: (*) is attributed to $[Au_2(NP_3)_2]X_2$ and (\bigcirc) to Au(NP₃)X.

assigned, from lower to higher field, to two apical, two terminal bridging and four terminal chelating phosphorus in accordance with each PP₃ acting as tridentate chelating and monodentate bridging ligand (Scheme 2). The ~ 130, 70 and 60 Hz coupling constants found are due to P involved in the five-membered rings, the unlike terminal P and internal and terminal P of the bridging arm, respectively. Furthermore, the digold fragments detected in the LSI MS mass spectra also support the existence of dinuclear species.

3.3. X-ray diffraction studies: crystal structures of 1, 7 and 11

The molecular structures with the numbering schemes of complexes 1, 7 and 11 are shown in Figs. 2 and 3. A summary of crystal parameters, data collection and refinement for the crystal structures is given in Table 2 and selected bond lengths and angles are listed in Table 3.

The X-ray crystal structures of 1, 7 and 11 consist of monomeric neutral CuLBr $[L = CP_3(1), NP_3(7)]$ and Au(NP₃)I (11) units with the metal bound to the three P atoms of the ligand and the halogen in a distorted tetrahedral geometry, confirming an identical behaviour for these complexes in solid state and solution.

The average for Cu–P bond lengths in 1 (2.2867(17) Å) is very close to the value found (2.2953(4) Å) in the chloro complex [10] and in both cases are in the expected range for four-coordinate Cu(I) systems (2.304 Å) [29a]. However, the Cu–Br distance of 7 (2.4965(13) Å) is longer than expected (literature values of 2.393 Å) and compared with that one found for 1 (2.3983(15) Å). This is indicative of a weaker coordination of the halide to Cu(I) compared with 1 as was also observed for NO₃⁻



Fig. 2. Molecular structure of 1.



Fig. 3. Molecular structure of 7 (a) and 11 (b).

in the complex Ag(NP₃)NO₃ [30] with Ag(I) achieving an AgP₃O arrangement. The averages for P–Cu–P and P–Cu–Br angles are very close to the ideal tetrahedral values in 7 (109.47(3) and 109.46(7)°, respectively) supporting the coordination of the bromide to the copper centre and show deviations in 1 (94.49(5) and 121.99(5)°, respectively) attributable to the strain imposed by the six-membered chelate rings formed [31]. It should be noted that in 7 the apical nitrogen of the ligand does not coordinate to copper (Cu–N: 3.070 Å) in contrast with the trigonal pyramidal structure found

Table 2 Summary of crystal parameters, data collection and refinement for 1, 7 and 11

	1	7	11
Empirical formula	C ₄₁ H ₃₉ CuBrP ₃	C42H42P3NCuBr	C ₄₂ H ₄₂ P ₃ NAuI
Formula weight	768.08	797.13	977.54
Temperature (K)	220(2)	293(2)	293(2)
Wavelength (Å)	1.54178	0.71073	0.71073
Crystal size (mm)	$0.50 \times 0.50 \times 0.15$	$1.13 \times 0.04 \times 0.04$	$0.94 \times 0.10 \times 0.06$
Colour/habit	colourless/plates	colourless/needles	yellow/needles
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	P21	P2 ₁	Cc
a (Å)	20.435(9)	10.224(2)	16.763(3)
b (Å)	10.272(5)	8.9741(18)	12.853(2)
<i>c</i> (Å)	17.010(10)	20.646(4)	17.745(3)
α (°)	90	90	90
β (°)	90	90.551(4)	93.180(3)
γ(°)	90	90	90
Volume (Å ³)	3576(3)	1894.2(6)	3817.2(11)
Ζ	4	2	4
Calculated density (mg m^{-3})	1.427	1.398	1.737
Absorption coefficient (mm^{-1})	3.649	1.788	1.701
F(000)	1576	820	1912
θ Range for data collection (°)	4.82-70.18	1.97-23.36	2.00-26.39
Index ranges	$-9 \le h \le 24, -6 \le k \le 12, -20 \le$	$-11 \le k \le 11, -9 \le l \le 9, 0 \le$	$-20 \le h \le 20, \ 0 \le k \le 16, \ -20 \le$
	$l \le 19$	$l \leq 22$	$l \leq 22$
Reflections collected	6829	8845	11 472
Independent reflections	2904 $[R_{int} = 0.0193]$	5236 $[R_{int} = 0.0512]$	6420 $[R_{int} = 0.0467]$
Max/min transmission	0.338/0.688	0.9319/0.2371	0.8650/0.5056
Data/restraints/parameters	2904/1/418	5229/1/433	6170/2/436
Goodness-of-fit on F^2	1.065	0.949	0.929
Final R indices	$R_1 = 0.0340, w R_2 = 0.0969$	$R_1 = 0.0482, wR_2 = 0.0900$	$R_1 = 0.0305, wR_2 = 0.0602$
Largest difference peak and hole (e ${\rm \AA^{-3}})$	0.351 and -0.420	0.637 and -0.619	1.385 and -0.745

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Selected distances (A	Å) and	l angles	(°)	for	complexes	1, '	7 and 11	
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	1	1 7	
Bond lengths			
M(1) - P(1)	2.2934(16)	2.306(2)	2.3903(16)
M(1)-P(2)	2.2787(18)	2.304(2)	2.4473(18)
M(1) - P(3)	2.2880(18)	2.3025(18)	2.3911(18)
M(1)-X(1)	2.3983(15)	2.4965(13)	3.0440(6)
Bond angles			
P(1)-M(1)-P(2)	92.49(5)	108.60(9)	108.04(6)
P(1)-M(1)-P(3)	94.55(5)	109.67(9)	112.57(6)
P(2)-M(1)-P(3)	96.43(6)	110.15(7)	112.25(6)
P(1)-M(1)-X(1)	121.30(6)	108.40(6)	109.24(4)
P(2)-M(1)-X(1)	126.11(5)	112.60(7)	103.52(4)
P(3)-M(1)-X(1)	118.56(5)	107.38(8)	110.78(4)

for $[Cu(NP_3)](BPh_4)$ (Cu-N: 2.288 Å) [32]. Thus, the change of bromide by the non-coordinating anion, BPh_4^- is responsible of the different resultant structure. On the other hand, for comparison purposes it is important to note that White et al. [33] reported the crystal structure of compounds $[Cu(P_3)X]_2$ (P₃ = bis[2-(diphenylphosphino)ethyl]phenylphosphine; X = Cl, Br, I) confirming the presence of neutral dimers, each

molecule of P_3 being coordinated to copper(I) in a bidentate chelating and a bridging fashion with two CuP₂PX environments. Both situations of complexes with tripodal and linear polyphosphines constitute an example of how the ligand arrangement influences its coordination mode and the nuclearity of the complexes formed.

The structure crystal of the cation in $[Au_2(NP_3)_2](BPh_4)_2$ [34] is identical to that one proposed for solutions of the dinuclear complexes $[Au_2(NP_3)_2]X_2$, X = Cl (9) and X = Br (10), which seem to coexist with the mononuclear species Au(NP₃)X. Although complex 11 was prepared using the same metal:ligand ratio and following the same procedure that for the chloro and bromo derivatives, the structural studies in solution showed a monomeric behaviour, the single-crystal analysis also confirming the existence of tetrahedral mononuclear units.

The average for Au–P bond distances (2.4095(17) Å) is close to that one found for the AuP₄ environment (2.4102 Å) in the complex [Au₃(CP₃)₂Cl₂]Cl (**3**) [16] and in the range expected for four-coordinate gold(I) compounds [29a]. The Au–I distance (3.0440(6) Å) is significantly longer than the 2.5–2.6 Å range usually observed for Au–I bond lengths [29b] and very close to

the value found in $[Au(EtTPA)_3]I_4 \cdot 3H_2O$ (EtTPA = $C_8H_{17}N_3P$) (2.9129(2) Å) showing an AuP₃ trigonalplanar arrangement with tetrahedral distortion (P-Au-P angles of 117.97(3)°) induced by one iodide [35]. However, the averages for P-Au-P (110.95(6)°) and P-Au-I (107.84(4)°) angles are very close to those corresponding to the ideal tetrahedral geometry, indicating as for complex 7 and for Ag(NP₃)Cl [8] that the halide is coordinated to the metal centre. Thus, the crystal structures of 7 and 11 constitute the first example of neutral mononuclear compounds for NP₃ with Cu(I) and Au(I), respectively.

3.4. Conversion to the 1:1 stoichiometry of complexes with n:1 (n = 3, 4) metal to ligand ratios

From solutions of $(1a) \cdot 2.5Et_2O$ in CHCl₃, crystals of $(1) \cdot 2Et_2O$ were obtained, the process being reproduced several times (eq. 1).

$$2Cu_{3}(CP_{3})Br_{3} \cdot 2.5Et_{2}O \xrightarrow{CHCl_{3}} \\ \times Cu(CP_{3})Br \cdot 2Et_{2}O + [Cu_{3}(CP_{3})(OEt_{2})_{3}Br][CuBr_{2}]_{2} \\ \xrightarrow{(1) \cdot 2Et_{2}O}$$
(1)

The ${}^{31}P{}^{1}H{}$ NMR spectrum of $(1a) \cdot 2.5Et_2O$ in CDCl₃ (Table 1) shows a broad signal at δ -25.3 attributable to (1) \cdot 2Et₂O and two signals at δ 31.2 and 32.7 with integration ratio 2:1 assignable to the ionic compound 1a'. Assuming linear geometries for copper in 1a' the signal with double integration could be attributed to two PCuOEt₂ fragments while the resonance at lower field to one POCuBr moiety. Although crystals of complex 2 were not achieved from solutions of $2a \cdot Et_2O$ ($2a = Cu_3(CP_3)I_3$) the ³¹P{¹H} NMR in DMSO-d₆ of this etherate also reveals the presence of the mononuclear system, 2, besides the iodo derivative 2a' analogous to 1a'. When complex 1a is prepared in absence of ether its ${}^{31}P{}^{1}H$ NMR spectrum in CDCl₃ shows a broad signal at $\delta -22.6$ ($\Delta \delta \sim 12$) assignable to 1 together with two clearly weaker resonances at δ 28.0 and 31.0 probably due to species containing totally and partially oxidised CP₃. Similar results leading to $Cu(CP_3)Cl(I)$ and other compounds (Table 1) seeming to contain PO, POCuCl, PCuCl and PCuP fragments (eq. 2) were observed when the ${}^{31}P{}^{1}H{}$ NMR spectrum of Cu₃(CP₃)Cl₃ (Ia) was recorded in CDCl₃.

$$4Cu_{3}(CP_{3})Cl_{3} \xrightarrow{\text{air}}_{CDCl_{3}} Cu(CP_{3})Cl + (ClCuOP)C(PCuCl)_{2} + [(ClCuOP)(OP)CPCuPC(PO)(POCuCl)]Cl + 5CuCl_{Ia''}$$

Thus, solutions in CDCl₃ or DMSO-d₆ of the systems $Cu_3(CP_3)X_3 \cdot nE_2O$ (n = 0, 1, 2.5) seem to generate the mononuclear compounds $Cu(CP_3)X$, its ³¹P resonance

(2)

being around 10 ppm lower field shifted due to the coexistence with other species. On the other hand, solutions of 1a and (1a) 2.5Et₂O in DMF show conductivity values in the lower range for 1:1 electrolytes in consistence with the coordinating behaviour of this solvent that could give rise to a process similar to that one described in eq. 1. Solutions of Ia in DMF exhibit a molar conductivity of 25 $Ohm^{-1} cm^2 mol^{-1}$ in accordance now with the process shown in eq. 2. The reactivity of Cu(CP₃)Cl (I) with CP₃ was studied by ${}^{31}P{}^{1}H$ NMR and the results (Fig. 4(A)) showed that by addition of 0.5 equiv. of CP₃ the starting compound (resonance at δ -33.5) coexists with free CP₃ (δ -27.6) and other species (δ -18.2, -11.5) containing dangling phosphorus (δ -29.8) and probably linear Cu(I) arrangements (eq. 3).

$$4\operatorname{Cu}(\operatorname{CP}_{3})\operatorname{Cl} + 2\operatorname{CP}_{3} \xrightarrow{\operatorname{CDCl}_{3}} \operatorname{Cu}(\operatorname{CP}_{3})\operatorname{Cl} + \operatorname{PC}(\operatorname{PCuCl})_{2}$$

$$I_{\mathbf{I}a_{1}} + [\operatorname{P}_{2}\operatorname{CPCuPCP}_{2}]\operatorname{Cl} + 2\operatorname{CP}_{3}$$
(3)

Further additions of CP_3 result in an increase of the intensity of the resonance due to free phosphine.

The titrations of **3a**, **9a** and **14a** with CP₃, NP₃ and PP₃, respectively, were also followed by ${}^{31}P{}^{1}H{}$ NMR (Table 1). Complex **3** was afforded when **3a** reacted with 1 molecular equiv. of CP₃, in consistence with a 3:2 metal to ligand ratio previously found for **3** (eq. 4). As expected, the formation of **9** as a mixture of a mononuclear and a dinuclear form (Scheme 3) required the addition of 2 molecular equiv. of NP₃ to **9a** (eq. 5). However, complex **14** was only species observed in solution by reaction of **14a** with 2 equiv. of PP₃ (eq. 6, Fig. 4(B)).

$$Au_{3}(CP_{3})Cl_{3}+CP_{3} \rightarrow [Au_{3}(CP_{3})_{2}Cl_{2}]Cl \qquad (4)$$

$$Au_{4}(NP_{4})Cl_{3}+2NP_{4}$$

$$\xrightarrow{\mathbf{y}_{a}} [\operatorname{Au}_{2}(\operatorname{NP}_{3})_{2}]\operatorname{Cl}_{2} + \operatorname{Au}(\operatorname{NP}_{3})\operatorname{Cl}$$

$$\xrightarrow{\mathbf{y}_{a}} (\operatorname{S}) \xrightarrow{\mathbf{y}_{a}} (\operatorname{S}) \operatorname{S} (\operatorname{S}) \xrightarrow{\mathbf{y}_{a}} (\operatorname{S}) \operatorname{S} (\operatorname{S}) \operatorname{S} (\operatorname{S}) \operatorname{S} (\operatorname{S}) \xrightarrow{\mathbf{y}_{a}} (\operatorname{S})$$

$$2\operatorname{Au}_{4}(\operatorname{PP}_{3})\operatorname{Br}_{4} + 4\operatorname{PP}_{3} \xrightarrow{-2\operatorname{Au}(I)\operatorname{Br}} 3[\operatorname{Au}_{2}(\operatorname{PP}_{3})_{2}]\operatorname{Br}_{2}$$
(6)

In all cases starting from neutral polynuclear compounds, with linear P-Au-X units, the addition of polyphosphine produces ring-closure reactions with formation of ionic complexes containing tetrahedrallinear (3), trigonal (9) or tetrahedral (14) environments for Au(I).

When 1 equiv. of CP_3 is added to 3 a dicationic complex $[Au_3(CP_3)_3Cl]Cl_2$ isostructural with 4 and 5 (Scheme 2) seems to be formed via a ring-closure process. Further additions of the appropriate polyphosphine to 9 and 14 result in the formation of complexes with new "AuP₄" arrangements and uncoordinated dangling phosphorus (Table 1) involving for 14 ringopening reactions.



Fig. 4. Titrations of Cu(CP₃)Cl(I) in CDCl₃ and Au₄(PP₃)Br₄ (14a) in CDCl₃-DMSO-d₆ with CP₃ (A) and PP₃ (B), respectively.



Scheme 3. Formation of 9 and 10 by reaction of $Au_3(NP_3)X_3$ [X = Cl (9a), Br(10a)] with NP₃.

4. Conclusions

The nature of the tripodal ligand modifies not only the structures of the resultant complexes, but also their reactivity. On the other hand, changes in the halogen lead to different structures in gold complexes with CP₃ (**3** vs. **4** and **5**) and NP₃ (**9** and **10** vs. **11**). Finally, substitution of copper(I) by gold(I) in complexes with CP₃ or NP₃ produce changes in their nuclearity and ionicity, the nuclearity of both metal complexes with PP₃ being not altered. The closed structures found for mononuclear compounds CuLCl lead to a partial (L = CP₃) or total (L = NP₃) retention of the CuP₃ arrangements by addition of the corresponding polyphosphine.

5. Supplementary material

A complete set of X-ray crystallographic studies for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 195347 (1), 195348 (7) and 195349 (11). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk). Fig. S1 shows the ³¹P{¹H} NMR spectra in CD₂Cl₂ for **3**, (**4**)·3H₂O and **5** at 183 K. Fig. S2 displays the ³¹P{¹H} NMR spectra for $Cu_3(CP_3)X_3$ complexes in CDCl₃ (X = Cl, Br) or DMSO-d₆ (X = I) with and without solvation. Figs. S3 and S4 contain the titrations followed by ³¹P{¹H} NMR of complexes **3a** (CDCl₃) and **9a** (CDCl₃–DMSO-d₆), respectively with the appropriate polyphosphine.

Acknowledgements

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