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Copper(I) and silver(I) azide complexes containing N-donor ligands

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Abstract

From the interaction of imidazole-type ligand L (L = imidazole (im), 1-methylimidazole (1-meim), 2-methylimidazole (2-meim), 4-methylimidazole (4-meim), benzimidazole (bzim), 1-benzylimidazole (bnim)) with $[Cu(N_3)(PPh_3)_2]_2$ the new mononuclear $[Cu(N_3)(PPh_3)_2(L)]$ and dinuclear $[Cu_2(N_3)_2(PPh_3)_3(L)]$ species have been obtained. Chelating bidentate ligands (L_2 = 2,2-bipyridyl (bipy), 1,10-phenanthroline (phen) or 2,9-dimethyl-1,10-phenanthroline (cupr)) react with $[M(N_3)(PPh_3)_2]_2$ (M = Cu or Ag) yielding $[M(N_3)(PPh_3)(L_2)]$. The S-donors 1-methyl-2-imidazol-2(3*H*)-thione (Hmimt), 2-benzothiazolethiol (Hbtt) and 2-pyridinethiol (Hpyt) react with $[Cu(N_3)(PPh_3)_2]_2$ in ethanol undergoing deprotonation and yielding $[Cu(mimt)(Ph_3P)]_n$, $[Cu(btt)]_n$ and $[Cu(pyt)]_n$, respectively. On the contrary, Hmimt and imidazoline-2(1,3*H*)thione (Himt) react in diethyl ether with $[Cu(N_3)(PPh_3)_2]_2$ yielding $[Cu(N_3)(Hmimt)_3]$ and $[Cu(N_3)(PPh_3)(Himt)]$, respectively. P(*o*-tolyl)$_3$ is able to displace the less basic phosphine PPh_3 from $[Cu(N_3)(PPh_3)(cupr)]$ yielding the complex $[Cu(N_3)\{P(o\text{-tolyl})_3\}(cupr)]$. 1,3-Bis(diphenylphosphino)propane (dppp) reacts with $[Cu(N_3)(PPh_3)(cupr)]$ yielding the complex $[Cu_2(N_3)_2(dppp)_3]$. $[Cu(N_3)(PPh_3)_2(im)]$ and $[Cu(N_3)(PPh_3)(phen)]$ react with CS_2 in benzene, in presence of excess of PPh_3 forming $[Cu(SCN)(PPh_3)_2]$ and $[Cu(tz)(PPh_3)(phen)]$ (Htz = 4-thia-1,2,3-triazole-5-thione), respectively. $[Ag(N_3)(PPh_3)(cupr)]$ reacts slowly with excess of CS_2 in diethyl ether giving [Ag(tz)(cupr)], whereas the same reaction in benzene in excess of PPh_3 yields immediately $[Ag(SCN)(PPh_3)_2]$. From the reaction of $[Ag(N_3)(PPh_3)(cupr)]$ with cyCN the complex $[Ag(N_3)(cyCN)(PPh_3)(cupr)]$ formed. All derivatives were characterized by IR and far-IR data, conductivity, ^1H NMR and in some cases also with $^{31}P\{^1H\}$ NMR and molecular weight measurements.

Keywords: Copper complexes; Silver complexes; Azole complexes; Phenanthroline; Spectroscopy

1. Introduction

Tertiary phosphine complexes of copper(I) have received great attention [1]. They can be used as precursors in chemical vapor deposition of copper films [2], as reagents in metal cluster [3], metallaborane [4] and organic chemistry [5]. Phosphine-ligated copper(I) complexes are known to produce a diversity of stoichiometries and structural prototypes which include complexes with ligand to copper ratios 3:1, 3:2, 2:1, 4:2, 2:2 and 4:4 [1,6]. The stoichiometry of phosphine copper(I) complexes depends primarily upon the steric bulk of the phosphine ligand and to a lesser extent on the choice of the counter-ion. We have recently found, however, that the interaction between $[MX(PR_3)_n]$ and N-donor ligands can yield complexes characterized by different stoichiometry, nuclearity and properties, also depending on the nature of the counter-ions [7–10].

Despite the large number of known copper(II) azide complexes [11], only a few papers have been published dealing with analogous copper(I) and silver(I) systems, although copper(I) azide phosphino complexes were obtained as early as 1971 by Ziolo and coworkers [12] with interest in this class of compounds continuing thereafter with La Monica et al. [13] who investigated the reactivity of the azido group bonded to copper. Copper complexes containing both N-donor ligands and azido groups also have been received recently particular attention: for example, a new synthetic route for designing homometallic chains of formula $[M(lig)(N_3)_2]_n$ [M = Mn or Cu; lig = 4,4-dimethyl-2,2′-

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bipyridine], exhibiting alternating ferromagnetic and antiferromagnetic properties, has been recently proposed [14].

Following a line of research whose major target is the chemical and structural characterization of Group 11 metal complexes containing N-donor ligands, structurally analogues of biologically important organic nucleobases, we have reported earlier the synthesis, structural and spectroscopic investigation of several triorganophosphine copper(I) and silver(I) containing halide or oxyanions [7–10]. As a part of these studies we were interested in extending the available literature data to include complexes incorporating N-donor, phosphine and the azide ligand.

2. Experimental

2.1. General procedures

All reactions were carried out under an atmosphere of dry-oxygen free dinitrogen, using Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent and further degassed before use where necessary. In some cases, as necessary, the reactions were protected from light by covering the reaction vessels with aluminum foil. Concentration was always carried out in vacuo (water aspirator). The samples for microanalysis were dried in vacuo to constant weight [20 °C, approximately 0.1 Torr (13.3 Pa)]. Elemental analyses (C, H, N, S) were performed with a Fison Instruments 1108 CHNS-O Elemental Analyzer. The IR spectra were recorded from 4000 to 150 cm^{-1} with a Perkin–Elmer System 2000 FT-IR instrument. ^{1}H and ^{31}P NMR spectra in a VXR-300 Varian spectrometer operating at room temperature (r.t.) (300 MHz for ^{1}H and 121.4 MHz for ^{31}P). Abbreviations: s = singlet, m = multiplet, d = doublet, dd = double doublet, t = triplet, br = broad. Relative intensity of signals in square brackets.

2.2. Syntheses

Safety note! Azide compounds are potentially explosive and should be treated with care and in small quantities.

The complexes $[M(N_3)(PPh_3)_2]_2$ (M = Cu or Ag) were prepared in accordance with literature procedures [12].

2.2.1. $[Cu(N_3)(PPh_3)_2]_2$

Recrystallised from chloroform–diethyl ether (yield 95%); m.p. 218–221 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.2–7.4 (m br, 30H, H_{arom}). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ −2.1s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ 23.7s, 5.5s, 2.0s, −1.5s, −2.8s, −4.5s. IR (Nujol mull, cm^{-1}): 3050w ($C–H_{azole} + C–H_{arom}$), 2052s, 2029m, 2002w (N_3), 1654w, 1584w, 1570w, (C⋯C, C⋯N), 524m, 507s, (PPh), 439m, 424m, 279w, 255w (δ_{azole}, Cu–N). Elemental analysis: *Anal.* Found: C, 68.88; H, 5.01; N, 6.51. Calc. for $C_{36}H_{30}N_3P_2Cu$: C, 68.62; H, 4.80; N, 6.67%. Λ_m (CH_2Cl_2, conc. = 1.0×10^{-3} mol l^{-1}): 2.2 Ω^{-1} mol^2 cm^{-1}.

2.2.2. $[Cu(N_3)(PPh_3)_2(im)]$ (1)

A solution/suspension of im (0.13 g, 1.9 mmol) in diethyl ether (30 ml) was added to $[Cu(N_3)(PPh_3)_2]$ (0.30 g, 0.48 mmol) in diethyl ether (40 ml) at 273 K. After the addition the suspension was stirred overnight at r.t., then filtered off and the colorless precipitate washed with 40 ml of diethyl ether–ethanol (3:1) and shown to be compound **1**. Recrystallized from acetonitrile–diethyl ether (1:1) (0.29 g, 0.4 mmol, yield 83%); m.p. 168–170 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 6.9 (s br, 1H, $H4 + H5$), 7.5 (s br, 2H, $H2$), 7.3 (m, 30H, H_{arom}). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ −2.4s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ −4.2s. IR (Nujol mull, cm^{-1}): 3150–2950br (N–H), 3120w, 3080w, 3050w ($C–H_{azole} + C–H_{arom}$), 2056s (N_3), 1618w, 1570w, 1560w, 1530m (C⋯C, C⋯N), 524m, 513s, 505s (PPh), 398w, 376w, 353w, 324w, 303w, 279w, 274 (δ_{azole}, Cu–N). Elemental analysis: *Anal.* Found: C, 66.88; H, 5.11; N, 10.42. Calc. for $C_{39}H_{34}N_5P_2Cu$: C, 67.09; H, 4.91; N, 10.03%. Λ_m (acetone, conc. = 1.0×10^{-3} mol l^{-1}): 19.3 Ω^{-1} mol^2 cm^{-1}.

2.2.3. $[Cu(N_3)(PPh_3)_2(1\text{-}meim)]$ (2)

This compound has been obtained as **1** (yield 62%); m.p. 134–136 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 3.75 (s br, 3H, CH_3), 6.9 (s br, 2H, $H4 + H5$), 7.3 (m, 30H, H_{arom}), 7.6 (s br, 1H, $H2$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ −3.8s. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): δ −4.1s br. IR (Nujol mull, cm^{-1}): 3180w ($C–H_{arom}$), 2029m, 2017m (N_3), 1684w, 1654w, 1646w, 1570w, 1522w, 1508w (C⋯C, C⋯N), 526w, 514s, 504m, 493m (PPh), 445w, 419w, 373w, 335w, 303w, 281w, 254w, 247w (δ_{azole}, Cu–N). Elemental analysis: *Anal.* Found: C, 66.99; H, 5.11; N, 9.93. Calc. for $C_{40}H_{36}N_5P_2Cu$: C, 67.45; H, 5.09; N 9.84%. Λ_m (CH_2Cl_2, conc. = 1.2×10^{-3} mol l^{-1}): 1.2 Ω^{-1} mol^2 cm^{-1}. MW ($CHCl_3$, 0.40×10^{-3} mol l^{-1}): 288.

2.2.4. $[Cu(N_3)(PPh_3)_2(2\text{-}meim)]$ (3)

This compound has been obtained as **1** (yield 83%); m.p. 169–171 °C. ^{1}H NMR ($CDCl_3$, 293 K): 2.2 (s br, 3H, CH_3), 6.9 (s br, 2H, $H4 + H5$), 7.3 (m, 30H, H_{arom}), 7.7 (s br, 1H, NH). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 293 K): 0.75s br. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 218 K): −1.1s br. IR (Nujol mull, cm^{-1}): 3110w, 3080w ($C–H_{arom}$), 3000–2500br (N–H) 2051m (N_3), 1684w, 1670w, 1628w, 1616w, 1576w, 1540w, 1506w (C⋯C, C⋯N), 525w, 514s, 504s, 494s (PPh), 442w, 430w, 417w, 377w, 271w (δ_{azole}, Cu–N). Elemental analysis: *Anal.* Found:

C, 67.32; H, 5.31, N, 9.97. Calc. for $C_{40}H_{36}N_5P_2Cu$: C, 67.45; H, 5.09; N 9.84%. Λ_m (acetone, conc. = 0.9×10^{-3} mol l^{-1}): 4.2 Ω^{-1} mol^2 cm^{-1}.

*2.2.5. [Cu(N$_3$)(PPh$_3$)$_2$(4-meim)] (**4**)*

This compound has been prepared as **1** (yield 63%). Washed with ethanol (10 ml); m.p. 174–177 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.2 (s br, 3H, CH_3), 6.85 (s br, 1H, *H*5), 7.3 (m, 30H, H_{arom}), 7.6 (s br, 1H, *H*2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ −2.4s. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ −4.4s br. IR (Nujol mull, cm^{-1}): 3050w (C–H_{arom}), 2059s (N_3), 1618w, 1584w, 1545w, 1508w (C⋯C, C⋯N), 513s, 504s, 492s (PPh), 442w, 418w, 367w, 277w (δ_{azole}, Cu–N). Elemental analysis: *Anal*. Found: C, 66.96; H, 5.23; N, 9.64. Calc. for $C_{40}H_{36}N_5P_2Cu$: C, 67.45; H, 5.09; N 9.84%. Λ_m (acetone, conc. = 1.1×10^{-3} mol l^{-1}): 6.9 Ω^{-1} mol^2 cm^{-1}.

*2.2.6. [Cu(N$_3$)(PPh$_3$)$_2$(bzim)] (**5**)*

This compound has been obtained as **1** by using a ligand-to-metal molar ratio of 1:1 (yield 54%); m.p. 157–160 °C. ^{1}H NMR (DMSO-d_6, 293 K): 7.15 (br, 33H, H_{arom} + CH_{bzim}), 7.3t (m, 2H, CH_{bzim}). $^{31}P\{^1H\}$ NMR (DMSO-d_6, 293 K): δ −26.34 [1], −3.3 br [20]. IR (Nujol mull, cm^{-1}): 3110w (C–H_{arom}), 3000–2400br (N–H), 2037s (N_3), 1684w, 1654w, 1622w, 1570w, 1560w, 1540w (C⋯C, C⋯N), 526w, 516s, 505m, 495m (PPh), 476sh, 442w, 429m, 322w, 304w, 284w, 230w (δ_{azole}, Cu–N). Elemental analysis: *Anal*. Found: C, 68.66; H, 4.97; N, 9.51. Calc. for $C_{43}H_{36}N_5P_2Cu$: C, 69.02; H, 4.85; N, 9.36%. Λ_m (CH_2Cl_2, conc. = 1.0×10^{-3} mol l^{-1}): 1.7 Ω^{-1} mol^2 cm^{-1}.

*2.2.7. [Cu$_2$(N$_3$)$_2$(PPh$_3$)$_3$(bnim)] (**6**)*

This compound has been obtained as **1** by using a ligand-to-metal molar ratio of 1:1 (yield 44%); m.p. 122–124 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 5.25 (s br, 2H, CH2), 7.1 (s br, 2H, *H*4 + *H*5), 7.2–7.5 (m br, 45H, H_{arom}), 7.6s br, 7.7 (s br, 1H, *H*2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ −1.0 (br). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ −0.5br, −3.7br. IR (Nujol mull, cm^{-1}): 3100w, 3050w (C–H_{arom}), 2024m (N_3), 1585w, 1560w, 1509w (C⋯C, C⋯N), 526m, 514sh, 507s, (PPh), 465w, 442w, 285w, 273w, 259w, 249w (δ_{azole}, Cu–N). Elemental analysis: *Anal*. Found: C, 66.26; H, 5.01; N, 9.51. Calc. for $C_{58}H_{55}N_8P_3Cu_2$: C, 66.49; H, 4.79; N, 9.69%. Λ_m (acetone, conc. = 1.1×10^{-3} mol l^{-1}): 11.11 Ω^{-1} mol^2 cm^{-1}.

*2.2.8. [Cu(N$_3$)(PPh$_3$)(phen)] (**7**)*

This compound has been obtained as **1** by using a ligand-to-metal molar ratio of 1:1 (yield 63%); m.p. 189–190 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.2–7.5 (m br, 15H, H_{arom}) 7.7 (br, 2H, H_{phen}), 7.8 (br, 2H, H_{phen}). 8.3 (br, 8H, H_{phen}), 8.9 (br, 2H, H_{phen}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ −0.7 (br). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 32.7s, 3.4s, 0.1s, −2.1s, −4.4s. IR (Nujol mull, cm^{-1}): 3060w (C–H_{arom}), 2033s (N_3), 1684w, 1670w, 1654w, 1636w, 1622m, 1582w, 1573m, 1509s (C⋯C, C⋯N), 527s, 502s (PPh), 440m, 352w, 283m, 244m (δ_{phen}, Cu–N). Elemental analysis: *Anal*. Found: C, 65.43; H, 4.40; N, 12.71. Calc. for $C_{30}H_{23}N_5PCu$: C, 65.75; H, 4.23; N, 12.78%. Λ_m (acetone, conc. = 0.9×10^{-3} mol l^{-1}): 16.2 Ω^{-1} mol^2 cm^{-1}.

*2.2.9. [Cu(N$_3$)(PPh$_3$)(cupr)] (**8**)*

This compound has been obtained as **1** by using a ligand-to-metal molar ratio of 1:1 (yield 94%); m.p. 235–238 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.8 (s, 6H, CH_3), 7.1–7.5 (m br, H_{arom}), 7.6 (d, 2H, CH_{cupr}), 7.8 (s, 2H, CH_{cupr}), 8.2 (d, 2H, CH_{cupr}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ −3.1br. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 23.7s, −2.7s, −4.5s. IR (Nujol mull, cm^{-1}): 3040w (C–H_{arom}), 2027s (N_3), 1684w, 1588w, 1558w, 1507w (C⋯C, C⋯N), 527s, 509s, 494w (PPh), 487w, 440w, 419w, 275w (δ_{cupr}, Cu–N). Elemental analysis: *Anal*. Found: C, 66.79; H, 4.91; N, 11.86. Calc. for $C_{32}H_{27}N_5PCu$: C, 66.71; H, 4.72; N, 12.16%. Λ_m (CH_2Cl_2, conc. = 1.1×10^{-3} mol l^{-1}): 5.4 Ω^{-1} mol^2 cm^{-1}.

*2.2.10. [Cu(N$_3$)(PPh$_3$)(bipy)]·Et$_2$O (**9**)*

This compound has been obtained as **1** by using a ligand-to-metal molar ratio of 4:1 (yield 44%); m.p. 191–193 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.1 (t, 6H, H_{ether}), 3.5 (q, 4H, H_{ether}), 7.2–7.5 (m br, H_{arom}), 7.6 (br, 4H, CH_{bipy}), 7.9 (br, 2H, CH_{bipy}), 8.56 (br, 2H, CH_{bipy}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ −2.3 br. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 32.6br, 2.2s, −0.1s, −2.3s. IR (Nujol mull, cm^{-1}): 3185w, 3160w, 3100w, 3060w, 3050w (C–H_{arom}), 2057s (N_3), 1592w, 1559w (C⋯C, C⋯N), 520s, 503m, 498m (PPh), 435w, 413w, 293w, 227w (δ_{azole}, Cu–N). Elemental analysis: *Anal*. Found: C, 64.01; H, 5.43; N, 11.83. Calc. for $C_{32}H_{33}N_5OPCu$: C, 64.26; H, 5.56; N, 11.71%. Λ_m (acetone, conc. = 1.0×10^{-3} mol l^{-1}): 24.2 Ω^{-1} mol^2 cm^{-1}.

*2.2.11. [Cu(N$_3$)(PPh$_3$)(Himt)] (**10**)*

This compound has been obtained as **1** by using a ligand-to-metal molar ratio of 2:1 (yield 40%); m.p. 184–186 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.0 (br, 2H, H_{Himt}), 7.2–7.5 (m br, 15 H_{arom}), 7.8 (br, 1H, NH_{Himt}), 12.1 (br, 1H, NH_{Himt}). $^{31}P\{^1H\}$ NMR (DMSO-d_6, 293 K): δ 43.1 [20], 36.0 [1], 26.4 [30], −3.8 [100], −6.8 [4]. IR (Nujol mull, cm^{-1}): 3185w, 3150w, 3050w (C–H_{arom}), 2056s (N_3), 1654w, 1583w, 1520m (C⋯C, C⋯N), 521s, 505s, 497s (PPh), 442w, 337w, 270w, 231w (δ_{azole}, Cu–N). Elemental analysis: *Anal*. Found: C, 54.02; H, 4.34; N, 14.84; S, 6.59. Calc. for $C_{21}H_{19}N_5PSCu$: C, 53.90; H, 4.09; N, 14.96; S, 6.85%.

Λ_m (DMSO, conc. = 1.0×10^{-4} mol l^{-1}): 3.3 Ω^{-1} mol^2 cm^{-1}.

*2.2.12. [Cu(mimt)(PPh$_3$)] (**11**)*

This compound has been obtained in refluxing ethanol by using a ligand-to-metal molar ratio of 2:1 (yield 54%). Washed with diethyl ether; m.p. 166–169 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 3.5 (br, 3H, NCH_3), 6.7 (br, 2H, CH_{mimt}), 7.2–7.5 (m br, 15H, H_{arom}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 29.7s [1], −3.4 br [30]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 32.7br [4], −2.8s [1]. −4.7s [2], −5.2s [1]. IR (Nujol mull, cm^{-1}): 3185w, 3110w (C–H$_{arom}$), 1584w, 1570m (C⋯C, C⋯N), 520sh, 518s, 508s, 489s (PPh), 449w, 435w, 419m, 279w, 246w (δ_{azole}, Cu–N). Elemental analysis: *Anal.* Found: C, 59.99; H, 4.72; N, 6.7; S, 7.02. Calc. for $C_{22}H_{20}N_2PSCu$: C, 60.19; H, 4.59; N, 6.38; S, 7.30%. Λ_m (acetone, conc. = 1.0×10^{-3} mol l^{-1}): 7.2 Ω^{-1} mol^2 cm^{-1}.

*2.2.13. [Cu(bimt)] (**12**)*

This compound has been obtained as **1** by using a ligand-to-metal molar ratio of 2:1 (yield 40%); m.p. (dec.) > 350 °C. ^{1}H NMR ($CDCl_3$, 293 K): 7.3 (br, 4H, CH_{arom}). IR (Nujol mull, cm^{-1}): 3050w (C–H$_{arom}$), 1550w (C⋯C, C⋯N), 429w, 387w, 379w, 353w, 327w, 316w, 303w, 280w (δ_{azole}, Cu–S, Cu–N). Elemental analysis: *Anal.* Found: C, 36.23; H, 1.81; N, 6.01; S, 27.81. Calc. for $C_7H_4NS_2Cu$: C, 36.59; H, 1.75; N, 6.10; S, 27.90%. Λ_m (DMSO, conc. = 1.0×10^{-3} mol l^{-1}): 1.8 Ω^{-1} mol^2 cm^{-1}.

*2.2.14. [Cu(pyt)] (**13**)*

This compound has been obtained as **1** by using a ligand-to-metal molar ratio of 2:1 (yield 35%); m.p. (dec.) 191 °C. ^{1}H NMR ($CDCl_3$, 293 K): 7.4 (br, 4H, CH_{arom}). IR (Nujol mull, cm^{-1}): 3050w (C–H$_{arom}$), 1617w, 1575w, 1547w (C⋯C, C⋯N), 508m 449m, 41m, 344w, 305m, 280w (δ_{azole}, Cu–S, Cu–N). Elemental analysis: *Anal.* Found: C, 34.32; H, 2.34; N, 7.92; S, 17.98. Calc. for C_5H_4NSCu: C, 34.57; H, 2.32; N, 8.06; S, 18.46%. Λ_m (acetone, conc. = 1.0×10^{-4} mol l^{-1}): 0.3 Ω^{-1} mol^2 cm^{-1}.

*2.2.15. [Cu(N$_3$)(Hmimt)$_3$] (**14**)*

This compound has been obtained as **1** by using a ligand-to-metal molar ratio of 5:1 (yield 63%); m.p. 128–130 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 3.6 (br, 9H, NCH_3), 6.7 (d, 6H, CH_{mimt}). IR (Nujol mull, cm^{-1}): 3060w (C–H$_{arom}$), 2034m (N_3), 1570w (C⋯C, C⋯N), 522s, 510s, 490s (PPh), 439w, 419w (δ_{azole}, Cu–N, Cu–S). Elemental analysis: *Anal.* Found: C, 32.41; H, 4.03; N, 27.92; S, 20.99. Calc. for $C_{12}H_{18}N_8S_3Cu$: C, 32.17; H, 4.05; N, 28.13; S, 21.47%. Λ_m (CH_2Cl_2, conc. = 1.0×10^{-3} mol l^{-1}): 0.9 Ω^{-1} mol^2 cm^{-1}. MW ($CHCl_3$, 0.40×10^{-3} mol l^{-1}): 299.

2.2.16. [Ag(N$_3$)(PPh$_3$)$_2$]

Recrystallized from tetrahydrofurane–chloroform–diethyl ether (yield 88%); m.p. 238–242 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.2–7.5 (m br, 30H, H_{arom}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 10.5s. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 32.1s [5], 23.7s [1], 15.8dd [2] ($^1J(^{109}Ag–^{31}P) = 713$ Hz, $^1J(^{107}Ag–^{31}P) = 620$ Hz), 8.05d br [200] ($^1J(Ag–^{31}P) = 413$ Hz). IR (Nujol mull, cm^{-1}): 3050w (C–H$_{azole}$ + C–H$_{arom}$), 2052s, 2029m, 2002w (N_3), 1654w, 1584w, 1570w, (C⋯C, C⋯N), 517m, 503s, 495m, 486m (PPh) 444w, 280w, 255w, 239w ($\delta_{phosphine}$, Ag–N). Elemental analysis: *Anal.* Found: C, 64.01; H, 4.59; N, 6.07. Calc. for $C_{36}H_{30}N_3P_2Ag$: C, 64.11; H, 4.48; N, 6.23%. Λ_m (CH_2Cl_2, conc. = 1.0×10^{-3} mol l^{-1}): 0.6 Ω^{-1} mol^2 cm^{-1}.

*2.2.17. [Ag(N$_3$)(PPh$_3$)(phen)] (**15**)*

This compound has been obtained as **1** by using a ligand-to-metal molar ratio of 4:1 (yield 94%); m.p. 205–207 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.2–7.5 (m br, 15H, H_{arom}) 7.7 (br, 2H, H_{phen}), 7.84 (d, 2H, H_{phen}), 8.30 (s, 2H, H_{phen}), 9.2 (br, 2H, H_{phen}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 29.5s [1], 12.6s [80]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 36.4s [1], 32.1s [5], 23.7s [2], 11.3dd ($^1J(^{109}Ag–^{31}P) = 669$ Hz, $^1J(^{107}Ag–^{31}P) = 583$ Hz). IR (Nujol mull, cm^{-1}): 3140w, 3110w, 3040w (C–H$_{arom}$), 2016s (N_3), 1616w, 1569w, 1507w (C⋯C, C⋯N), 520s, 504s (PPh), 484m, 471m, 443w, 419w (δ_{phen}, Cu–N). Elemental analysis: *Anal.* Found: C, 60.62; H, 3.84; N, 12.00. Calc. for $C_{30}H_{23}N_5PAg$: C, 60.83; H, 3.90; N, 11.82%. Λ_m (acetone, conc. = 1.0×10^{-3} mol l^{-1}): 2.3 Ω^{-1} mol^2 cm^{-1}.

*2.2.18. [Ag(N$_3$)(PPh$_3$)(cupr)] (**16**)*

This compound has been obtained as **1** by using a ligand-to-metal molar ratio of 4:1 (yield 99%); m.p. 232–234 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.87 (s, 6H, CH_3), 7.3–7.5 (m br, H_{arom}), 7.55 (d, 2H, CH_{cupr}), 7.77 (s, 2H, CH_{cupr}), 8.21 (d, 2H, CH_{cupr}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 10.7br. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 36.1s [1], 32.0s [10], 23.7s [8], 10.1d br [60] ($^1J(Ag–^{31}P) = 650$ Hz,). IR (Nujol mull, cm^{-1}): 3045w (C–H$_{arom}$), 2013s (N_3), 1599w, 1559w, 1500w (C⋯C, C⋯N), 545m, 523s, 500s, 494s (PPh), 435m, 422sh, 340br, 318w, 275w (δ_{cupr}, Cu–N). Elemental analysis: *Anal.* Found: C, 61.77; H, 4.57; N, 10.98. Calc. for $C_{32}H_{27}N_5PAg$: C, 61.95; H, 4.39; N, 11.29%. Λ_m (CH_2Cl_2, conc. = 1.0×10^{-3} mol l^{-1}): 6.6 Ω^{-1} mol^2 cm^{-1}.

*2.2.19. [Cu(N$_3$){P(o-tolyl)$_3$}(cupr)] (**17**)*

Tri-*o*-tolylphosphine P(*o*-tolyl)$_3$ (0.608 g, 2.0 mmol) was added to a diethyl ether suspension (100 ml) of compound **8** (0.58 g, 1.0 mmol). After 24 h stirring, the solid was filtered and washed with diethyl ether affording product **17** (0.309 g, 0.5 mmol) (yield 50%); m.p.

230–232 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.37 (s, 9H, $CH_{3P(o\text{-}tolyl)3}$), 2.78 (s, 6H, CH_{3cupr}), 6.7 (d, 2H, H_{arom}), 7.05 (t, 2H, H_{arom}), 7.2–7.4 (m br, 8H, H_{arom}), 7.48 (d, 2H, CH_{cupr}), 7.74 (s, 2H, CH_{cupr}), 8.17 (d, 2H, CH_{cupr}). IR (Nujol mull, cm^{-1}): 3045w (C–H_{arom}), 2025s (N_3), 1616w, 1584w, 1558w, 1505m (C⋯C, C⋯N), 546m, 526s, 517m, 502s, 498sh (PPh), 457m, 436m, 422sh, 320br, 274w (δ_{cupr}, Cu–N). Elemental analysis: *Anal.* Found: C, 68.15; H, 5.47; N, 11.23. Calc. for $C_{35}H_{33}N_5PCu$: C, 68.0; H, 5.38; N, 11.33%. Λ_m (CH_2Cl_2, conc. = 1.0×10^{-3} mol l^{-1}): 0.2 Ω^{-1} mol^2 cm^{-1}.

*2.2.20. [$Cu_2(N_3)_2(dppp)_3$] (**18**)*

1,2-Bis(diphenylphosphino)propane (0.41 g, 1.0 mmol) was added to a diethyl ether–dichloromethane 1:1 solution (50 ml) of compound **8** (0.58 g, 1.0 mmol). After 2 h stirring the solid was filtered and washed with diethyl ether to afford compound **18** (0.295 g, 0.2 mmol, 60%); m.p.: dec., 113 °C; char. 218 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.6 (br, 4H, CH_{2dppp}), 2.8 (br, 2H, CH_{2dppp}) 7.0–8.0 (m br, 20H, H_{arom}). IR (Nujol mull, cm^{-1}): 3060w (C–H_{arom}), 2011m (N_3), 1587w, 1556w, 1482sh (C⋯C, C⋯N), 548s, 511s (PPh) 450sh br, 332w, 308w. Elemental analysis: *Anal.* Found: C, 67.00; H, 5.67; N, 5.45. Calc. for $C_{81}H_{78}N_6P_6Cu_2$: C, 67.17; H, 5.43; N, 5.80%. Λ_m (CH_2Cl_2, conc. = 1.0×10^{-3} mol l^{-1}): 0.1 Ω^{-1} mol^2 cm^{-1}.

*2.2.21. [Cu(tz)(PPh_3)(phen)] (**19**)*

PPh_3 (0.52 g, 2 mmol) and CS_2 (4 mmol) were added to a benzene solution (50 ml) of compound **7** (0.55 g, 1.0 mmol). After 2 h stirring the solution was concentrated to 20 ml. A red–orange precipitate formed (0.500 g, 0.8 mmol, 80% yield) which has been filtered and washed with *n*-hexane (20 ml); m.p. 79–80 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.2–7.4 (m br, 15H, H_{arom}), 7.4–8.0 (m 8H, CH_{phen}). IR (Nujol mull, cm^{-1}): 3065w (C–H_{arom}), 1965w, 1888w, 1817w, 1665w, 1582m, 1570sh (C⋯C, C⋯N), 541m, 513s, 498sh (PPh), 430m, 420m, 398w, 310w, 300w, 280w, 265w, 252w, 245w, 226w (δ_{cupr}, Cu–N). Elemental analysis: *Anal.* Found: C, 59.82; H, 3.83; N, 11.23; S, 10.56. Calc. for $C_{31}H_{23}N_5PS_2Cu$: C, 59.65; H, 3.71; N, 11.22; S, 10.27%. Λ_m (CH_2Cl_2, conc. = 0.8×10^{-3} mol l^{-1}): 0.1 Ω^{-1} mol^2 cm^{-1}.

*2.2.22. [Ag(tz)(cupr)] (**20**)*

CS_2 (0.76 g, 10 mmol) was added to a diethyl ether solution of compound **16** (0.52 g, 1.0 mmol). The suspension was stirred overnight. The colorless precipitate obtained was then filtered off, washed with diethyl ether and shown to be compound **20** (0.141 g, 0.32 mmol, 32%); m.p. 171–172 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.85 (s, 6H, CH_{3cupr}), 7.4, 7.8, 8.2 (br, 6H, CH_{cupr}). IR (Nujol mull, cm^{-1}): 1650w, 1620w, 1595w, 1556w, 1511m, 1500m (C⋯C, C⋯N), 550m, 491m, 452w, 433w, 398w, 313w (δ_{cupr}, Cu–N). Elemental analysis: *Anal.* Found: C, 41.78; H, 2.90; N, 15.80; S, 14.26. Calc. for $C_{15}H_{12}N_5S_2Ag$: C, 41.49; H, 2.79; N, 16.13; S, 14.76%. Λ_m (CH_2Cl_2, conc. = 0.5×10^{-3} mol l^{-1}): 0.1 Ω^{-1} mol^2 cm^{-1}. From the filtered solution the complex [Ag(SCN)(PPh_3)$_2$] was recovered.

*2.2.23. [Ag(N_3)(PPh_3)(cyCN)(cupr)] (**21**)*

cyCN (0.56 g, 5 mmol) was added to a diethyl ether solution of compound **16** (0.52 g, 1.0 mmol). A clear solution has been obtained immediately. After 4 h stirring a microcrystalline precipitate formed, which has been filtered off, washed with diethyl ether and shown to be compound **21** (0.255 g, 0.35 mmol, 35%); m.p. 212–215 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.4, 1.7, 1.9 (m br, 11H, H_{cyCN}), 2.85 (s, 6H, CH_{3cupr}), 7.2–7.5 (m, 15H, CH_{arom}), 7.52 (d, 2H, CH_{cupr}), 7.73 (s, 2H, CH_{cupr}), 8.18 (s, 2H, CH_{cupr}). IR (Nujol mull, cm^{-1}): 3060w, 3045 (C–H_{arom}), 2190m (CN), 2011s, 1967sh (N_3) 1619w, 1595m, 1558m, 1500m (C⋯C, C⋯N), 546m, 522s, 501sh, 494s (PPh), 435m, 422m, 398w, 315w, 300w, 281w, 265w, 251w, 226w (δ_{cupr}, Cu–N). Elemental analysis: *Anal.* Found: C, 63.91; H, 4.93; N, 11.26. Calc. for $C_{39}H_{38}N_6PAg$: C, 64.20; H, 5.25; N, 11.52%. Λ_m (CH_2Cl_2, conc. = 0.4×10^{-3} mol l^{-1}): 0.05 Ω^{-1} mol^2 cm^{-1}.

3. Results and discussion

3.1. Syntheses

By the interaction of $[Cu(N_3)(PPh_3)_2]_2$ with monodentate nitrogen donors L (L = im, 1-meim, 2-meim, 4-meim and bzim) in diethyl ether the complexes $[Cu(N_3)(PPh_3)_2(L)]$ (**1**–**5**) (Scheme 1) have been immediately obtained upon breaking of the bridging copper(I)–azide bond in the dimeric starting reagent. On the contrary, the donor bnim reacts slowly with $[Cu(N_3)(PPh_3)_2]_2$, displacing only one molecule of PPh_3 from the dimer and yielding the likely dinuclear complex $[Cu_2(N_3)_2(PPh_3)_3(bnim)]$ (**6**) (Scheme 1).

The chelating bidentate ligands bipy, phen and cupr reacts immediately with $[Cu(N_3)(PPh_3)_2]_2$ yielding the mononuclear complexes $[Cu(N_3)(PPh_3)(L_2)]$ **7**–**9** upon breaking of the bridging Cu–(N_3)–Cu bonds and displacement of one PPh_3 molecule from the Cu(I) coordination sphere (Scheme 1). The 1:1 adduct $[Cu(N_3)(PPh_3)(Himt)]$ (**10**) was obtained when Himt reacts with $[Cu(N_3)(PPh_3)_2]$ in 1:1 ligand to metal molar ratio, whereas when Hmimt reacts with $[Cu(N_3)(PPh_3)_2]$ in ethanol, deprotonation of the sulfur ligand occurs with the formation of the poorly soluble [Cu(mimt)-(PPh_3)] (**11**).

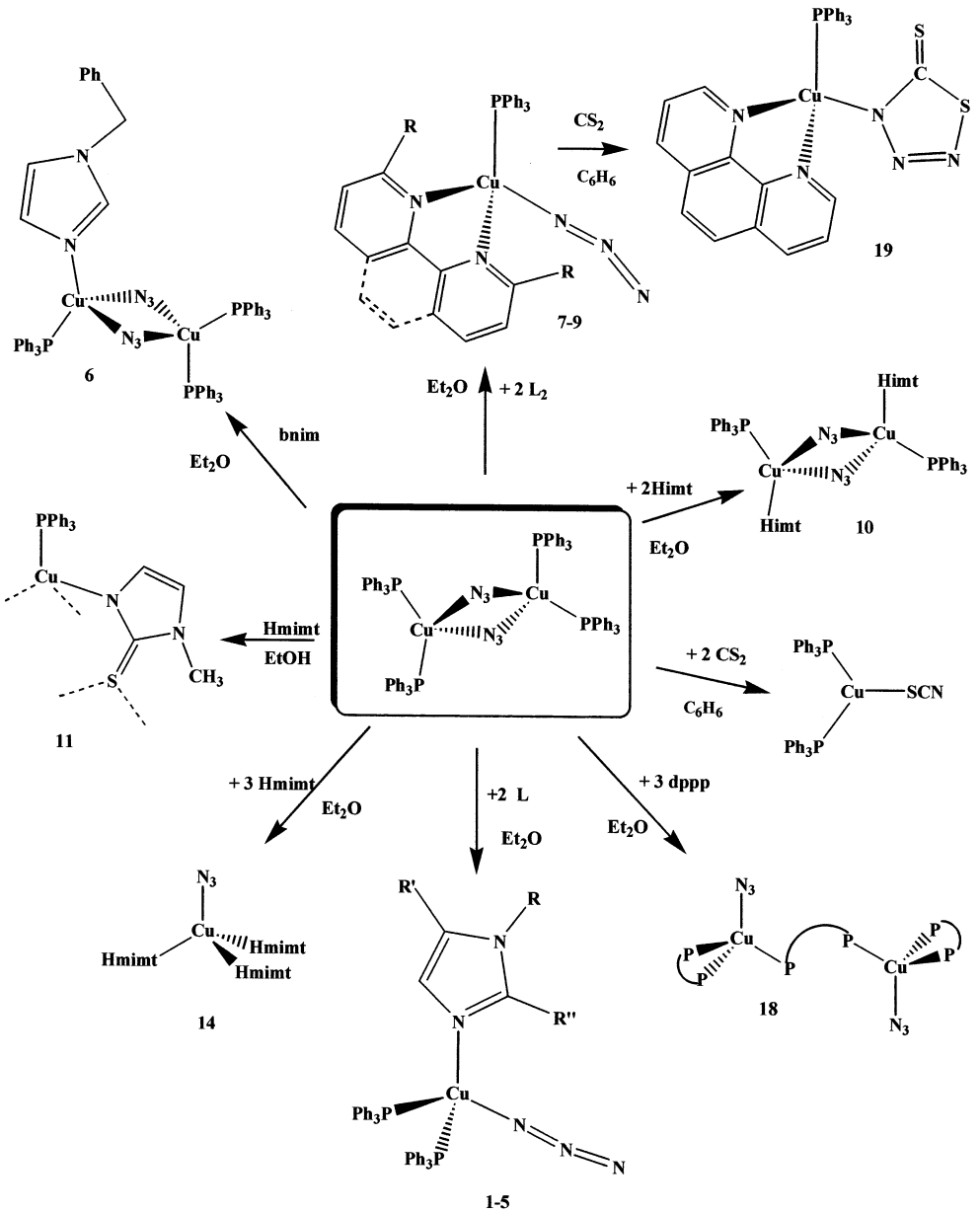
The two *S*-donor acid ligands Hbtt and Hpyt react similarly through elimination of HN_3 and lead to the formation of the insoluble likely polynuclear copper(I) complexes $[Cu(bimt)]_n$ (**12**) and $[Cu(pyt)]_n$ (**13**).

Unexpectedly, the reaction of $[Cu(N_3)(PPh_3)_2]_2$ with an excess of Hmimt in diethyl ether proceeds in a different way, to give a white solid formulated as $[Cu(N_3)(Hmimt)_3]$ (**14**) the two PPh_3 molecules being easily displaced by three Hmimt ligands.

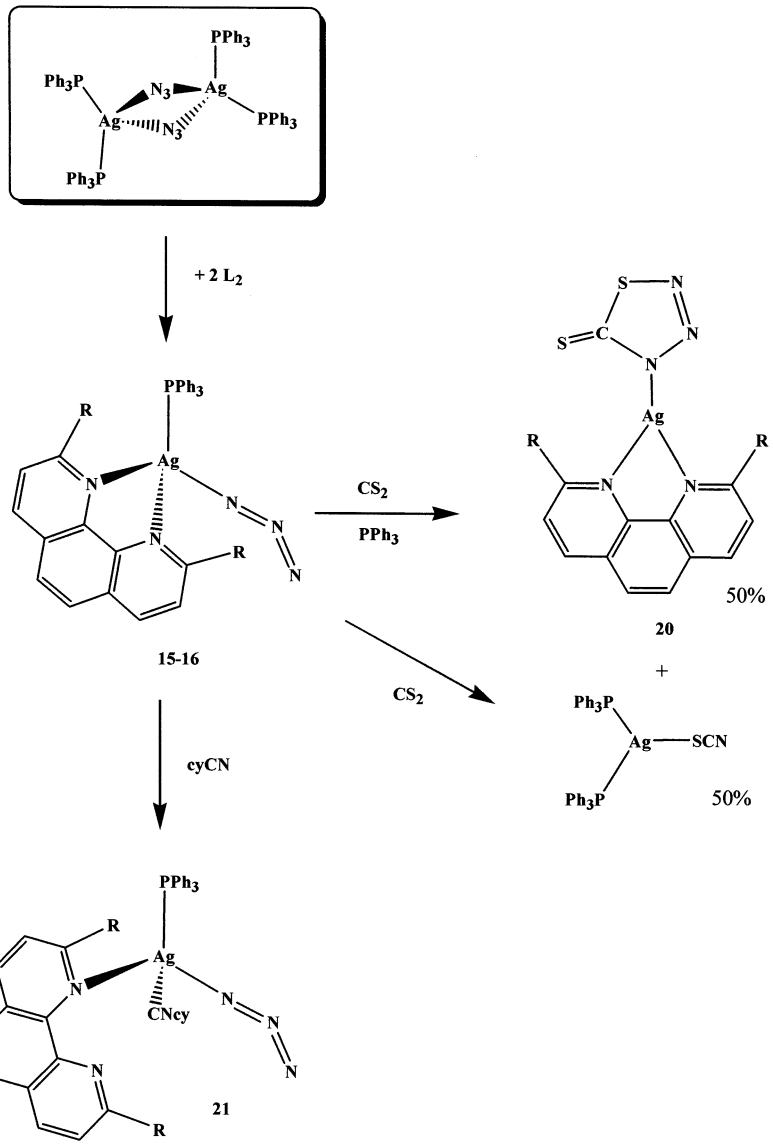
Attempts to obtain imidazole derivatives of silver(I)phosphino azide by using the appropriate stoichiometric amount or a strong excess of the N-donor ligand were unsuccessful, the starting reagents being always recovered. The reaction of $[Ag(N_3)(PPh_3)_2]_2$ with the S-donors led instead to complex mixtures and were not reproducible.

The chelating ligands phen and cupr reacts with $[Ag(N_3)(PPh_3)_2]_2$ yielding the complexes $[Ag(N_3)(PPh_3)(phen)]$ (**15**) and $[Ag(N_3)(PPh_3)(cupr)]$ (**16**) analogous to those of copper(I) (Scheme 2).

The reaction between 1 equiv. of compound **8** with 2 equiv. of P(*o*-tolyl)$_3$ in diethyl ether results in the rapid formation of the compound $[Cu(N_3)\{P(o\text{-tolyl}_3)\}(cupr)]$ (**17**) upon displacement of the less basic PPh_3. A different pattern was found with the chelating diphosphine dppp which easily displaced both cupr and PPh_3 from the copper complex **8** affording derivative having a 2:2:3 stoichiometry: $[Cu_2(N_3)_2(dppp)_3]$ (**18**). The reac-



Scheme 1.



Scheme 2.

tion of **4** with CS_2 in benzene and in presence of excess of PPh_3 yields immediately the well-known $[Cu(SCN)(PPh_3)_2]$ [12], whereas under the same conditions CS_2 reacts with $[Cu(N_3)(PPh_3)(phen)]$ yielding the thiotriazolate complex $[Cu(tz)(PPh_3)(phen)]$ (**19**). The reaction of the silver complex $[Ag(N_3)(PPh_3)(cupr)]$ (**16**) with CS_2 in benzene in presence of PPh_3 proceeds instantaneously resulting in the complete displacement of cupr and in the condensation of CS_2 with N_3 to yield $[Ag(SCN)(PPh_3)_2]$ [15]. The same reaction carried out in diethyl ether without excess of phosphine proceeds slowly yielding equimolar quantity of the thiotriazolate complex [Ag(tz)(cupr)] (**20**) and of $[Ag(SCN)(PPh_3)_2]$. Finally the reaction of $[Ag(N_3)(PPh_3)(cupr)]$ (**16**) with cyCN produces the mixed-ligand complex $[Ag(N_3)(PPh_3)(cyCN)(cupr)]$ (**21**), but not condensation products as the tetrazole obtained by Beck and Felhammer [16].

All the compounds are insoluble in diethyl ether and ethanol, and, with the exception of **11**–**13**, insoluble in all common organic solvents, they are soluble in acetone, DMSO, chlorinated solvents and acetonitrile. The conductivity measurements, carried out only on the stable solutions, show that our compounds are non-electrolytes not only in dichloromethane, but also in more ionizing solvents such as acetone, in agreement with their non-ionic structure proposed in Schemes 1 and 2. The ratio between the vaporimetric molecular weight ($CHCl_3$ solution) and the formula weight for compounds **2** and **14** is 0.40 and 0.68, respectively, in accordance with a partial dissociation of this kind of complexes in chloroform solution.

All attempts to crystallize complexes **1**–**21** failed due to their instability towards dissociation in organic solvents.

3.2. Spectroscopy

3.2.1. IR spectra

The IR spectra of the silver and copper complexes show several bands which may be taken as diagnostic for the presence of azole and pyridine-type ligands: a ring breathing band between 1600 and 1500 cm^{-1} and the ν(CH) stretching vibrations due to heterocyclic ring above 3000 cm^{-1} can often be detected. In the spectra of compounds **1**–**5**, **10** and **14** the presence of NH stretching vibrations between 3100 and 2400 cm^{-1}, with no significant shift from the free ligand values, is consistent with a monodentate neutral azole, coordinated through the pyridine nitrogen (compounds **1**–**5**) or the thione sulphur (**10** and **14**).

Changes to the Hmimt and Himt spectra upon coordination in **10** and **14** involve a slight perturbation to the thioamide II band (1275 cm^{-1}) and major perturbation to thioamide IV (770, 740 cm^{-1}) which is converted from its clearly resolved component in the uncoordinated molecule [17] into a peak (733 cm^{-1}) with associated shoulders (720–746 cm^{-1}) in the complexes. Slight shift (± 20 cm^{-1}) together with band splitting also occurs with δ(C–S) (675 cm^{-1}) and π(C–S) (520 cm^{-1}). All these significant perturbations (changes) in the thione region indicate sulfur donation by the ligand [18]. Weak bands at approximately 300 cm^{-1}, not present in the spectra of the free donors and of the starting Cu(azide) complexes, are tentatively assigned to Cu–S stretching bands. This fact further supports the coordination of the thione ligands through the S atoms.

In the spectra of **1**–**18** the IR-active N–N asymmetric stretch of the N_3 ligand is in the range 2060–2020 cm^{-1}. The position of this band cannot be used generally to infer bridging or non-bridging coordination mode to the azide group [19]. However, due to the fact that the N–N asymmetric stretching frequency differs by about 30 cm^{-1} from that of the starting $[M(N_3)(Ph_3P)_2]_2$ species where the azide is symmetric, and that the N–N asymmetric stretch for terminal azides generally falls at 2030 cm^{-1}, structures containing monocoordinate terminal azide ligands, as those in the Schemes 1 and 2, are likely for our compounds.

The band due to the cyCN ligand in complex **21** appears at 2190 cm^{-1}. This C–N stretching frequency is in the expected range being the isocyanide coordinate to a metal center [20].

In the far-IR region of derivatives **1**–**11**, **15**–**19** and **21** we always found a strong broad multiplet absorption near 500 cm^{-1}, assignable to Whiffen's y-vibrations [21]. A second group of medium intensity generally appeared near 410–420 cm^{-1}, whereas the u- and x-vibrations appeared as bands of weak intensity between 270 and 250 cm^{-1}. These bands are not very sensitive to the nature of the azole donor and of the counter-ion. It was not possible to assign the ν(Cu–P) vibrations, because they are likely hidden under some absorptions characteristic of the azole ring system.

The IR spectra of **19** and **20** show the disappearance of the asymmetric azide stretching bands and the appearance of the characteristic IR bands of the five-membered heterocyclic anion that has formed by the 1,3-dipolar cycloaddition of the azido moiety to the dipolarophile CS_2. A strong band at approximately 1200 cm^{-1} appears which can be assigned to the thiocarbonyl group [22]. The photolytical conversion of the bonded azide in **7** to the bonded thiocyanate in $[Cu(SCN)(PPh_3)_2]$ can be followed by the disappearance of the N–N stretching band and the appearance of a strong band at approximately 2090 cm^{-1} typical of a thiocyanate group [13].

3.2.2. NMR spectra

In the ^{1}H NMR spectra of **1**–**10** and **15**–**17** the signals due to azole or chelating ligands are always deshielded with respect to the free donors: the higher the Δ ($\Delta = \delta_{adduct} - \delta_{N\text{-}donor}$), the higher is the donation from the donor to the metal, and the stronger the corresponding M–N interaction. The Δ values further confirm the existence, at least partial, of complexation in solution. On the basis of the molecular weight determinations mentioned above we hypothesize that the complexes dissociated partly in solution. The resonances observed are averaged between those of the complex and the free ligand owing to a rapid exchange reaction between both. This has been confirmed from the spectra of compounds **1** and **7** recorded in presence of N-donor ligand excess. No additional signal appeared, but only a greater Δ has been found.

The solution ^{31}P NMR spectrum for each triphenylphosphine complex at r.t. consists of a broad singlet, presumed to be consequent on the presence of rapid exchange equilibria. A unique absorption is generally detected at lower fields than that of the free phosphine. The chemical shit values move upfield towards the values of the free PPh_3 with increasing coordination number, the $\Delta = \delta_{adduct} - \delta_{free\ phosphine}$ being generally greater for the complexes containing one P-donor molecule and for silver with respect to copper(I) derivatives.

Lability of the phosphorus ligands was evident in the temperature dependence of the ^{31}P NMR spectra of some derivatives: the cooled (218 K) $CDCl_3$ solutions of derivatives $[Cu(N_3)(PPh_3)_2]_2$, **1**, **5**, **6**, **7**–**10** show two or more different signals, one of them generally due to the free PPh_3.

The spectra at 223 K of $[Ag(N_3)(PPh_3)_2]_2$, **15** and **16** show splitting for the signal at approximately 10 ppm due to $^1J(Ag–^{31}P)$ coupling. The $^1J(^{107,109}Ag–^{31}P)$ coupling constant values observed are in the range typical for the monophosphino complexes [23]. They provide a

useful guide for the hybridization of the silver atom and hence to its solution coordination number. For example, the averaged $^1J(Ag-^{31}P)$ coupling constant value of **16** corresponds to sp silver hybridization in association with a coordination number of two whereas the $^1J(Ag-^{31}P)$ coupling constant found for the signal at approximately 8 ppm in the spectrum of $[Ag(N_3)(PPh_3)_2]_2$ is approximately 400 Hz, corresponding to an sp^2 hybridization and coordination number three [23].

4. Conclusions

A series of copper(I) and silver(I)–tertiary phosphine adducts containing coordinated azide and heterocyclic N-donor or S-donor ligands has been prepared and characterized. A different pattern of reactivity has been found for $[Cu(N_3)(PPh_3)_2]_2$ with respect to $[Ag(N_3)(PPh_3)_2]_2$. Monodentate N- and S-donors are able to displace phosphine ligands from the copper center, but not from silver. The reactivity of the azide group bonded to copper is also different from that of the azide bonded to silver. In the first case condensation of CS_2 with N_3 is generally fast and yield a tetrathioazolate derivative, in the second case the reaction of CS_2 with N_3 is slow and the main product is a thiocyanate derivative. From the reaction of $[Cu(N_3)(PPh_3)_2]_2$ with N-donors mixed-ligand complexes having coordination number four were always obtained. With S-donor displacement of the azide group was observed when the reaction was carried out in polar solvents such as EtOH. None of the complexes synthesized are very stable in solution, undergoing extensive ligand dissociation and rapid ligand exchange even at low temperature and in non-polar solvents. Azido groups bound to metal can be used to obtain tetrathioazole complexes.

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