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Synthesis and spectroscopic characterization of new Cu(I) complexes containing triaryl-, tricycloalkylphosphines and heterocyclic anionic or neutral N-donor ligands. Crystal and molecular structure of $[(Cy_3P)_2(pzH)Cu]ClO_4\cdot CH_3OH$ (Cy = cyclohexyl, pzH = pyrazole)

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Abstract

The reaction of $(PPh_3)_4CuClO_4$, $(PPh_3)_2CuCl$, $(Cy_3P)_2CuNO_3$ and $(Cy_3P)_2CuClO_4$ with an excess of monodentate heterocyclic N-donor ligand (QH in general, in detail: ImH = imidazole, 1-MeimH = 1-methylimidazole, 2-MeimH = 2-methylimidazole, 4-PhimH = 4-phenylimidazole, BimH = benzimidazole, 1-BzimH = 1-benzylimidazole, pzH = pyrazole, pz'H = 3,5-dimethylpyrazole) in diethyl ether or benzene resulted in the formation of new 2:2:1 $[(PPh_3)_2(QH)_2Cu]ClO_4$ (QH = ImH, 1-MeimH, 2-MeimH, 4-PhimH, BimH, pzH) and $[(PCy_3)_2(QH)_2Cu]NO_3$ (QH = 4-PhimH, BimH), 1:3:1 $[(PPh_3)(1\text{-}BzimH)_3Cu]ClO_4$, $[(PCy_3)(1\text{-}MeimH)_3Cu]ClO_4$ and $[(PCy_3)(QH)_3Cu]NO_3$ (QH = ImH, 1-MeimH, pzH), 2:1:1 $[(PPh_3)_2(QH)CuCl]$ (QH = ImH, 2-MeImH, 4-PhimH, BimH, 1-BzimH), $[(PCy_3)_2(QH)Cu]NO_3$ (QH = 1-BzimH, pz'H) and $[(PCy_3)_2(QH)Cu]ClO_4$ (QH = 2-MeimH, 4-PhimH, BimH, 1-BzimH, pzH, pz'H), 1:2:1 $[(PCy_3)(2\text{-}MeimH)_2Cu]NO_3$ and $[(PCy_3)(ImH)_2Cu]ClO_4$ and 1:1:1 $[(PPh_3)(1\text{-}MeimH)CuCl]$ adducts. With the bidentate donors bis(pyrazol-1-yl)methane (L^1), bis(3,5-dimethylpyrazol-1-yl)methane (L^2) and bis(4-methylpyrazol-1-yl)methane (L^4), 2:1:1 $[(PPh_3)_2(L)Cu]ClO_4$ and 1:1:1 $[(PCy_3)(L)Cu]ClO_4$ complexes were obtained, whereas the exopolydentate bis(1,2,4-triazol-1-yl)methane (L^3) in similar conditions yielded 1:1:1 $[(PPh_3)(L^3)Cu]ClO_4$ and $[(PCy_3)(L^3)Cu]NO_3$, and 1:2:1 $[(PCy_3)(L^3)_2Cu]ClO_4$ derivatives. Breaking of the bridging $C(sp^3)$–N bond in the bidentate bis(pyrazol-1-yl)methane occurred when the reaction between L^1 and $(PCy_3)_2CuNO_3$ was carried out in diethyl ether under aerobic conditions, the derivative $[(PCy_3)(pzH)_3Cu]NO_3$ being formed. In methanol in the presence of base, ImH, 2-MeimH, 4-PhimH and BimH react with $(PPh_3)_2CuCl$ giving the sparingly soluble complexes $[(PPh_3)_2(Im)Cu]\cdot 1/2H_2O$, $[(PPh_3)_2(2\text{-}Meim)Cu]\cdot H_2O$, $[(PPh_3)(4\text{-}Phim)Cu]$ and $[(PPh_3)(Bim)Cu]$, respectively. Reaction of $[(PPh_3)_2(ImH)_2Cu]ClO_4$ with PCy_3, PBz_3 (Bz = benzyl), $P(p\text{-}tolyl)_3$ and $(Ph_2PCH_2)_2$ (abbreviated Diphos) resulted in the formation of compounds $[(PPh_3)(PCy_3)(ImH)_2Cu]ClO_4$, $[(PPh_3)(PBz_3)(ImH)Cu]ClO_4$, $[(PPh_3)P(p\text{-}tolyl)_3(ImH)_2Cu]ClO_4$ and $[(Diphos)_2Cu]ClO_4$, respectively, whereas reaction with 1,10-phenanthroline (Phen) and 2,2'-bipyridyl (Bipy) produced $[(PPh_3)_2(ImH)(Phen)Cu]ClO_4$ and $[(PPh_3)_2(ImH)(Bipy)Cu]ClO_4$, respectively. While PCy_3, PBz_3 and $P(p\text{-}tolyl)_3$ were not able to displace the triphenylphosphine from $[(PPh_3)_2(L^1)Cu]ClO_4$, Phen and Bipy in the same conditions formed the derivatives $[(PPh_3)_2(Phen)Cu]ClO_4$ and $[(PPh_3)_2(Bipy)Cu]ClO_4$. All of the complexes were characterized by IR and far-IR data, conductivity, ^1H NMR and in some cases also with UV, ^{13}C and ^{31}P NMR and molecular weight measurements. The structure of $[(Cy_3P)_2(pzH)Cu]ClO_4\cdot CH_3OH$ was determined by single crystal X-ray diffraction: monoclinic, space group Pn, $Z=2$, $a=9.949(7)$, $b=13.128(4)$, $c=16.588(8)$ Å, $\beta=91.15(7)°$. The copper atom exhibited a distorted ideal trigonal planar geometry involving two phosphine groups (Cu–P: 2.262(9) and 2.272(6) Å; P–Cu–P: 132.3(7)°) and one pyrazole ligand (Cu–N: 2.047(18) Å) coordinating through a pyridine-like nitrogen atom. The pyrazole donor of one molecule was hydrogen bonded to a molecule of methanol, which in turn was hydrogen bonded to the ionic perchlorato group.

Keywords: Crystal structures; Copper complexes; Tertiary phosphine complexes; N-ligand complexes

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1. Introduction

Copper(I) derivatives are of importance for understanding the mechanism of several catalytic processes [1]. Copper(I) catalysts are very versatile in oxidation reactions and play a relevant role in the redox-active copper containing proteins [2]. Several copper(I) compounds are also suitable molecular precursors for CVD due to their high vapor pressure, low decomposition temperature and facile decomposition mechanism in the pure metal deposit and supporting ligands [3].

Following a line of research whose major target is the chemical and structural characterization of metal complexes containing N-donor ligands, structural analogues of biologically important organic nucleobases, we have reported in the earlier papers [4,5] the synthesis and spectroscopic investigations of several triarylphosphino copper(I)-nitrato and -halide derivatives containing anionic or neutral pyrazole- and imidazole-type ligands. We have shown that the diversity of stoichiometries, coordination number and geometries of complexes containing Group 15 ligands are strongly dependent on the steric and electronic requirements of the donors employed. The coordination number 4 was by far the most frequently observed conformation in the case of copper(I) compounds containing small donor molecules, whereas tricoordination was limited to more sterically hindered derivatives [6].

Now we have decided to extend our research to study the interaction of the N-donor ligands given in Fig. 1 with other phosphinocopper(I) complexes and here we report the synthesis and spectroscopic characterization of a number of new derivatives of $(Ph_3P)_nCuX$ ($n=0$, 1 or 2; X = Cl or ClO_4) and $(Cy_3P)_nCuX$ ($n=0$, 1 or 2; X = NO_3 or ClO_4). The factors affecting the stoichiometry and the coordination number are discussed and rationalized on the basis of steric (for example Tolman's cone angle [7]) and electronic arguments (presence of a non-coordinating anion, basicity of the donors, etc.) [8]. The X-ray crystal structure of $[(Cy_3P)_2(pzH)Cu]ClO_4 \cdot CH_3OH$ (Cy = cyclohexyl) is also reported. To date, this is the first structurally characterized ionic mononuclear Cu(I) compound containing two phosphines and one N-donor azole-type ligand.

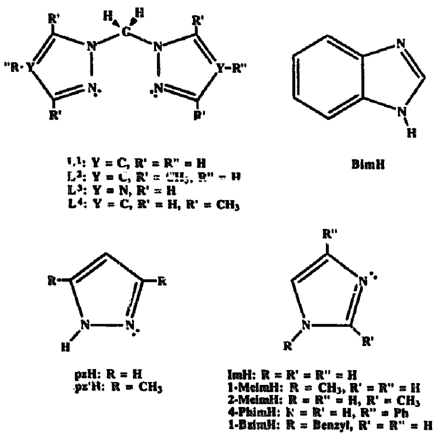

Fig. 1. Structure of the N-donor ligands.

2. Experimental

All solvents were dried by standard techniques. The reagents were obtained from Aldrich Chemical Co. and from Alfa. The samples were dried in vacuo to constant weight (20 °C, ~0.1 Torr). Elemental analyses were carried out in-house with a Fisons Instruments 1108 CHNS-O elemental analyzer. IR spectra from 4000 to 100 cm^{-1} were recorded with a Perkin-Elmer System 2000 FT-IR instrument. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a VX-300 Varian spectrometer operating at room temperature (300 for ^1H, 75 for ^{13}C and 121.4 MHz for ^{31}P). Melting points were taken on an IA 8100 Electrothermal instrument. The electrical resistances of solutions were measured with a Crison CDTM 522 conductimeter at room temperature. The osmometric measurements were carried out at 37 °C over a range of concentrations with a Knauer KNA0280 vapor pressure osmometer calibrated with benzil. The solvent was Baker Analyzed Spectrophotometric grade chloroform or acetone. The results were reproducible to ±2%.

2.1. *Synthesis of the ligands*

The donors L^1, L^2, L^3 and L^4 were prepared by published methods [9,10].

2.2. *Synthesis of the Cu(I) complexes*

The derivatives $[(PPh_3)_4Cu(ClO_4)]$, $[(Ph_3P)_2CuCl]$ and $[(PCy_3)_2CuX]$ (X = ClO_4 or NO_3) were prepared by published methods [11–13] and their analytical and spectral data are consistent with those reported in the literature.

2.2.1. *Perchloratobis(triphenylphosphine)-bis(imidazole)copper(I)*

(a) Imidazole (0.14 g, 2.0 mmol) was added to a diethyl suspension (100 cm^3) of $[(PPh_3)_4Cu](ClO_4)$ (1.21 g, 1.0 mmol). After 3 h stirring the solid was filtered and washed with ether (20 cm^3), affording product **1** (0.70 g, 0.85 mmol). Compounds **2–8**, **10**, **13–24** and **28–39** were obtained similarly.

(b) Triphenylphosphine (1.31 g, 5.0 mmol) was added to an ethanol suspension of tetrakis(imidazole)copper(II)-diperchlorate (0.53 g, 1.0 mmol) previously prepared according to the literature [14]. The solution was refluxed for 2 days. Et_2O was then added and a white precipitate was immediately formed, which was filtered and washed with Et_2O. The residue was recrystallized from 100 cm^3 of methanol/diethyl ether 1:1 to give 0.35 g (40% yield) of **1**.

2.2.2. *Perchloratobis(tricyclohexylphosphine)-bis(triazol-1-yl)methane copper(I)*

Bis(triazol-1-yl)methane (0.30 g, 2.0 mmol) was added to an acetone suspension (120 cm^3) of [(PPh$_3$)$_4$Cu](ClO$_4$) (1.21 g, 1.0 mmol). After 1.5 days stirring, the solid was filtered and washed with acetone (30 cm^3), affording product **9** (0.22 g, 0.38 mmol). Compound **27** was obtained similarly.

2.2.3. *Perchloratobis(triphenylphosphine)bis(pyrazole)-copper(I)*

Pyrazole (0.14 g, 2.0 mmol) was added to a benzene solution (100 cm^3) of [(PPh$_3$)$_4$Cu](ClO$_4$) (1.21 g, 1.0 mmol). The solution was refluxed for 2 days and evaporated to dryness; the residue was washed twice with diethyl ether, leaving product **11** (0.54 g, 0.65 mmol). Compounds **12**, **25** and **26** were prepared similarly.

2.2.4. *Imidazolatobis(triphenylphosphine)copper(I)*

Imidazole (0.14 g, 2.0 mmol) and KOH (0.11 g, 2.0 mmol) were added to a methanol suspension (100 cm^3) of CuI(PPh$_3$)$_3$ (1.95 g, 2.0 mmol). The suspension was refluxed for 2 days, then filtered and washed with hot methanol (20 cm^3), leaving product **40** (1.089 g, 1.64 mmol). Compounds **41–43** were obtained similarly.

2.2.5. *Perchlorato(triphenylphosphine)(1,10-phenanthroline)(imidazole) copper(I)*

1.10-Phenanthroline (0.180 g, 1.0 mmol) was added under nitrogen to a benzene solution of compound **1** (0.82 g, 1.0 mmol). A black precipitate was immediately formed which was refluxed for 2 days, filtered off and recrystallized from dichloromethane/diethyl ether, leaving product **44** (0.673 g, 1.00 mmol).

2.2.6. *Perchlorato(triphenylphosphine)(tricyclohexylphosphine)imidazole copper(I)*

Tricyclohexylphosphine (0.28 g, 1.0 mmol) was added to a diethyl ether suspension (110 ml) of compound **1** (0.82 g, 1.0 mmol). After 1.5 days stirring, the solid was filtered and washed with diethyl ether, affording product **46** (0.71 g, 0.84 mmol). Compounds **45**, **47** and **48** were prepared similarly.

2.2.7. *Perchloratobis(triphenylphosphine)(1,10-phenanthroline)copper(I)*

1.10-Phenanthroline (0.180 g, 1.0 mmol) was added under nitrogen to a benzene solution of compound **7** (0.77 g, 1.0 mmol). A black precipitate was formed which was crystallized from hot dichloromethane/diethyl ether leaving the yellow product **49** (0.716 g, 0.90 mmol). Compound **50** was prepared similarly using diethyl ether as solvent of reaction.

2.2.8. *Perchloratobis(1,2-diphenylphosphinoethane)-copper(I)*

1,2-Diphenylphosphinoethane (0.80, 2.0 mmol) was added under a stream of N$_2$ to a diethyl ether suspension of compound **1** (0.82 g, 1.0 mmol). After 1.5 days stirring, the solid was filtered and washed with diethyl ether, affording the product (Diphos)$_2$CuClO$_4$ (0.86 g, 0.90 mmol). M.p. 235–236 °C. IR data: ν(ClO$_4$): 1092s, 625s; ν(Ph): 515s, 489s. *Anal.* Found: C, 65.3; H, 5.0. Calc.: C, 65.1; H, 5.0%.

Caution! Perchlorate salts with organic ligands are potentially explosive and should be handled with the necessary precautions [15].

2.3. *X-ray crystallography*

Crystals of [(Cy$_3$P)$_2$Cu(pzH)]ClO$_4$·CH$_3$OH were obtained by slow evaporation of methanol/diethy ether.

2.3.1. *Crystal data*

C$_{40}$H$_{74}$N$_2$O$_5$P$_2$CuCl, $M=893.982$, monoclinic, $a=9.949(7)$, $b=13.128(4)$, $c=16.588(8)$ Å, $\beta=91.15(7)°$, $U=2166.044$ Å^3 (by least-squares refinement on diffractometer angles for 9 automatically centered reflections, $\lambda=0.71069$ Å), space group *Pn* (alt. *Pc*, No. 7), $Z=2$, $D_c=1.264$ g cm^{-3}, $F(000)=888.0$. Colorless prisms, 0.9×0.5×0.4 mm, μ(Mo Kα) = 7.034 cm^{-1}.

2.3.2. *Data collection and processing*

Huber CS diffractometer [16], ω scan mode with $\Delta\omega=1.5°$, ω scan speed 1.0–30.0° min^{-1}, graphite-monochromatized Mo Kα radiation, 3838 reflections collected ($1.5\leq\theta\leq30°$, h, k, $\pm l$) 3323 unique (merging $R=0.019$), giving 3126 with $|F_o|\geq6\sigma|F_o|$. Three reflections, periodically monitored, showed no decay.

2.3.3. *Structure analysis and refinement*

Direct methods followed by Fourier synthesis. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens, clearly located by difference syntheses, in idealized positions (X–H = 0.96 Å with X = C, N). The hydrogen atom of the OH group of the methanol molecule was not clearly localized by difference syntheses and not included in the final calculations. Each hydrogen atom was assigned the equivalent isotropic temperature factor of the parent non-hydrogen atom and allowed to ride on it. The CH$_3$ group of the methanol solvent was kept fixed to the position revealed by Fourier synthesis. Corrections for the anomalous dispersion for Cu, P and Cl atoms were included in the final refinement. The weighting scheme $w=1/(a+b|F_o|+c|F_o|^2)$, with $a=0.34131$, $b=0.06039$, $c=0.00011$ gave $S=1.078$. The final difference Fourier map, with a root-mean-square deviation of electron density of 0.05 e Å^{-3}, showed values not exceeding 0.30 e Å^{-3}, which, however, are not of chemical significance. Final R and R_w values are 0.0363 and 0.0487. Programs and computers used and sources of scattering factors are given in Refs. [17,18].

3. Results and discussion

3.1. *Synthesis of the complexes [(PPh$_3$)$_{4-n}$(QH)$_n$Cu]ClO$_4$ and [(PPh$_3$)$_y$(L)$_x$Cu]ClO$_4$*

The copper(I) perchlorato complexes **1–10** listed in Table 1, together with their relevant physical and analytical

Table 1
Analytical [a] and physical data for the copper(I) compounds

Complex	M.p. [b] (°C)	Yield [c] (%)	Analysis (%)			Conductivity data [d]			Selected IR data [e] (cm^{-1})		
			C	H	N	Solv.	Conc.	Λ	$\nu(ClO_4)/\nu(NO_3)$ ν(Cu–Cl)	ν(N–H) ν(O–H)	ν(C–H) azole
1 $[(PPh_3)_2(ImH)_2Cu]ClO_4$	199–202	85	61.2	4.9	6.8	CH_3CN	1.01	121.5	1120s, 920m	3291s br	3150w, 3110w
$C_{42}H_{38}ClCuN_4O_4P_2$			(61.2)	(4.6)	(6.8)	CH_2Cl_2	1.02	20.6	624s	2900s br	3080w, 3060m
2 $[(PPh_3)_2(2\text{-MeimH})_2Cu]ClO_4$	183–185	99	62.2	5.1	6.2	CH_3CN	0.61	133.8	1092s, 927w	3378s br	3123w, 3110w
$C_{44}H_{42}ClCuN_4O_4P_2$			(62.0)	(5.0)	(6.6)	DMSO	0.72	30.8	622s	3270s br	3080w, 3060m
3 $[(PPh_3)_2(1\text{-MeimH})_2Cu]ClO_4$	171–173	88	61.6	5.1	6.3	CH_3CN	0.88	81.5	1095s, 935w		3122w, 3071w
$C_{44}H_{42}ClCuN_4O_4P_2$			(62.0)	(5.0)	(6.6)				623ss		3053w
4 $[(PPh_3)_2(4\text{-PhimH})_2Cu]ClO_4$	147–149	88	67.0	5.1	5.3	CH_3CN	0.61	114.3	1091s, 943w	3270s br	3120w, 3080w
$C_{54}H_{46}ClCuN_4O_4P_2$			(66.5)	(4.8)	(5.7)				624s	2850sbr	
5 $[(PPh_3)_2(BimH)_2Cu]ClO_4$	165–167	99	65.4	4.8	5.6	CH_3CN	0.69	118.5	1093s, 932w	3395s br	3120w, 3070w
$C_{50}H_{42}ClCuN_4O_4P_2$			(65.0)	(4.6)	(6.1)				623s	3237s br	
6 $[(PPh_3)(1\text{-BzimH})_3Cu]ClO_4$	129–131	98	64.5	5.3	9.5	CH_3CN	0.70	129.7	1083s, 934w		3140w, 3121w
$C_{48}H_{45}ClCuN_6O_4P$			(64.1)	(5.0)	(9.3)				623s		3080w, 3065w
7 $[(PPh_3)_2(L^1)Cu]ClO_4$	212–215	89	62.3	4.3	6.5	CH_3CN	0.86	122.0	1080s, 930w		3140w, 3118w
$C_{43}H_{38}ClCuN_4O_4P_2$			(61.8)	(4.6)	(6.7)				624s		3080w, 3050w
8 $[(PPh_3)_2(L^2)Cu]ClO_4$	213–214	80	63.6	5.0	6.2	CH_3CN	0.80	125.0	1083s		3129w, 3090w
$C_{47}H_{46}ClCuN_4O_4P_2$			(63.3)	(5.2)	(6.3)	CH_2Cl_2	0.98	39.0	624s		3080w
9 $[(PPh_3)(L^3)Cu]ClO_4$	232–236	38	48.5	3.9	15.0	CH_3CN	0.90	114.8	1092s, 931w		3140w, 3107w
$C_{23}H_{21}ClCuN_6O_4P$			(48.0)	(3.7)	(14.6)				623s		3080w, 3050w
10 $[(PPh_3)_2(L^4)Cu]ClO_4\cdot 2H_2O$	229–230	97	59.6	5.0	6.2	CH_3CN	0.88	115.7	1104s, 932w		3140w, 3107w
$C_{45}H_{46}ClCuN_4O_6P_2$			(60.1)	(5.1)	(6.2)				624s		3080w, 3050w
11 $[(PPh_3)_2(pzH)_2Cu]ClO_4$	188–191	65	61.6	4.4	6.8	CH_3CN	0.85	121.6	1080s, 933w	3271s br	3140w, 3080w
$C_{42}H_{38}ClCuN_4O_4P_2$			(61.2)	(4.7)	(6.8)				623s		
12 $[(L^2)_2Cu]ClO_4$	244–246	75	46.6	5.5	20.0	CH_3CN	0.80	133.0	1082s, 930sh		3140w, 3080w
$C_{22}H_{32}ClCuN_8O_4$			(46.2)	(5.6)	(19.6)	CH_2Cl_2	1.04	51.2	623s		
13 $[(PPh_3)_2(ImH)CuCl]$	195–200	53	67.4	5.2	4.5	CH_3CN	0.71	40.9	213br	3230s br	
$C_{39}H_{34}ClCuN_2P_2$			(67.7)	(5.0)	(4.1)						
14 $[(PPh_3)_2(2\text{-MeimH})CuCl]$	180–184	99	67.8	5.3	4.1	CH_3CN	0.67	38.2	203br	3190s br	3140w, 3110w
$C_{40}H_{36}ClCuN_2P_2$			(68.1)	(5.1)	(4.0)	CH_2Cl_2	0.75	0.1			
15 $[(PPh_3)(1\text{-MeimH})CuCl]$	152–157	98	60.0	5.0	6.1	CH_3CN	1.05	34.7	180m br		3119w, 3103w
$C_{22}H_{21}ClCuN_2P$			(59.6)	(4.8)	(6.3)				160m br		3053w
16 $[(PPh_3)_2(4\text{-PhimH})CuCl]$	124–128	99	69.8	5.5	3.8	CH_3CN	0.81	29.4	225m	3200br	3117w, 3080w
$C_{45}H_{38}ClCuN_2P_2$			(70.4)	(5.0)	(3.6)						3050sh
17 $[(PPh_3)_2(BimH)CuCl]$	140–142	95	69.1	5.2	3.8	CH_3CN	0.83	31.7	234m	3250br	3140w
$C_{43}H_{36}ClCuN_2P_2$			(69.6)	(4.9)	(3.8)						
18 $[(PPh_3)_2(1\text{-BzimH})CuCl]\cdot 1.5(H_2O)$	195–200	99	68.4	5.7	3.6	CH_3CN	0.76	42.8	211br	3250br	3150w, 3140w,
$C_{46}H_{43}ClCuN_2O_{1.5}P_2$			(68.3)	(5.4)	(3.5)	CH_2Cl_2	0.79	0.2			3080w
19 $[(PCy_3)(ImH)_3Cu]NO_3$	92–94	82	53.5	7.2	15.7	CH_3CN	0.64	133.1	1360s br	3200br	3196w, 3139w
$C_{27}H_{45}CuN_7O_3P$			(53.1)	(7.4)	(16.1)				826m		3050w
20 $[(PCy_3)(2\text{-MeimH})_2Cu]NO_3$	179–180	84	55.2	7.8	11.9	CH_3CN	0.88	108.5	1408s, 1003w	3200br	3176w, 3132br
$C_{26}H_{45}CuN_5O_3P$			(54.8)	(8.0)	(12.3)				1330s		3100br
21 $[(PCy_3)(1\text{-MeimH})_3Cu]NO_3$	88–89	42	55.6	8.0	14.6	CH_3CN	0.76	124.9	1370s, 829w		3110w
$C_{30}H_{51}CuN_7O_3P$			(55.2)	(7.9)	(15.0)						

22 $[(PCy_3)_2(4\text{-PhimH})_2Cu]NO_3\cdot 2(H_2O)$ $C_{54}H_{86}CuN_5O_5P_2$	164–168	58	63.8 (64.2)	8.6 (8.6)	7.3 (6.9)	CH_3CN	0.85	85.8	1370s, 829w	3200br	3050w
23 $[(PCy_3)_2(BimH)_2Cu]NO_3\cdot 2(Et_2O)$ $C_{58}H_{98}CuN_5O_5P_2$	176–186	66	64.7 (65.1)	9.6 (9.2)	6.2 (6.5)	CH_3CN	0.67	168.7	1370s br 826w	3250br	3140w
24 $[(PCy_3)_2(1\text{-BzimH})Cu]NO_3$ $C_{46}H_{76}CuN_3O_3P_2$	177dec	71	65.5 (65.4)	9.2 (9.1)	5.2 (5.0)	CH_3CN	0.79	135.9	1365s br 821w		3138w, 3108w 3083w
25 $[(PCy_3)(pzH)_3Cu]NO_3$ $C_{27}H_{45}CuN_7O_3P$	144–146	84	53.2 (53.1)	7.6 (7.4)	16.3 (16.1)	CH_3CN	0.65	138.7	1370s br 826w	3250br	3140w, 3110w
26 $[(PCy_3)_2(pz'H)Cu]NO_3$ $C_{41}H_{74}CuN_3O_3P_2$	223–226	30	62.9 (62.9)	9.6 (9.5)	5.2 (5.4)	CH_3CN	0.42	88.5	1400s br, 826w 1360sbr, 1310w	3200br	3110w
27 $[(PCy_3)(L^3)Cu]NO_3$ $C_{23}H_{39}CuN_7O_3P$	159–161	53	49.5 (49.7)	7.4 (7.1)	18.0 (17.6)	CH_3CN	0.90	135.0	1416sbr, 1360sbr 1290s br		3122w
28 $[(PCy_3)(ImH)_2Cu]ClO_4$ $C_{24}H_{41}ClCuN_4O_4P$	136–139	84	49.8 (49.7)	7.3 (7.1)	9.9 (9.7)	CH_3CN	1.01	90.3	1102s br, 1069s 622s, 612s	3271 sbr	3138w
29 $[(PCy_3)_2(2\text{-MeimH})Cu]ClO_4$ $C_{40}H_{72}ClCuN_2O_4P_2$	185–195	85	59.9 (59.6)	9.2 (9.0)	3.7 (3.5)	CH_3CN	1.03	119.1	1108s, 926sw 623s	3212s br	3126w
30 $[(PCy_3)(1\text{-MeimH})_3Cu]ClO_4$ $C_{30}H_{51}ClCuN_6O_4P$	115–118	90	52.5 (52.2)	7.8 (7.5)	11.8 (12.2)	CH_3CN	0.96	121.4	1076s br, 928m 622s		3119w
31 $[(PCy_3)_2(4\text{-PhimH})Cu]ClO_4\cdot 2(H_2O)$ $C_{45}H_{78}ClCuN_2O_6P_2$	179–182	84	59.8 (59.8)	8.7 (8.7)	3.0 (3.1)	CH_3CN	0.94	129.1	1100s br, 916w 624s	3250b 3170br	3050w
32 $[(PCy_3)_2(BimH)Cu]ClO$ $C_{43}H_{72}ClCuN_2O_4P_2$	186–190	99	61.6 (61.3)	8.6 (8.6)	3.6 (3.3)	CH_3CN	0.97	115.0	1103s, 934w 623s	3195br	3098w
33 $[(PCy_3)_2(1\text{-BzimH})Cu]ClO_4\cdot(Et_2O)$ $C_{50}H_{86}ClCuN_2O_5P_2$	180–185	87	63.2 (62.8)	9.4 (9.1)	2.8 (2.9)	CH_3CN	1.00	128.4	1095s, 936w 623s		3140w 3123w
34 $[(PCy_3)_2(pzH)Cu]ClO_4\cdot(CH_3OH)$ $C_{40}H_{74}ClCuN_2O_5P_2$	143–147	50	58.4 (58.3)	9.4 (9.1)	3.5 (3.4)	CH_3CN	0.95	129.7	1116s br 928w, 623s	3390s br 3177s br	3125w 3060w
35 $[(PCy_3)_2(pz'H)Cu]ClO_4$ $C_{41}H_{74}ClCuN_2O_4P_2$	162–165	43	60.6 (60.1)	9.2 (9.1)	3.0 (3.4)	CH_3CN	0.96	133.9	1113s,1060s 1032s, 1020s 926w, 623s	3212br	3150w 3116w
36 $[(PCy_3)(L^1)Cu]ClO_4\cdot 1/2(Et_2O)$ $C_{27}H_{46}ClCuN_4O_{4.5}P$	206–211	96	51.8 (51.6)	7.6 (7.4)	8.9 (8.9)	CH_3CN	0.91	130.2	1083s, 917w 623s		3125w
37 $(PCy_3)(L^2)Cu]ClO_4$ $C_{29}H_{49}ClCuN_4O_4P$	193–197	75	53.9 (53.8)	7.4 (7.6)	8.5 (8.7)	CH_3CN	0.91	124.5	1081s, 929w 623s		3080w 3060w
38 $[(PCy_3)(L^3)_2Cu]ClO_4$ $C_{28}H_{45}ClCuN_{12}O_4P$	198–203	99	45.2 (45.2)	6.4 (6.1)	22.4 (22.6)	CH_3CN	0.93	125.3	1083s, 919w 624s		3112w
39 $[(PCy_3)(L^4)Cu]ClO_4$ $C_{27}H_{45}ClCuN_4O_4P$	200–203	93	52.7 (52.3)	7.4 (7.3)	8.9 (9.0)	CH_3CN	0.98	121.1	1082s, 918w 623s		3163w, 3120w 3104w, 3024w
40 $[(PPh_3)_2(Im)Cu]\cdot 1/2(H_2O)$ $C_{39}H_{34}CuN_2O_{0.5}P_2$	176–177	82	70.4 (70.5)	5.2 (5.1)	4.0 (4.2)	 CH_2Cl_2	 1.09	 0.0		3350br	3144w 3040w
41 $[(PPh_3)_2(2\text{-Meim})Cu]\cdot(H_2O)$ $C_{40}H_{37}CuN_2OP_2$	153–167	60	70.0 (69.9)	5.4 (5.4)	4.2 (4.1)	 CH_2Cl_2	 0.93	 0.0		3350br	3126w
42 $[(PPh_3)(4\text{-Phim})Cu]$ $C_{27}H_{22}CuN_2P$	116–125	70	68.8 (69.1)	5.0 (4.7)	5.8 (6.0)	 CH_2Cl_2	 0.01	 0.0			3042w
43 $[(PPh_3)(Bim)Cu]\cdot 1/2(H_2O)$ $C_{25}H_{21}CuN_2O_{0.5}P$	135–139	99	66.4 (66.4)	4.6 (4.7)	6.3 (6.2)	 CH_2Cl_2	 0.01	 0.0		 3300br	3071w 3046w
44 $[(PPh_3)(Phen)(ImH)Cu]ClO_4$ $C_{33}H_{27}ClCuN_4O_4P$	174–182	99	58.4 (58.8)	4.0 (4.1)	8.3 (8.3)	CH_3CN	0.82	127.7	1103s, 1063s 929w, 622s	3251br	3126w
45 $[(PPh_3)(Bipy)(ImH)Cu]ClO_4$ $C_{31}H_{27}ClCuN_4O_4P$	157–161	89	57.7 (57.3)	4.5 (4.2)	8.2 (8.6)	CH_3CN	0.62	132.3	1098s, 1065s 927w, 622w	3271br	3119w

(continued)

Table 1 (*continued*)

Complex	M.p. [b] (°C)	Yield [c] (%)	Analysis (%) [a] C	H	N	Conductivity data [d] Solv.	Conc.	Λ	Selected IR data [e] (cm^{-1}) $\nu(ClO_4)$/$\nu(NO_3)$ ν(Cu–Cl)	ν(N–H) ν(O–H)	ν(C–H) azole
46 $[(PPh_3)(PCy_3)(ImH)_2Cu]ClO_4$ $C_{42}H_{56}ClCuN_4O_4P_2$	156–162	84	60.3 (59.9)	6.5 (6.7)	6.4 (6.7)	CH_3CN	0.65	131.6	1117s, 1064s 918w, 623s	3260s br	3071w
47 $[(PPh_3)(PBz_3)(ImH)Cu]ClO_4$ $C_{42}H_{40}ClCuN_2O_4P_2$	156–164	95	63.6 (63.2)	5.4 (5.1)	4.0 (3.5)	CH_3CN	0.72	117.9	1090s, 1064s 917w, 623s		
48 $[(PPh_3)(Ptolyl_3)(ImH)_2Cu]ClO_4$ $C_{45}H_{44}ClCuN_4O_4P_2$	186–192	71	62.2 (62.4)	4.9 (5.1)	6.8 (6.5)	CH_3CN	0.73	142.3	1117s, 1069s 919w, 624s		
49 $[(PPh_3)_2(Phen)Cu]ClO_4$ $C_{48}H_{38}ClCuN_2O_4P_2$	226–228	90	66.3 (66.4)	4.5 (4.4)	3.2 (3.2)	CH_3CN	0.86	136.8	1080s, 930w 624s		
50 $[(PPh_3)_2(Bipy)Cu]ClO_4$ $C_{46}H_{38}ClCuN_2O_4P_2$	181–183	90	65.3 (65.5)	4.6 (4.5)	3.4 (3.3)	CH_3CN	0.90	137.4	1085s br, 929w 624s		

[a] Required values are given in parentheses.
[b] With decomposition.
[c] Based on copper.
[d] In ohm^{-1} cm^2 mol^{-1} at room temperature; conc. is molar concentration (×10^3).
[e] In Nujol mull and/or in $CHCl_3$ solution.

data, were prepared by reacting a strong excess of the N-donor ligand with a diethyl ether suspension containing one equivalent of $[(PPh_3)_4Cu]ClO_4$, previously synthesized according to the literature [11]. When less than two equivalents of the ligand were used, some unreacted starting material was often recovered from the reaction. The derivative $[(PPh_3)_2(pzH)_2Cu]ClO_4$ (**11**) was obtained by reacting one equivalent of $(PPh_3)_4CuClO_4$ with two equivalents of pyrazole (pzH) in refluxed benzene under an N_2 stream. It is noteworthy that in refluxed benzene the ligands L^1 and L^2 reacted in a different manner: while with L^1 the 1:1 adduct $[(PPh_3)_2(L^1)Cu]ClO_4$ (**7**) was again obtained, with L^2, which was more basic and more sterically hindered, the 2:1 adduct $[(L^2)_2Cu]ClO_4$ (**12**) was afforded upon displacement of all the phosphine donors. The sparingly soluble compound $[(PPh_3)(L^3)Cu]ClO_4$ (**9**) was also obtained when the reaction was carried out in acetone. The displacement of three phosphines from $(PPh_3)_4CuClO_4$ by the ligand L_3 is likely due to the polydentate nature of this N-donor which has often been shown to yield polymeric insoluble complexes [9]. The imidazole derivatives can also be synthesized by a method considerably more convenient with respect to the above synthesis: reduction of the 4:1 copper(II) complexes $[(QH)_4Cu](ClO_4)_2$ [14] with triphenylphosphine yields again the 2:2:1 adducts **1**–**5** and the 1:3:1 adduct **6**. The imidazole derivatives may be crystallized in good yield by slow diffusion of diethyl ether into an acetonitrile solution whereas the pyrazole derivative **11** was generally unstable in chloroform, acetone or benzene solution: it was readily oxidized by air, giving a blue solution in a very short time. Studies of the reaction of ImH, 1-MeimH, 2-MeimH and pzH with $[(PPh_3)_4Cu]ClO_4$ have indicated a pronounced preference for the isolation of 2:2:1 adducts compared to 3:1:1 ones also when the reaction is carried out by using an equimolar quantity of the reactants. All the compounds are insoluble in diethyl ether and ethanol and soluble in acetone, DMSO, chlorinated solvents and acetonitrile. Compounds **2**, **6**, **7**, **10** are moderately soluble in benzene. The conductivity measurements carried out only on the stable solutions show that our compounds are electrolytes not only in acetonitrile but also in non-ionizing solvents such as dichloromethane, which is in reasonable agreement with their ionic structure proposed in Fig. 2(a). In molecular weight measurements performed on selected sufficiently soluble derivatives, in $CHCl_3$ and/or acetone (concentration in the range 1.0–2.0×10^{-2} m), the ratio r between the vaporimetric molecular weight and the formula weight lies in the range 0.40–0.80 and indicates that complexes **1**–**12** presumably dissociate partly in these solvents, in accordance with their ionic nature or ligand loss in solution (Eqs. (1)–(5)).

$$[(PR_3)_n(QH)_xCu]X \rightleftarrows [(PR_3)_2CuX] + x(QH) \qquad (1)$$

$$[(PR_3)_n(QH)_xCu]X \rightleftarrows [(PR_3)_{n-1}(QH)_xCuX] + PR_3 \qquad (2)$$

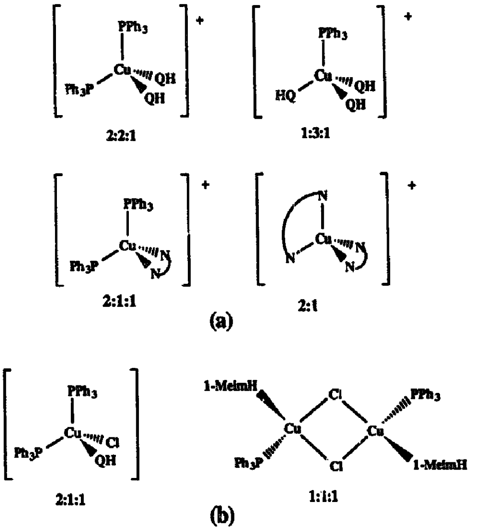

Fig. 2. Ionic perchlorato– (a) and neutral chloride– (b) copper(I)phosphino derivatives of azoles.

$$[(PR_3)_n(QH)_xCu]X \rightleftarrows$$
$$[(PR_3)_{n-1}CuX] + x(QH) + (PR_3) \qquad (3)$$
$$[(PR_3)_n(L)CuX] \rightleftarrows [(PR_3)_nCuX] + L \qquad (4)$$
$$[(PR_3)_n(L)CuX] \rightleftarrows [(PR_3)_{n-1}(L)CuX] + PR_3 \qquad (5)$$

We have also found that dissociation is strongly dependent upon the concentration of the solutions: for example r for **9** is ~0.70 at conc. 1.0×10^{-2} m, whereas it is ~0.50 at conc. 5×10^{-3} m.

The steric effects determine to a great extent the success of the reaction and the coordination environment on the copper center; for example, no adduct was obtained even under forcing conditions with 3,5-dimethylpyrazole which is more basic but provides greater steric hindrance with respect to pyrazole. The ligand *N*-benzylimidazole, which is less basic but more sterically hindered than imidazole, displaces three phosphines from $(PPh_3)_4CuClO_4$ giving the 1:3:1 adduct $[(PPh_3)(1\text{-}BzimH)_3Cu]ClO_4$.

3.2. *Synthesis of the complexes* $[(PPh_3)_n(QH)_xCuCl]$

The copper(I) chloride complexes **13–18** (Table 1) were prepared by reacting two equivalents of the monodentate N-donor ligand with one equivalent of $(PPh_3)_2CuCl$ in diethyl ether under an N_2 stream.

The donor 1-MeImH displaces one phosphine from $(PPh_3)_2CuCl$, the 1:1:1 adduct $[(PPh_3)(1\text{-}MeimH)CuCl]$ (**15**) being formed. This compound is sparingly soluble in acetonitrile and chlorinated solvents; instead, with all the other imidazole-type ligands, adducts of stoichiometry $[(PPh_3)_2(QH)CuCl]$ were always obtained (Fig. 2(b)). On the basis of IR data (see below) and of previous reports on copper(I) chloride complexes of the type [(PPh_3)(N-donor)CuX] [19] a dimeric structure of the type shown in Fig. 2(b) is suggested for compound $[(PPh_3)(1\text{-}MeimH)CuCl]$.

In the molecular weight determination in $CHCl_3$, r for compound **15** lies in the range 0.80–1.10, whereas for the other halide complexes it is of the order of ~0.40–0.70. This further supports our hypothesis.

The chloride phosphino copper(I) compounds are less soluble than the analogous perchlorato derivatives. The conductivity measurements indicate that complexes **13–18** are non-electrolytes in dichloromethane and also in ionizing solvents such as acetonitrile or DMSO.

3.3. *Synthesis of the complexes* $[(PCy_3)_n(QH)_xCu]X$ *and* $[(PCy_3)_n(L)_xCu]X$ *(X = NO_3 or ClO_4)*

The reactions between the N-donor ligands in Fig. 1 and bis(tricyclohexylphosphine)copper(I) nitrate or perchlorate are generally more complicated than the analogous reactions with triphenylphosphinecopper(I) compounds. This is likely due to greater instability to hydrolysis and the remarkable steric hindrance of PCy_3 with respect to PPh_3. The stoichiometries of the products synthesized (Table 1) are very different (Fig. 3): for example ImH, 1-MeimH and pzH reacted with $[(PCy_3)_2CuNO_3]$ and 1-MeimH reacted with $[(PCy_3)_2CuClO_4]$ in diethyl ether or benzene giving the 1:3:1 adducts $[(PCy_3)(QH)_3CuNO_3]$ (**19**, **21** and **25**) and $[(PCy_3)(1\text{-}MeimH)_3Cu]ClO_4$ (**30**), respectively, upon displacement of one tricyclohexylphosphine ligand, whereas the 1:2:1 and 2:2:1 adducts $[(PCy_3)(2\text{-}MeimH)_2Cu]NO_3$ (**20**), $[(PCy_3)_2(4\text{-}PhimH)_2Cu]NO_3$ (**22**), $[(PCy_3)_2(BimH)_2Cu]NO_3 \cdot 2Et_2O$ (**23**) and $[(PCy_3)Cu(ImH)_2ClO_4]$ (**28**) were obtained from the reaction of

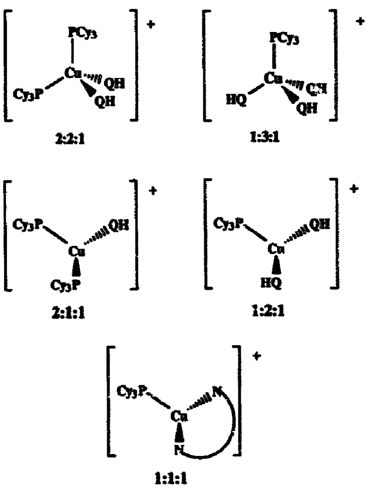

Fig. 3. Tricyclohexylphosphinocopper(I) azole derivatives.

[$(PCy_3)_2CuNO_3$] with 2-MeImH, 4-PhimH and BimH and of [$(PCy_3)_2CuClO_4$] with ImH. Finally the 2:1:1 adducts [$(PCy_3)_2$(1-BzimH)Cu]NO_3 (**24**), [$(PCy_3)_2$(pz'H)Cu]NO_3 (**26**) [$(PCy_3)_2$(2-MeimH)Cu]ClO_4 (**29**), [$(PCy_3)_2$(4-PhimH)Cu]ClO_4 (**31**), [$(PCy_3)_2$(BimH)Cu]ClO_4 (**32**), [$(PCy_3)_2$(1-BzimH)Cu]$ClO_4 \cdot Et_2O$ (**33**), [$(PCy_3)_2$(pzH)Cu]$ClO_4 \cdot CH_3OH$ (**34**) and [$(PCy_3)_2$(pz'H)Cu]ClO_4 (**35**) were afforded when 1-BzimH in diethyl ether and pz'H in benzene interacted with [$(PCy_3)_2CuNO_3$] and when 2-MeimH, 4-PhimH, BimH, 1-BzimH, pzH or pz'H, respectively, were added to a methanol or a diethyl ether suspension of [$(PCy_3)_2CuClO_4$].

The bis(azol-1-yl)alkanes L^1, L^2, L^3 and L^4 showed a different behavior: while their reaction with [$(PCy_3)_2CuClO_4$] was always successful, the 1:1:1 adducts **36**–**38** and the 1:2:1, **39**, being formed, respectively, in good yield, the polydentate ligand L^3 was the only one able to coordinate the [$(PCy_3)_2CuNO_3$] acceptor, yielding the derivative [$(PCy_3)(L^3)$Cu]NO_3 (**27**) upon displacement of one PCy_3. Finally, when the reaction between L^1 and [$(PCy_3)_2CuNO_3$] was carried out in aerobic conditions breaking of the bridging $C(sp^3)$–N bond occurred and the derivative [$(PCy_3)(pzH)_3CuNO_3$] was again synthesized. This behavior is similar to that previously found with poly(azol-1-yl)alkanes and tin(IV), zinc(II) and vanadium(IV) acceptors [20].

The tricyclohexylphosphinocopper(I) complexes are generally insoluble in diethyl ether and alkanes, soluble in acetone, DMSO, chlorinated solvents and acetonitrile, and somewhat soluble in benzene and alcohols. Stereochemical factors are largely responsible for the relative stabilities of the complexes in solutions: for example the derivatives containing tricyclohexylphosphine, a ligand which has a cone angle of 170° [21], are more unstable in solution than the analogous complexes containing triphenyphosphine (cone angle: 145°) [7]. We have also observed that the monophosphine derivatives are more oxygen sensitive than the bistriorganylphosphinecopper(I) complexes, and that the former, upon exposure to air, rapidly turn deep green or blue, the characteristic colors of copper(II) complexes.

Also the steric hindrance of the N-donors considerably influence the coordination number of copper(I). This is well illustrated by the reaction of [$(PCy_3)_2CuNO_3$] with imidazoles: while the 1:3:1 adduct was synthesized with ImH and 1-MeimH, introduction of a single methyl group in the 2-position of the imidazole ring decreased the coordination number to three with formation of the 1:2:1 adduct.

With the exception of **22** and **28**, all the tricylohexylphosphine complexes, in acetonitrile and dichloromethane solution, exhibit conductivity values similar to those of a typical 1:1 electrolyte such as tetra-n-butylammonium bromide. The values observed are in agreement with the ionic formulation proposed in Fig. 3 and in Table 1. The molecular weight measurements suggests that dissociations (1)–(5) take place in $CHCl_3$ and/or acetone also for these compounds. For example $r=0.60$, 0.50 and 0.54 (conc. $\sim 1\times10^{-2}$ m) for complexes **20**, **26** and **28**, respectively.

3.4. *Synthesis of the complexes [$(PPh_3)_n(Q)Cu$]$\cdot xH_2O$*

The imidazolato complexes **40**–**43** were synthesized by reacting one equivalent of the N-donor ligand with one equivalent of $(PPh_3)_2CuCl$ in boiling methanol in the presence of one equivalent of potassium hydroxide under an N_2 stream. The precipitate obtained was washed with hot methanol repeatedly. No complications associated with difficulty in separating potassium chloride from the final product were encountered. Separation of the salt is further aided by the complete insolubility of the imidazolate copper(I) derivatives in hot methanol. All attempts at recrystallization with chloroform, dichloromethane or acetonitrile have proved useless due to the instability of these compounds in almost all solvents. The bis(triphenylphosphine)copper(I)imidazolate derivatives **40** and **41** are poorly soluble in chlorinated solvents and insoluble in acetone, acetonitrile, alcohols and DMSO, whereas the monotriphenylphosphine derivatives **42** and **43** are completely insoluble in all the common organic solvents. Polymeric or oligomeric structures containing a bridging imidazolato group between copper(I) centers are suggested on the basis of a previous report on imidazolato complexes of gold(I), mercury(II) and organotin(IV) acceptors [22].

3.5. *Reactivity of complexes [$(PPh_3)_2(ImH)_2Cu$]ClO_4 (1) and [$(PPh_3)_2(L^1)Cu$]ClO_4 (7)*

Compound **1** reacts with Phen in benzene under an N_2 stream or with Bipy in diethyl ether yielding the 1:1:1 adducts [(PPh_3)(ImH)(Phen)Cu]ClO_4 (**44**) and [(PPh_3)(ImH)(Bipy)Cu]ClO_4 (**45**) respectively, upon displacement of one imidazole and one triphenylphosphine. These reactions are highly dependent on the temperature, reaction time, donor/acceptor ratio and solvent employed. For example only intractable material was afforded when the reaction between Phen and **1** was carried out in diethyl ether or when the ligand/metal ratio employed was greater than 4:1, but also when **1** interacted with Phen or Bipy at ~ 60 °C. On the other hand, the less basic L^1 and the monodentate pzH and pyridine are not able to displace the imidazole donor from the copper center.

The reaction between one equivalent of compound **1** and two equivalents of PCy_3 in diethyl ether results in the rapid formation of the compound [$(PPh_3)(PCy_3)(ImH)_2Cu$]ClO_4 (**46**) upon displacement of the less basic PPh_3. Similar behavior is found with P(*p*-tolyl)$_3$, the complex [(PPh_3)(*p*-tolyl)$_3(ImH)_2Cu$]ClO_4 (**47**) being obtained, while with Bz_3P displacement of one molecule of imidazole and formation of [$(PPh_3)(PBz_3)(ImH)Cu$]ClO_4 (**48**) were observed. No displacement of the second molecule of PPh_3 was observed when the reaction was carried out in strong excess of PCy_3, PBz_3 or P(*p*-tolyl)$_3$. A different pattern was found with ligand Diphos: this chelating phosphine easily displaced both the imidazole and PPh_3 from the copper(I) complex **1** and afforded the derivative [$(Diphos)_2Cu$]ClO_4.

The reaction between one equivalent of compound **7** and two or more equivalents of PCy_3, PBz_3 and $P(p\text{-tolyl})_3$ was unsuccessful and the starting materials were always recovered. The chelating effect, which is supposedly acting in the reactions with L^1 can explain the reactivity of this compound. The reaction of **7** with ImH proceeded instantaneously resulting in complete displacement of L^1 by ImH to form compound **1**. Phen and Bipy reacted with **7** similarly and the derivatives $[(PPh_3)_2(Phen)Cu]ClO_4$ (**49**) and $[(PPh_3)_2(Bipy)Cu]ClO_4$ (**50**), respectively, were obtained [23].

3.6. *Infrared data*

The IR spectra (some selected data are reported in Table 1) show all of the bands required by the presence of the organic N-donor and phosphine ligand. In detail the derivatives of ImH, 2-MeimH, 4-PhimH, BimH, pzH and pz'H show a band in the 3300–2800 cm^{-1} region which is assigned to ν(N–H) stretching. In some cases, a hydrogen bond between the amine proton and the oxygen atoms of perchlorato, nitrato or solvent molecules is suggested by both the broadness and the range (lower limit 2800 cm^{-1} for compound **4**) of the absorption; the higher limit is generally 3250 cm^{-1}, except in the case of compound **34** where it is found at 3390 cm^{-1} owing to the presence of one molecule of methanol. The existence of hydrogen bonds in perchlorato derivatives is also confirmed by IR spectra in $CHCl_3$ solution. In fact, whereas the spectra of the bis(azolyl)alkane derivatives recorded in $CHCl_3$ are unchanged with respect to those in nujol mull, several changes are observed in the spectra of complexes containing ImH, 2-MeimH, pzH and 4-PhimH: the broad $\nu(ClO_4)$ becomes more sharp and ν(N–H) shifts to a higher field. When the region is not covered by the N–H absorption, weak C–H stretching vibrations due to the pseudo-aromatic ring are observed in the range 3150–3050 cm^{-1}, similar to those previously found in several imidazole, imidazolato, pyrazole and pyrazolato derivatives of gold(I), mercury(II), zinc and copper(II) [22,24]. Here again the vibrations found between 1500 and 1600 cm^{-1} may be due to a ring breathing mode. In the region 900–650 cm^{-1} some absorptions, assignable with certainty to C–H bending and ring deformation, were always detected [25].

In the spectra of compounds **40–43** N–H stretchings and bendings are absent in accordance with the coordination of the imidazoles in the anionic mono- or bidentate form.

The IR spectra of the azole perchlorato copper(I) derivatives **1–12** show two absorptions characteristic of a perchlorate group: a strong band in the range 1110–1080 cm^{-1} (ν_3) and a sharp medium or strong band at ~625 cm^{-1} (ν_4) [26]. These absorptions are very similar to those reported for $[(PPh_3)_4Cu]ClO_4$ and different from those found in the strongly distorted trigonal planar $[(Cy_3P)_2CuClO_4]$ [12]. They are indicative of an ionic uncomplexed ClO_4^- group, in accordance with the structure proposed in Fig. 2(a) and with the behavior shown by these complexes in solution.

The copper(I) nitrato derivatives exhibit spectra in the region 1400–1100 cm^{-1} which differ considerably from the spectra of the starting bis(tricyclohexyl)phosphinecopper(I)nitrate [13]. In particular in $[(Cy_3P)_2CuNO_3]$ the two highest frequency bands which arise from removal of the degeneracy of the ν_3 NO_3^- mode, are separated by ~164 cm^{-1}. In derivatives **20**, **26** and **27**, ν_1 and ν_4 differ in frequency by ~70–90 cm^{-1}. This suggests for this compound in the solid state the presence of a monodentate nitrato group. Whereas, derivatives **19** and **21–25** show three absorptions at ~1370, 1040 and 830 cm^{-1} characteristic of ionic nitrato groups. This further supports the hypothesis that a nitrato group can be displaced from copper(I) provided a suitable nitrogen donor ligand is chosen.

In the far-IR region of compounds **13**, **14** and **16–18** we observed the copper(I)–chloride stretching band at ~230–210 cm^{-1}. We noted that ν(Cu–Cl) decreased by ~60 cm^{-1} on going from the starting three-coordinate copper(I) complex to four-coordinate imidazole derivatives, in agreement with the trends previously indicated [27]. The compound $[(PPh_3)(1\text{-MeimH})CuCl]$ showed surprisingly two broad Cu–Cl absorptions at ~180 and 160 cm^{-1}. On the basis of previous assignments reported for complexes containing a bridging halide group [28], we suggest that in this derivative, having a different stoichiometry with respect to those found in the other imidazole and pyrazole phosphinocopper(I) chloride compounds, the copper(I) center is coordinated by two bridging chlorides, in reasonable agreement with the dimeric structure shown in Fig. 2(b). Additional support for our hypothesis is given by the molecular weight measurement in chloroform solution and by the well-known preference of copper(I) for tetracoordination with respect to tricoordination.

In the triphenylphosphine derivatives, we always noted a strong broad triplet absorption near 500 cm^{-1} assignable to Whiffen's *y*-vibrations [29]. A second group (Whiffen's *t*-vibrations) of medium intensity generally appeared near 410–420 cm^{-1}, whereas the *u*- and *x*-vibrations appeared as bands of weak intensity at ~270–250 cm^{-1} [30]. All these absorptions are generally not very sensitive to the nature of the azole donor and of the counterion.

We are not able to assign the ν(Cu–P) vibrations [31], because they are likely hidden under some absorptions characteristic of the azole ring system and of phosphines, whereas in the spectra of some of our copper(I) complexes, bands of medium and weak intensity appeared at ~300 cm^{-1}, which are not present in the spectra of the starting copper(I) derivatives and of neutral imidazole, pyrazole and poly(azolyl)alkane ligands; these bands are similar to those described in the literature for some copper(I)azolato derivates [32] and could be tentatively assigned to ν(Cu–N) vibrations.

3.7. *UV spectra*

The UV spectra recorded only for some stable complexes (see Section 5) in acetonitrile solution are dominated by one main broad band in the region 200–230 nm, ascribed from the existence of intraligand transitions of azole [33], and by one broad medium absorption due to n–π transitions of the phosphine [34]. When an aryl group (derivatives **4**, **16**, **22** and **31**) is attached to a ring carbon, some intense bands appear between 250 and 300 nm as a consequence of conju-

Table 2
^1H and ^{31}P NMR data [a] for the copper(I) compounds

Complex	$\delta(^1H)$ [b]		$\delta(^{31}P)$
	Phosphine	N-donor ligand	
$[(PPh_3)_4Cu]ClO_4$	7.1m, 7.2m, 7.4m, 7.5m		0.65
1	7.1–7.3m br, 7.4m	6.8s br, 7.5br	−2.34
2	7.1–7.3m, 7.4m	2.0s br, 6.8br	−2.78
3	7.1–7.3m, 7.4m	3.7s, 7.2s	−2.47
4	7.1–7.3m, 7.4m	6.9br, 7.5–7.8br	−1.86
5	7.1–7.3m, 7.4m	7.0s br, 7.4–7.7m br, 7.8 br	−2.23
6	7.1–7.4m br	5.20s br, 7.1s br, 7.1–7.4m br	−2.11
7	7.1d, 7.2t, 7.4t	6.1pt (2.2), 6.9d (2.2) 8.3d (2.5)	−1.09
8	7.3–7.5m br, 7.6–7.7m	1.8s, 2.5s, 5.9s, 6.4s	−1.26
9	7.2br, 7.3br	6.6br, 7.7br, 8.8br	
10	7.0d, 7.2t, 7.4t	1.8s, 6.0s, 6.7s, 8.0s	−1.18
11	7.2d, 7.35t, 7.48t	6.3pt, 7.6br [c]	
12		1.9s, 2.5s, 5.8s, 6.3s	
$[(PPh_3)_2CuCl]$	7.20m, 7.40m		−3.85
13	7.2–7.5m	7.1br, 7.6br [c]	
14	7.2–7.4m	2.2s, 6.8br	−3.90
15	7.3–7.5m	3.7s, 7.3pt, 7.6pt, 7.3–7.5m	−1.67
16	7.1–7.5m	7.1–7.5m br, 7.7s br	
17	7.2–7.5m	7.1br, 7.2–7.5m	
18	7.2–7.5m br	5.1s, 7.1m, 7.2d	
$[(PCy_3)_2CuNO_3]$	1.0–1.5m br, 1.6–2.0m br		
19	1.1–1.5m br, 1.6–2.0m br	7.1s br, 7.6s br	19.86
20	1.0–1.5m br, 1.6–2.0 m br	2.2br, 7.0br	
	1.0–1.5m br, 1.6–2.0m	2.1br, 7.0br [c]	
21	1.1–1.5m, 1.6–2.0br	3.73s br, 7.0–8.0br	
22	1.1–1.5m, 1.6–1.9m br	7.2–7.3m, 7.3–7.4m, 7.6–7.8br	
23	1.0–1.5m, 1.6–2.0br	7.3m, 7.7m br, 8.1 sbr	
24	1.2–1.6m, 1.6–2.0m	5.20s br, 7.1br, 7.3–7.4m br	13.60
25	1.0–1.5m, 1.6–1.9m	6.8br, 8.1br, 12.3br	
26	1.1–1.5m, 1.6–1.9m	2.2s, 6.1br	
$[(PCy_3)_2CuClO_4]$	1.2–1.6m, 1.7–2.1m		17.19
28	1.1–1.5m br, 1.6–2.0m br	7.0–8.0 br	
29	1.1–1.5m, 1.6–2.0m	2.6br, 7.0s	11.72
30	1.1–1.5m, 1.6–2.0m	3.8s br, 7.3br, 7.6 br, 7.8br	
31	1.1–1.6m, 1.6–2.0m	7.3br, 7.3–7.5m, 7.7d, 7.8–7.9m	
32	1.1–1.5m, 1.6–2.0m	7.4m, 7.5m, 7.7m, 7.9m, 8.3br, 8.4s	
33	1.1–1.5m, 1.6–2.1m	5.4br, 7.1br, 7.2s, 7.3s	
34	1.0–1.5m, 1.6–2.0m	6.4s, 7.7br, 12.2br	
35	1.1–1.5m, 1.6–2.1m	2.3br, 5.7br	
36	1.1–1.6m, 1.6–2.1m	6.4br, 6.7br, 7.6br, 8.4br	
37	1.2–1.5m, 1.6br, 1.7–2.2m	2.3s, 2.5s, 5.9s, 6.4s	
38	1.2–1.6m, 1.6–2.2m	6.5br, 8.0br, 8.6br	
39	1.1–1.5m, 1.6–2.0m	2.1s, 6.5s, 7.3s, 8.0s	27.31
40	7.1–7.5br	6.9br, 7.7br	
41	7.2–7.6br	2.30br, 6.90br, 7.7br	
44	7.1–7.4br	6.9br, 7.7br, 8.0br, 8.5d br, 8.8br	2.30
45	7.0–7.4br	6.9br, 7.5br, 8.0t, 8.3d, 8.4br	1.45
46	1.1–1.5m, 1.6–1.9m, 7.1–7.4m	4.0–5.0br, 6.9br, 7.5br	−3.11; 17.95
47	2.9s, 3.0s, 7.0br, 7.1–7.5m	6.9br, 7.5br	−6.03; 40.04
48	2.2s, 7.1–7.5m	6.9br, 7.6br	−2.45
49	7.1d, 7.2t, 7.3t	7.7dd, 8.0s, 8.6d, 8.7br	3.40
50	7.0–7.7m br	8.2br, 8.4br, 8.6br	2.60

[a] In $CDCl_3$, unless otherwise stated.

[b] s = singlet, d = doublet, t = triplet, pt = pseudotriplet, dd = double doublet, m = multiplet, br = broad, *J* in Hz in parentheses.

[c] In CD_3CN.

gation between the aromatic and the heteroaromatic system [35]. In the BimH derivatives **5**, **17**, **23** and **32**, absorption maxima appear also at ~270–280 and 250–260 nm. The short wavelength bands are assigned to electron transitions localized in the imidazole ring, whereas the longer one is regarded as a displaced B band of benzene [36].

3.8. NMR data

The ^1H (Table 2), ^{31}P (Table 2) and ^{13}C NMR spectra (Table 3), carried out only when the compounds were sufficiently soluble and the solution sufficiently stable in chloroform, support the formulae proposed and show that our N-donors have not undergone any structural changes upon coordination. On comparison between the chemical shift related to the same type of proton in the free bases [9,10] and in their phosphinocopper(I) derivatives and when the molecular weight determinations mentioned above are considered, we hypothesize that the complexes dissociate partially in solution. The observed resonances are averaged between those of the complex and free ligand owing to a rapid exchange reaction between both (Eq. (2)). The small coordination shifts are perhaps therefore attributable to the small fraction of the complex present in solution. In the spectra of bis(azol-1-yl)alkane derivatives we found a pattern of chemical shifts in keeping with what has been previously described [10]. The signals due to the heterocyclic ring and methylene bridges are generally shifted downfield upon complexation, whereas the ring and bridging carbon move downfield and upfield, respectively. Also in complexes of pyrazoles and imidazole, the ligand proton signals shift to lower field upon coordination: the shift could be caused by a change in the electron density of the donor owing to the formation of the Cu–N bond. The ^1H spectra of the pyrazole derivatives exhibit only one broad resonance instead of the two expected for the protons in 3 and 5 positions, the same being found for the 4 and 5 positions in imidazoles. This is due to the fluxional behavior of these compounds which likely requires a concomitant prototropy and metallotropy of the ligand [37]. Variable temperature NMR experiments confim the hypothesis that on cooling a $CDCl_3$ solution of compound **29**, the resonance at 6.9 ppm due to 4- and 5-H of 2-MeimH broadened and split into two broad resonances at 273 K, which sharpened to two resonances at 6.6 and 7.1 ppm at 253 K.

The ^{31}P NMR spectra of complexes **1**–**46** show a single resonance. This is due to a fluxional behavior of these complexes. Notice that every free phosphine appears upfield of its corresponding copper(I) complex [38]. $\Delta\delta^{31}P = \delta^{31}P_{complex} - \delta^{31}P_{ligand}$, the difference in shift between each free phosphine and corresponding copper complex is in the order of 2–5 ppm for PPh_3 and of 3–8 ppm for PCy_3. The smaller shift, compared with those observed for example in platinum and gold complexes [39], together with the broadening of the spectra, are likely due to instability of complexes in solution which undergo rapid ligand exchange in accordance with equilibria (1)–(5) previously described.

A study was performed on compound **3**, lowering the temperature of the sample tube from 298 to 200 K in approximately 10 K increments: at 228 K the broad resonance at −2.5 ppm splits into three broad resonances at ~0.1, −4.5 and −5.6 ppm, the last of these signals being due to free PPh_3.

We found that the ^{31}P NMR spectra of our copper(I) complexes showed a shift of the signals to lower field as the number of phosphine ligands in the complexes increased in accordance with a smaller shielding of this nucleus. This is likely due to reduction in the π-contribution to the Cu–P bond as the number of phosphines increases [40].

3.9. Crystallographic study of $[(PCy_3)_2(pzH)Cu]ClO_4 \cdot CH_3OH$ (34)

To probe the nature of $[(PCy_3)_2(pzH)Cu]ClO_4 \cdot CH_3OH$ further, single crystals were grown from methanol/diethyl

Table 3
^{13}C NMR data [a] for some $[(PPh_3)_nCu]ClO_4$ derivatives

Complex	$\delta(^{13}C)$ [b]	
	Phosphine	N-donor ligand
$[(PPh_3)_4Cu]ClO_4$	129.1d, 133.4d, 130.6s 128.6d, 132.1d, 131.0d	
1	129.3d, 130.4s, 133.9d	118.9s, 133.9s, 137.0s
2	129.4d, 130.6s, 133.9d	14.5s, 133.1s, 133.6s
7	129.5s br, 130.8s, 137.7br 132.4d	66.3s, 107.5s, 134.1s, 143.0s
8	129.0d, 129.7d, 131.3s 132.6s, 134.1d	11.5s, 14.2s, 58.2s, 107.4s 118.9s, 143.1s
10	128.9s br, 130.2s br 132.3s	8.6s, 62.2s, 117.2s, 131.8s 142.8s
11	128.8d, 130.0s, 132.6d 133.5d	105.6br, 135.2br

[a] In $CDCl_3$.
[b] s = singlet, d = doublet, br = broad.

ether solution and studied by single crystal X-ray diffraction. A summary of the crystal data is presented in Section 2. Atomic coordinates are given in Table 4 and bond lengths and angles involving non-H atoms in Table 5. A drawing of the molecular structure of **34** with the atom numbering scheme is shown in Fig. 4.

Table 4
Atomic coordinates vith their e.s.d.s in parentheses for non-hydrogen atoms for complex **34**

Atom	*x*	*y*	*z*
Cu(1)	0.318(1)	0.2665(1)	0.0343(7)
Cl(1)	0.863(1)	0.2326(2)	−0.2213(7)
P(1)	0.259(1)	0.4124(1)	0.0972(7)
P(2)	0.337(1)	0.1030(1)	0.0780(7)
O(1)	0.760(2)	0.257(1)	−0.268(2)
O(2)	0.967(2)	0.201(1)	−0.266(1)
O(3)	0.819(3)	0.1532(8)	−0.185(1)
O(4)	0.896(2)	0.3182(7)	−0.1773(9)
O(5)	0.700(1)	0.3518(6)	−0.0576(8)
N(1)	0.332(1)	0.2838(4)	−0.0878(8)
N(2)	0.447(1)	0.3006(5)	−0.1282(8)
C(1)	0.426(2)	0.2864(7)	−0.2067(8)
C(2)	0.298(2)	0.2594(7)	−0.2192(8)
C(3)	0.242(1)	0.2594(6)	−0.1435(8)
C(4)	0.408(1)	0.4862(5)	0.1294(8)
C(5)	0.488(1)	0.5215(7)	0.0572(8)
C(6)	0.614(1)	0.5811(7)	0.0842(8)
C(7)	0.702(1)	0.5169(8)	0.1395(9)
C(8)	0.623(1)	0.4832(7)	0.2123(8)
C(9)	0.498(1)	0.4232(5)	0.1873(8)
C(10)	0.165(1)	0.5024(5)	0.0325(8)
C(11)	0.138(2)	0.6066(5)	0.0651(9)
C(12)	0.080(2)	0.6774(6)	0.0020(9)
C(13)	−0.031(2)	0.6343(7)	−0.0472(9)
C(14)	−0.009(1)	0.5303(7)	−0.0761(8)
C(15)	0.051(1)	0.4589(6)	−0.0144(8)
C(16)	0.167(1)	0.3875(5)	0.1912(8)
C(17)	0.161(1)	0.4718(6)	0.2542(8)
C(18)	0.098(1)	0.4316(7)	0.3320(8)
C(19)	−0.039(1)	0.3865(7)	0.3163(8)
C(20)	−0.039(1)	0.3075(7)	0.2507(9)
C(21)	0.029(1)	0.3436(6)	0.1745(8)
C(22)	0.431(1)	0.0767(5)	0.1729(8)
C(23)	0.578(1)	0.1066(6)	0.1663(8)
C(24)	0.657(1)	0.0800(7)	0.2435(8)
C(25)	0.595(1)	0.1326(7)	0.3161(8)
C(26)	0.449(1)	0.1050(6)	0.3227(8)
C(27)	0.370(1)	0.1302(5)	0.2457(8)
C(28)	0.400(1)	0.0077(5)	0.0046(8)
C(29)	0.504(1)	0.0522(6)	−0.0512(8)
C(30)	0.545(1)	−0.0228(7)	−0.1163(8)
C(31)	0.595(1)	−0.1222(6)	−0.0805(8)
C(32)	0.489(1)	−0.1677(6)	−0.0271(9)
C(33)	0.451(1)	−0.0922(5)	0.0397(8)
C(34)	0.163(1)	0.0624(5)	0.0980(8)
C(35)	0.143(1)	−0.0450(6)	0.1277(8)
C(36)	−0.004(1)	−0.0651(7)	0.1477(9)
C(37)	−0.094(1)	−0.0456(7)	0.0754(9)
C(38)	−0.077(1)	0.0604(7)	0.0442(8)
C(39)	0.070(1)	0.0841(6)	0.0253(8)
C(40)	0.7370	0.2792	−0.0031

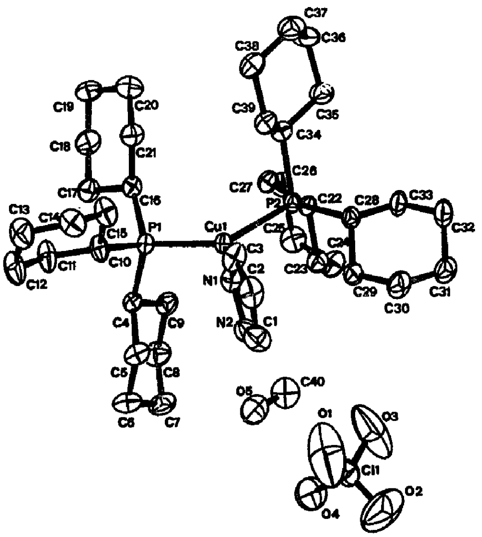

Fig. 4. A drawing of the molecule of $[(Cy_3P)_2(pzH)Cu]ClO_4 \cdot CH_3OH$ in the crystal, showing the anisotropy of the thermal motion. The thermal ellipsoids of the non-H atoms have been scaled to the 30% probability level. The drawing is based on the atomic parameters from the final refinement.

The coordination geometry of the copper atom is distorted trigonal. The P–Cu–P bond angle (132.3(6)°) differs significantly from the idealized value of 120°. This finding is probably due to the remarkable steric hindrance of the two bulky tricyclohexylphosphine ligands. However, the P–Cu–P bond angle is smaller than those reported for sterically hindered three- or four-coordinated bis(tricyclohexyl)-phosphine copper(I) derivatives [12,13,41] whereas the Cu–P bond length is comparable with those reported in the literature for similar complexes. The Cu–N bond length (2.046(17) Å) is somewhat longer than that observed previously in copper(I)–azole compounds [42], suggesting a weak bonding interaction between the poor donor pyrazole and the copper(I) acceptor. However, the value of the Cu–N bond length is in agreement with the values observed in phosphinocopper(I) compounds containing more basic and more sterically hindered pyridines or bipyridines [43–45]. The two N–Cu–P bond angles (112.7(4) and 114.4(4)°), together with the P–Cu–P bond (132.3(6)°) imply that the coordination at the copper atom is not planar; however it lies 0.09 Å from the plane of the nitrogen and phosphorus donors. The pyrazole ring is essentially planar to within experimental accuracy. When comparing the molecular geometry of the pyrazole ring in $[(PCy_3)_2(pzH)Cu]ClO_4 \cdot CH_3OH$ with that reported for other similar derivatives, it is found that also in this case the bond angles agree with the empirical rules concerning pyrazoles, previously indicated by Bonati on the basis of an accurate analysis of more than two hundred independent molecules [46]. The interatomic bond lengths and angles within the tricyclohexylphosphine group are consistent with those commonly found in coordinated phosphine donors, but,

Table 5

Bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Cu(1)–P(1)	2.262(9)		
Cu(1)–P(2)	2.272(6)		
Cu(1)–N(1)	2.046(17)		
P(1)–C(4)	1.837(15)	P(2)–C(22)	1.848(17)
P(1)–C(10)	1.843(15)	P(2)–C(28)	1.865(13)
P(1)–C(16)	1.856(17)	P(2)–C(34)	1.850(17)
Cl(1)–O(1)	1.311(26)	N(1)–C(3)	1.312(19)
Cl(1)–O(2)	1.348(22)	N(2)–C(1)	1.329(18)
Cl(1)–O(3)	1.287(16)	N(1)–N(2)	1.358(18)
Cl(1)–O(4)	1.375(13)	O(5)–C(40)	1.359(11)
C(1)–C(2)	1.336(21)	C(20)–C(21)	1.521(19)
C(2)–C(3)	1.383(19)	C(22)–C(23)	1.518(18)
C(4)–C(5)	1.525(18)	C(22)–C(27)	1.532(17)
C(4)–C(9)	1.542(17)	C(23)–C(24)	1.533(19)
C(5)–C(6)	1.532(18)	C(24)–C(25)	1.530(18)
C(6)–C(7)	1.515(18)	C(25)–C(26)	1.502(19)
C(7)–C(8)	1.523(19)	C(26)–C(27)	1.525(19)
C(8)–C(9)	1.521(18)	C(28)–C(29)	1.514(18)
C(10)–C(11)	1.497(12)	C(28)–C(33)	1.517(12)
C(10)–C(15)	1.477(19)	C(29)–C(30)	1.524(17)
C(11)–C(12)	1.505(18)	C(30)–C(31)	1.516(15)
C(12)–C(13)	1.472(21)	C(31)–C(32)	1.514(19)
C(13)–C(14)	1.463(14)	C(32)–C(33)	1.541(16)
C(14)–C(15)	1.502(17)	C(34)–C(35)	1.508(12)
C(16)–C(17)	1.523(14)	C(34)–C(39)	1.532(19)
C(16)–C(21)	1.508(18)	C(35)–C(36)	1.524(20)
C(17)–C(18)	1.541(18)	C(36)–C(37)	1.505(21)
C(18)–C(19)	1.496(19)	C(37)–C(38)	1.496(14)
C(19)–C(20)	1.504(17)	C(38)–C(39)	1.526(19)
P(2)–Cu(1)–P(1)	132.3(6)		
N(1)–Cu(1)–P(1)	112.7(4)		
N(1)–Cu(1)–P(2)	114.4(4)		
C(4)–P(1)–Cu(1)	111.6(7)	C(22)–P(2)–Cu(1)	119.1(5)
C(10)–P(1)–Cu(1)	114.0(7)	C(28)–P(2)–Cu(1)	117.0(7)
C(16)–P(1)–Cu(1)	112.0(4)	C(34)–P(2)–Cu(1)	104.8(6)
C(10)–P(1)–C(4)	103.3(5)	C(28)–P(2)–C(22)	105.0(6)
C(16)–P(1)–C(4)	105.1(8)	C(34)–P(2)–C(22)	104.7(8)
C(16)–P(1)–C(10)	110.2(8)	C(34)–P(2)–C(28)	104.7(6)
O(2)–Cl(1)–O(1)	110(1)	O(4)–Cl(1)–O(3)	119(1)
O(3)–Cl(1)–O(1)	102(1)	C(3)–N(1)–N(2)	105(1)
O(3)–Cl(1)–O(2)	107(1)	C(1)–N(2)–N(1)	110(1)
O(4)–Cl(1)–O(1)	107(1)	C(2)–C(1)–N(2)	109(1)
O(4)–Cl(1)–O(2)	112(1)	C(3)–C(2)–C(1)	105(1)
C(2)–C(3)–N(1)	111(1)		
C(9)–C(4)–C(5)	110(1)	C(27)–C(22)–C(23)	109.5(9)
C(6)–C(5)–C(4)	111(1)	C(24)–C(23)–C(22)	111(1)
C(7)–C(6)–C(5)	110.7(9)	C(25)–C(24)–C(23)	110(1)
C(8)–C(7)–C(6)	110(1)	C(26)–C(25)–C(24)	111(1)
C(9)–C(8)–C(7)	112(1)	C(27)–C(26)–C(25)	112(1)
C(8)–C(9)–C(4)	110.7(8)	C(26)–C(27)–C(22)	110.7(9)
C(15)–C(10)–C(11)	114(1)	C(33)–C(28)–C(29)	110(1)
C(12)–C(11)–C(10)	112(1)	C(30)–C(29)–C(28)	112.3(8)
C(13)–C(12)–C(11)	114.8(9)	C(31)–C(30)–C(29)	112(1)
C(14)–C(13)–C(12)	115(1)	C(32)–C(31)–C(30)	110(1)
C(15)–C(14)–C(13)	115(1)	C(33)–C(32)–C(31)	110.7(8)
C(14)–C(15)–C(10)	114.1(8)	C(32)–C(33)–C(28)	111(1)
C(21)–C(16)–C(17)	111(1)	C(39)–C(34)–C(35)	110.7(9)
C(18)–C(17)–C(16)	110.3(7)	C(36)–C(35)–C(34)	111.5(9)
C(19)–C(18)–C(17)	112(1)	C(37)–C(36)–C(35)	111(1)
C(20)–C(19)–C(18)	113(1)	C(38)–C(37)–C(36)	111(1)
C(21)–C(20)–C(19)	112.9(9)	C(39)–C(38)–C(37)	112(1)
C(20)–C(21)–C(16)	113(1)	C(38)–C(39)–C(34)	111(1)

as previously mentioned, two different sets of Cu–P–C bond angles are detected (111.6(7), 112.0(4) and 114.0(7)° around P(1), and 104.8(6), 117.0(7) and 119.1(5)° around P(2)) in accordance with the non-equivalence of the cyclohexyl rings found also in the ^1H and ^{13}C NMR spectra in $CDCl_3$ solution.

The crystal structure consists of discrete molecules of **34** separated by normal van der Waals contacts. The methanol molecule is bonded to the ionic perchlorato group, which exhibits a distorted tetrahedron geometry due to the large thermal motion, via the O(4)···O(5) hydrogen bond (2.84(2) Å) and to the pyrazole ring via the O(5)···N(2) hydrogen bond (2.84(2) Å) of the same asymmetric unit. The O(4)···O(5) and O(5)···N(2) separations compare with the hydrogen bond contacts found in $[(PPh_3)_2(Phen)Cu]NO_3\cdot 1.5EtOH$ [47], (O···O: 2.722(7) and 2.798(4) Å) and in $[(PPh_3)_2(tzdtH)_2Cu]NO_3$ [48], (tzdtH = 1,3-thiazolidine-2-thione) (N···O = 2.779 and 2.815 Å).

4. Conclusions

The present study has shown that from the interaction of several triphosphinocopper(I) acceptors with monodentate and bidentate N-donor ligands, complexes with different stoichiometries and geometries have been obtained. The different metal–ligand molar ratios vary with the steric hindrance and pK_a of the phosphorous donors, with the basicity and steric requirements of the azole-type N-donor ligands and finally with the nature of the counterion. For example the coordination number 3 is often found in cyclohexylphosphino complexes, whereas it is rare in triphenylphosphino derivatives. It is generally more easy to displace PPh_3 from Cu(I) ($pK_a = 2.73$) than PCy_3 ($pK_a = 9.70$). The ligand 2-methylimidazole, which has a methyl group near to the coordination site, is the only imidazole-type donor able to form tricoordinated compounds.

None of the complexes synthesized are very stable in solution. We have found that substitution of triphenylphosphine for the tricyclohexylphosphine reduces the dissociation of the copper(I) complexes. This behavior serves to illustrate further the influence of steric factors on the properties of d^{10} phosphine complexes [49].

The presence of clathrated or hydrogen bonded molecules, such as CH_3OH or H_2O, seems to be fairly common and is probably connected with the packing requirements of the rigid hydrogen-bonding azole ligands. This complicating factor suggests that caution should be used when data obtained with adducts of simple heterocycles are extrapolated to other azoles such as purines or natural products.

The X-ray crystal structure determination of $[(Cy_3P)_2(pzH)Cu]ClO_4\cdot CH_3OH$ (**34**) shows that tricoordination is possible for Cu(I) when bulky ligands are employed, and also indicates that hydrogen bonding might be relevant in the interaction of Cu(I) with NH groups belonging to purines or to proteins.

5. Supplementary material

The following additional data are available from the authors on request: table of UV data, tables of observed and calculated structure factors, tables of atomic coordinates and isotropic thermal parameters, as well as hydrogen parameters.

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References

[1] G. La Monica, M.A. Angaroni and G.A. Ardizzoia, *J. Organomet. Chem.*, *348* (1988) 279; G.A. Ardizzoia, G. La Monica, M.A. Angaroni and F. Cariati, *Inorg. Chim. Acta*, *158* (1989) 159; G. La Monica, M.A. Angaroni, F. Cariati and S. Cenini, *Inorg. Chim. Acta*, *143* (1988) 239.

[2] H.B. Gray and E.I. Solomon, in T.G. Spiro (ed.), *Copper Proteins*, Wiley-Interscience, New York, 1981, Ch. I; H. Sigel (ed.), *Metal Ions in Biological Systems*, Vol. 13. *Copper Proteins*, Marcel Dekker, New York, 1981.

[3] M.J. Hampden-Smith, T.T. Kodas, M. Paffett, J.D. Farr and H.-K. Shin, *Chem. Mater.*, 2 (1990) 636; J. Farkas, M.J. Hampden-Smith and T.T. Kodas, *J. Phys. Chem.*, *98* (1994) 6753.

[4] F. Bonati, A. Cingolani, G. Gioia Lobbia, D. Leonesi, A. Lorenzotti and C. Pettinari, *Gazz. Chim. Ital.*, *120* (1990) 341.

[5] C. Pettinari, G. Gioia Lobbia, G. Sclavi, D. Leonesi, M. Colapietro and G. Portalone, *Polyhedron*, *14* (1995) 1709.

[6] J.T. Gill, J.J. Mayerle, P.S. Welcker, D.F. Lewis, D.A. Ucko, D.J. Barton and D. Stovens, *Inorg. Chem.*, *15* (1976) 155.

[7] C.A. Tolman, *J. Am. Chem. Soc.*, *92* (1970) 2956; *Chem. Rev.*, *77* (1977) 313.

[8] M.R. Grimmett, Imidazoles and their benzo derivatives: (i) Structure, in A.R. Katritzky and C.W. Rees (eds. in chief), and K.T. Potts (ed.), *Comprehensive Heterocyclic Chemistry*, Vol. 5, Part 4A, Pergamon, Oxford, 1984, p. 345.

[9] G. Gioia Lobbia and F. Bonati, *Synth. React. Inorg. Met.-Org. Chem.*, *551* (1988) 551.

[10] A. Lorenzotti, A. Cingolani, G. Gioia Lobbia and D. Leonesi, *Gazz. Chim. Ital.*, *117* (1987) 191; D. Leonesi, A. Cingolani, G. Gioia Lobbia, A. Lorenzotti and F. Bonati, *Gazz. Chim. Ital.*, *117* (1987) 491.

[11] F.A. Cotton and D.M.L. Goodgame, *J. Chem. Soc.*, (1960) 5267.

[12] R.J. Restivo, A. Costin, G. Ferguson and A.J. Carty, *Can J. Chem.*, *53* (1975) 1949.

[13] W.A. Anderson, A.J. Carty, G.J. Palenik and G. Schreiber, *Can. J. Chem.*, *49* (1971) 761.

[14] D.M.L. Goodgame, M. Goodgame, P.J. Hayward and G.W. Rayner-Canham, *Inorg. Chem.*, *7* (1968) 2447.

[15] W.C. Wolsey, *J. Chem. Educ.*, *55* (1973) A355.

[16] M. Colapietro, L. Barba, C. Marciante, A. Pifferi and R. Spagna, personal communication.

[17] *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, UK, 1974, pp. 99–149.

[18] M. Camalli, D. Capitani, G. Cascarano, S. Cerrini, C. Giacovazzo and R. Spagna, *Ital. Patent No. 35403c/86*; SIRCAOS USERGUIDE, Istituto di Strutturistica Chimica CNR.

[19] J. Zukerman-Schpector, E.E. Castellano, A.E. Mauro and M.R. Roveri, *Acta Crystallogr., Sect. C*, *42* (1986) 302; L.M. Engelhardt, P.C. Healy, J.D. Kildea and A.H. White, *Aust. J. Chem.*, *42* (1989) 913; *44* (1991) 729; G.A. Bowmaker, J.V. Hanna, R.D. Hart, P.C. Healy and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1994) 2621.

[20] C. Pettinari, A. Cingolani and B. Bovio, *Polyhedron*, *15* (1996) 115.

[21] M.M. Rahman, H.-Y. Liu, K. Eriks, A. Prock and W.P. Giering, *Organometallics*, *8* (1989) 1.

[22] D. Leonesi, A. Lorenzotti, A. Cingolani and F. Bonati, *Gazz. Chim. Ital.*, *111* (1981) 483; A. Lorenzotti, A. Cingolani, D. Leonesi and F. Bonati, *Inorg. Chim. Acta*, *89* (1984) 113; J.G.A. Luijten and G.J.M. Van der Kerk, *Recl. Trav. Chem. Pays-Bas*, *82* (1963) 1181; J.G.A. Luijten, M.J. Janssen and G.J.M. Van der Kerk, *Recl. Trav. Chem. Pays-Bas*, *81* (1962) 202; R. Gassend, J.C. Maire and J.C. Pommier, *J. Organomet. Chem.*, *132* (1977) 69.

[23] L.M. Engelhardt, C. Pakawatchai, A.H. White and P.C. Healy, *J. Chem. Soc., Dalton Trans.*, (1985) 125.

[24] K. Nakamoto, in K. Nakamoto (ed.), *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 4th edn., 1986; J.G. Vos and W.L. Groeneveld, *Inorg. Chim. Acta*, *24* (1977) 123.

[25] H. Okkersen, W.L. Groeneveld and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, *92* (1973) 945.

[26] M.R. Rosenthal, *J. Chem. Educ.*, *50* (1973) 331.

[27] G.A. Bowmaker and D. A Rogers, *J. Chem. Soc., Dalton Trans.*, (1984) 1249.

[28] K. Nakamoto, Coordination compounds, in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 4th edn., 1986, pp. 328–331.

[29] K. Shobatake, C. Postmus, J.R. Ferraro and K. Nakamoto, *Appl. Spectrosc.*, *23* (1969) 12.

[30] J Bradbury, K.P. Forest, R.H. Nuttall and S.W. A Sharp, *Spectrochim. Acta*, *23* (1967) 2701.

[31] J.G. Verkade, *Coord. Chem. Rev.*, *9* (1972) 1.

[32] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 4th edn., 1986, pp. 201–220.

[33] R.C.R. Pozharskii, A.D. Garnovskii and A.M. Simonov, *Russ. Chem. Rev. (Engl. Transl.)*, *35* (1966) 122.

[34] E.W. Abel, R.A.N. Mc Lean and I.H. Sabherwal, *J. Chem. Soc. A*, (1969) 133.

[35] M.R. Grimmett, *Adv. Heterocycl. Chem.*, *11* (1970) 1.

[36] M.R. Grimmett, Imidazoles and their benzo derivatives: (i) Structure, in A.R. Katritzky and C.W. Rees (eds. in chief), and K.T. Potts (ed.), *Comprehensive Heterocyclic Chemistry*, Vol. 5, Part 4A, Pergamon, Oxford, 1984, p. 356.

[37] N.F. Borkett and M.I. Bruce, *J. Organomet. Chem.*, *65* (1974) C51; R. Gassend, J.C. Marie and J.C. Pommier, *J. Organomet. Chem.*, *132* (1977) 69; M.A. Angaroni, G.A. Ardizzoia, T. Beringhelli, G. D'Alfonso, G. La Monica, N. Masvciocchi and M. Moret, *J. Organomet. Chem.*, *363* (1989) 409.

[38] S.J. Berners-Price and P.J. Sadler, *Inorg. Chem.*, *25* (1986) 3822, and Refs. therein.

[39] S. Attar and J. Malito, *Polyhedron*, *11* (1992) 2409.

[40] A.M. Leiva, L. Rivera and B. Loeb, *Polyhedron*, *10* (1991) 347.

[41] H.-K. Shin, M.J. Hampden-Smith, E.N. Duesler and T. Kodas, *Can. J. Chem.*, *70* (1992) 2954.

[42] T.N. Sorrell and D.J. Jameson, *J. Am. Chem. Soc.*, *105* (1983) 6013; L.M. Engelhardt, C. Pakawatchai, A.H. White and P.C. Healy, *J. Chem. Soc., Dalton Trans.*, (1985) 125.

[43] R. Hamalainen, U. Turpeinen, M. Ahlgreen and T. Raikas, *Finn. Chem. Lett.*, (1978) 199; R. Hamalainen, M. Ahlgreen, U. Turpeinen and T. Raikas, *Cryst. Struct. Commun.*, *8* (1979) 75; G. Dessy and V. Fares, *Cryst. Struct. Commun.*, *8* (1979) 507.

[44] B.E. Gree, C.H.L. Kennard, G. Smith, B.D. James and A.H. White, *Acta Crystallogr., Sect. C, 40* (1984) 426.
[45] L.M. Engelhardt, C. Pakawatchai, A.H. White and P.C. Healy, *J. Chem. Soc., Dalton Trans.*, (1985) 125.
[46] F Bonati, *Gazz. Chim. Ital., 119* (1989) 291.
[47] J.R. Kirkhhoff, D.R. McMillin, W.R. Robinson, D.R. Powell, A.T. McKenzie and S. Chen, *Inorg. Chem., 24* (1985) 3928.
[48] P. Karagiannidis, P Aslanidis, S. Papastefanou, D. Mentzafos, A. Hountas and A. Terzis, *Inorg. Chim. Acta, 156* (1989) 265.
[49] S.J. Lippard and G.J. Palenik, *Inorg. Chem., 10* (1971) 1322.