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SYNTHESIS AND CHARACTERIZATION OF DERIVATIVES OF COPPER(I) WITH N-DONOR LIGANDS—I. AZOLE AND BIS(AZOLYL)ALKANE COMPOUNDS. CRYSTAL STRUCTURE OF NITRATO BIS(TRI-*p*-TOLYLPHOSPHINE)COPPER(I)

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Abstract—Several new complexes of the type $[Cu(NO_3)(PPh_3)_2(L)_m]$ (L = 3-methylpyrazole, 4-methylpyrazole, 3,5-dimethylpyrazole, 4-bromopyrazole or bis(4-methylpyrazol-1-yl)methane, $m = 1$; L = pyrazole, 1,2,4-triazole or 2-methylimidazole, $m = 2$), $[Cu(NO_3)(PPh_3)(L)]$ (L = 3,4,5-trimethylpyrazole or 4-phenylimidazole), $[Cu(NO_3)(PAr_3)_n(L)_3]$ (Ar = *p*- or *m*-tolyl, $n = 0$ or 1, L = pyrazole), $[CuX(PPh_3)_2(L)]$ (X = Cl, Br or I, L = pyrazole or 3,5-dimethylpyrazole) and $[CuX(PPh_3)(L)]$ (X = Cl or Br, L = bis(pyrazol-1-yl)methane, bis(3,5-dimethylpyrazol-1-yl)methane or bis(triazol-1-yl)methane) have been prepared and characterized by analytical and spectral data. The compounds $[CuX(PPh_3)_2(L)]$ (X = Cl, Br or I, L = pyrazole or 3,5-dimethylpyrazole) are fluxional at temperature above 240 K. The dinuclear compound $[Cu_2(PPh_3)_3(pzH)_2]$ was obtained when the reaction between $[CuI(PPh_3)_3]$ and pyrazole (pzH) was carried out in methanol containing alkali. In the crystal structure of the title compound, the copper atom is found in a strongly distorted tetrahedral coordination [P—Cu—P: 128.0(1)°] with two long Cu—O distances [2.217(9) and 2.184(9) Å].

During our investigation into the coordination chemistry of pyrazole and its derivatives, several zinc, cadmium, mercury, tin and silver compounds were obtained and characterized.[1] These complexes display a diversity of stable structural types in which the pyrazole ring can be N- or C-bonded to metal.

Coordination compounds of copper(I) and copper(II) with nitrogen-donor ligands have been extensively synthesized and described,[2] but much less work is available on $(Ar_3P)_n(L)_yCu^IX$ derivatives (L = nitrogen donor ligands).[3,4]

Interest in such systems, often air-sensitive and labile in solution, arises because of their structural features,[5] potential application in catalysis[6] and well-described relevance of copper(I) centres at the active sites of several proteins.[7]

In the previous work[8] the interaction between $Cu(NO_3)(Ar_3E)_n$ (E = P, Sb or As; $n = 2$ or 3) and various poly(azol-1-yl)alkanes (Fig. 1), a family of stable and flexible bidentate ligands, has been reported and it has been shown that only the less

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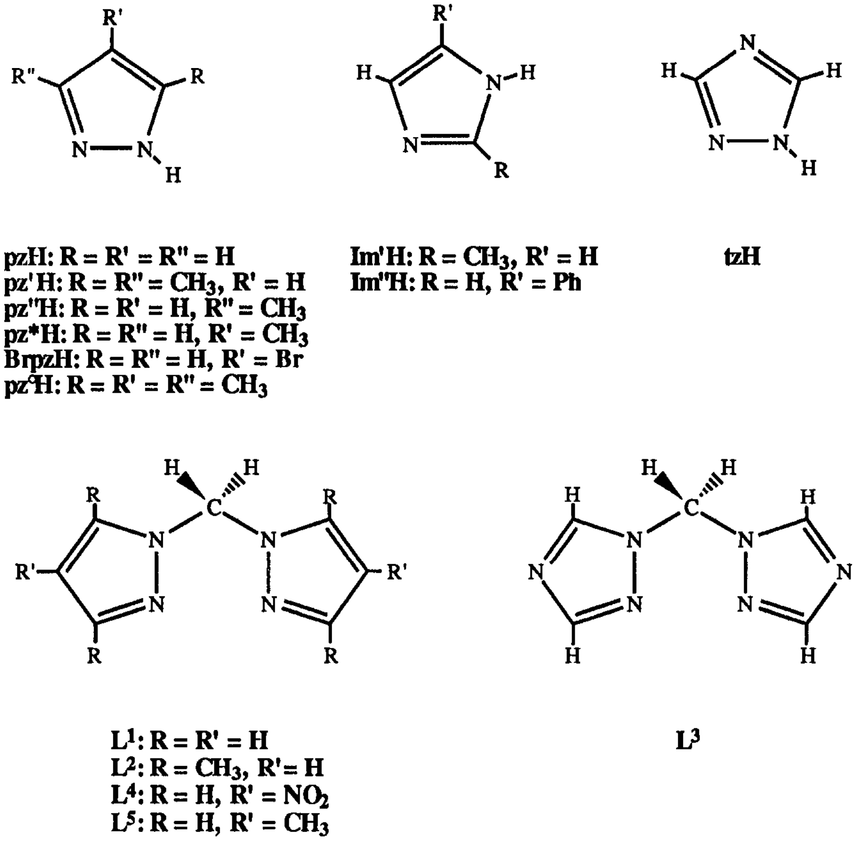


Fig. 1. Structures of the ligands employed in this work.

hindered (L^1, L^3 and L^4) and the more basic nitrogen donors (L^2) are able to displace the phosphine ligands and/or the nitrato group from the starting copper(I) derivatives.

So, it seemed pertinent to extend this investigation to the study of the interaction of $Cu(No_3)(Ar_3P)_2$ with the bis(4-methylpyrazol-1-yl)methane, (abbreviated L^5), more basic than L^1 and less hindered than L^2, and with the simplest azotate molecule also shown in Fig. 1.

The interaction between $CuX(Ar_3P)_n$ (X = Cl, Br, I, CN or SCN) and pzH, pz'H, L^1, L^2, L^3 and L^4 has been also investigated. The X-ray crystal structure of $[Cu(NO_3)\{(p\text{-tolyl})_3P\}_2]$ and a comparison with some related compounds has been reported.

EXPERIMENTAL

All solvents were dried by standard techniques. The reagents were purchased from the Aldrich Chemical Co. and from Alfa. The samples were dried *in vacuo* to constant weight (20°C, *ca* 0.1 torr). Elemental analyses were carried out in-house with an Elemental analyser 1108 CHNS-O Fisons Instruments. IR spectra from 4000 to 100 cm^{-1} were recorded with a Perkin–Elmer instrument System 2000 FT-IR. ^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 resistance of solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

Synthesis of the ligands

The donors L^1, L^2, L^3, L^4 and L^5 were prepared by the published methods.[9,10]

Synthesis of the complexes

The derivatives $Cu(NO_3)(Ar_3P)_2$ (Ar = phenyl, *p*-tolyl and *m*-tolyl) and $CuX(Ph_3P)_3$ (X = Cl, Br or I) were prepared by the published methods[11,12] and their analytical and spectral data are consistent with those reported in the literature.

Nitratobis(tri-o-tolylphosphine)copper(I). Tri-*o*-tolylphosphine (5.0 g, 12.1 mmol) in warm methanol (20 cm^3) was treated with $Cu(NO_3)_2 \cdot 3H_2O$ (1.0 g, 4.0 mmol) in methanol (10 cm^3). The copper(II) salt dissolved immediately; the blue colour of solution discharged and a pale green colour persisted. The solution was heated at reflux for 2 h, and then stirred to ambient temperature for 8 h. White needles (2.0 g, 2.7 mmol, 67.5%) appeared when the solution was cooled overnight in a freezer compartment. M.p.: 145–7°C. Found: C, 68.8; H, 5.8; N, 1.6. Calc. for $C_{42}H_{42}CuNO_3P_2$: C, 68.7; H, 5.8; N, 1.9%.

Cyanobis(triphenylphosphine)copper(I). To a solution of triphenylphosphine (14.46 g, 55.0 mmol) in 200 cm^3 of chloroform, CuCN (1.22 g, 14.0 mmol) was added. The reaction solution was stirred overnight at room temperature. Et_2O (200 cm^3) was added and a precipitate was formed immediately, which was filtered and washed with Et_2O (50 cm^3). The residue was recrystallized from 200 cm^3 of hot methanol to give 5.16 (60% yield) of $[CuCN[P(C_6H_5)_3]_2]$, m.p. 180–182°C. Found: C, 72.7; H, 5.0; N, 2.1. Calc. for $C_{37}H_{30}CuNP_2$: C, 72.4; H, 4.9; N, 2.3%.

Thiocyanatebis(triphenylphosphine)copper (I). This complex was prepared as described for $[CuCN\{P(C_6H_5)_3\}_2]$ by using PPh_3 (7.75 g, 29 mmol) and CuSCN (0.9 g, 7.0 mmol) to yield a colourless solid (2.39 g, 50% yield). M.p. 233–236°C. Found: C, 68.6; H, 4.8; N, 2.1. Calc. for $C_{37}H_{30}CuNP_2S$: C, 68.8; H, 4.7; N, 2.2%.

Nitratobis(triphenylphosphine)bis(pyrazole)copper(I). Pyrazole (0.14 g, 2.0 mmol) was added to a diethyl suspension (100 cm^3) of $Cu(NO_3)(Ph_3P)_2$ (0.65 g, 1.0 mmol). After 3 h stirring the solid was filtered and washed with ether (20 cm^3), affording the products **1** (0.75 g, 0.96 mmol). Compounds **2**–**23** and **25** were obtained similarly.

Chloro(triphenylphosphine)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 $CuCl(Ph_3P)_3$ (0.89 g, 1.0 mmol). After 1.5 day stirring, the solid was filtered and washed with acetone (30 cm^3), affording the product **24** (0.49 g, 0.96 mmol). Compound **26** was obtained similarly.

$[Cu_2(PPh_3)_3(pzH)_2]$. Pyrazole (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 the product **27** (1.05 g, 0.96 mmol).

X-ray crystallography

Crystal and experimental data are summarized in Table 1. A crystal of $C_{42}H_{42}NO_3CuP_2$, obtained from a methanol solution, was mounted on a CS automatic four-circle diffractometer equipped with a Huber goniometer[13] using graphite monochromatized Mo-K_α radiation ($\lambda = 0.71069$ Å). The cell parameters were refined by least squares from the angular position of 11 reflections in the range $8 < 2\theta < 17°$. The data were collected at room temperature for $3.0 < 2\theta < 60°$ from colourless crystal of approximate 0.2 × 0.2 × 0.3 mm using an ω scan technique. The scan rate was automatically chosen according to the peak intensity in the range 2.0–30.0° min^{-1}. Background counts were taken with stationary crystal with an offset of 0.5° at each end of the scan, and a total background to scan time ratio of 0.5. The intensities of three standard reflections, monitored every 97 reflections during the data collections, decayed by *ca* 20.0%. Data were corrected for Lorentz and polarization effects and for decay, but not for absorption. A total of 2459 independent reflections having $F_0 > 6\sigma F_0$ were used in all subsequent calculations.

Table 1. Crystallographic data

Formula	$C_{42}H_{42}NO_3CuP_2$
Formula weight	734.29
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.929 (7)
b (Å)	33.805 (45)
c (Å)	11.601 (7)
β (°)	117.41 (5)
V ($Å^{-3}$)	3804.9
Z	4
D_c ($g\ cm^{-3}$)	1.282
μ (cm^{-1})	7.212
$F(000)$	1536.0
No. of measured reflections	8366
No. of unique reflections	6477
No. of observed reflections, $\lvert F_0\rvert > 6\sigma\lvert F_0\rvert, n$	2459
Function minimized	$\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2$
Variables refined, m	442
a, b and c values in the weighting function[a]	7.959, 0.039, 0.004
R[b]	0.0563
R_w[c]	0.0725
Goodness of fit, S[d]	0.6

[a] $w = 1.0/(a+b|F_0|+c|F_0|^2)$.

[b] $R = \Sigma(|F_0|^2-|F_c|^2)/\Sigma F_0^2$.

[c] $R_w = \Sigma w(|F_0|-|F_c|)^2/\Sigma wF_0^2$.

[d] $S = \Sigma w(|F_0|-F_0|)^2/(n\text{-}m)$.

The structure was solved by Patterson and Fourier techniques. All non-hydrogen atoms were refined by full-matrix least-squares methods with anisotropic thermal parameters. The hydrogen atoms were introduced in the final refinement in idealized positions (C—H = 0.96 Å). Each hydrogen atom was assigned the equivalent isotropic temperature factor of the parent carbon atom and allowed to ride on it. The final difference Fourier map, with a root-mean-square deviation of electron density of 0.1 $e\text{Å}^{-3}$, showed values not exceeding 0.9 $e\text{Å}^{-3}$ which, however, are not of chemical significance. Atomic scattering factors were taken from ref. 14. All calculations were done on a PC using the SIR CAOS structure determination package.[15]

RESULTS AND DISCUSSION

The results of the reactions described here are reported in Scheme 1. Different types of products have been obtained, depending on the particular nitrogen-donor ligand and on the starting copper(I) derivative employed. The compounds were characterized through analytical and conductivity data (Table 2), infrared spectra (Table 3), ^{1}H and in some cases also through ^{13}C and ^{31}P NMR spectra (Table 4B).

By the reaction of $Cu(NO_3)(PPh_3)_2$ with an excess of pyrazole (abbreviated pzH) or of 2-methylimidazole (Im′H) in diethyl ether, the complexes **1** and **2** respectively are obtained according to eq. (1), whereas when $Cu(NO_3)(PPh_3)_2$ reacts with the sterically hindered 3,5-dimethylpyrazole (pz′H), 3-methylpyrazole (pz″H), 4-methylpyrazole (pz*H) or with the less donor 4-bromopyrazole (BrpzH), the complexes **3–6** were obtained (eq. 2). 3,4,5-Trimethylpyrazole ($pz^{\circ}H$) is a sterically hindered ligand because of the methyl group near the coordination sites, but is the more basic donor ($pK_a = 4.63$)[16] with respect to the other pyrazoles here employed and from its interaction with Cu$(NO_3)(PPh_3)_2$ the 2 : 1 adduct $[Cu(NO_3)(PPh_3)(pz^{\circ}H)_2]$, **7**, was obtained (eq. 3).

The influence of ligands with bulky substituent groups on coordination mode of copper(I), is also well illustrated by the reaction of $Cu(NO_3)(PPh_3)_2$ with Im″H (4-phenylimidazole) which afforded the $[Cu(NO_3)(PPh_3)(Im''H)_2]$ derivative, **8**, with displacement of one phosphine (eq. 3′). One phosphine is displaced also from the $[Cu(CO_3)\{p\text{-}CH_3C_6H_4)_3P\}_2]$ and $[Cu(NO_3)\{m\text{-}CH_3C_6H_4)_3P\}_2]$ by pzH (compounds **9** and **10**, eq. 4), while the introduction of a single methyl group in the *ortho* position of the phenyl rings causes a displacement of all the phosphines coordinated to copper, which is observed when pzH reacts with $[Cu(NO_3)\{o\text{-}CH_3C_6H_4)_3P\}_2]$, **11** (eq. 5).

The reaction of equimolar amounts of 1,2,4-triazole (tzH) and $Cu(NO_3)(PPh_3)_2$ gave the compound **12** (eq. 6), whereas when an excess of tzH was employed the derivative **13** is obtained (eq. 6′).

Reaction of L^5 with $Cu(NO_3)(PPh_3)_2$ leads to compound **14**, $[Cu(L^5)(PPh_3)_2]NO_3$, analogous to the compound previously described with the ligand L^1 (eq. 7).

The compounds **15–20** were readily isolated when pzH or pz′H reacts in diethyl ether with $CuX(PPh_3)_3$ (X = Cl, Br or I), in accordance with eq. (8).

The compound CuI(PPh$_3$)(pz′H), **21**, was obtained when the reaction between pz′H and $CuI(PPh_3)_3$ was carried out for 2 days. This is in agreement with the behaviour shown by most of the copper(I)phosphino derivatives,[17] which generally when stirred for a long reaction time dissociate in solution losing some of the P-donor ligands.

The ligands L^1, L^2 and L^3 displace two phosphine groups from $CuX(PPh_3)_3$ (X = Cl or Br) and yield the derivatives **22–26** (eq. 9).

Finally, if the reaction between a large excess of pzH and $CuI(PPh_3)_3$ was executed in refluxing methanol and KOH, the derivative **27**, empirical formula $C_{30}H_{25.5}CuN_2P_{1.5}$, in accordance with the stoichiometry $[Cu(pz)(PPh_3)_{1.5}]$, was afforded. This unusual and curious stoichiometry has been previously reported for several copper(I) halide derivatives $Cu_2X_2(Ar_3P)_3$ [X = Cl, Br or I; Ar = phenyl or *m*-tolyl].[12b,18] It has been suggested, also on the basis of X-ray crystal structure determinations, that these compounds are true complexes rather than mixtures and they can be formulated as bridged-halide dimers. In our case, two pyrazolate anions are probably bridging between two different copper(I) centres, one of which is three-coordinate and the other four-coordinate, as in Fig. 2. The dimeric structure is also supported by the fact that complexes having monohapto pyrazolate ligands are rare.[19] The steric effects determine to a great extent the coordination environment of the copper(I) atom: the formation of $Cu_2(pz)_2(PPh_3)_4$ seems to be precluded by the strong interligand repulsions between the bulky PPh_3 molecules.

The compound **27** is unstable in chloroform and acetone solution: it was readily oxidized by air, giving blue solutions in a very short time.

No reaction was observed with $Cu(NO_3)(PPH_3)_2$ when the ligand was benzotriazole or 3,5-dimethyl-4-iodopyrazole, or with L^1, L^2, L^3, pzH or pz′H when the copper reagent was $CuX(PPh_3)_3$ (X = CN or SCN).

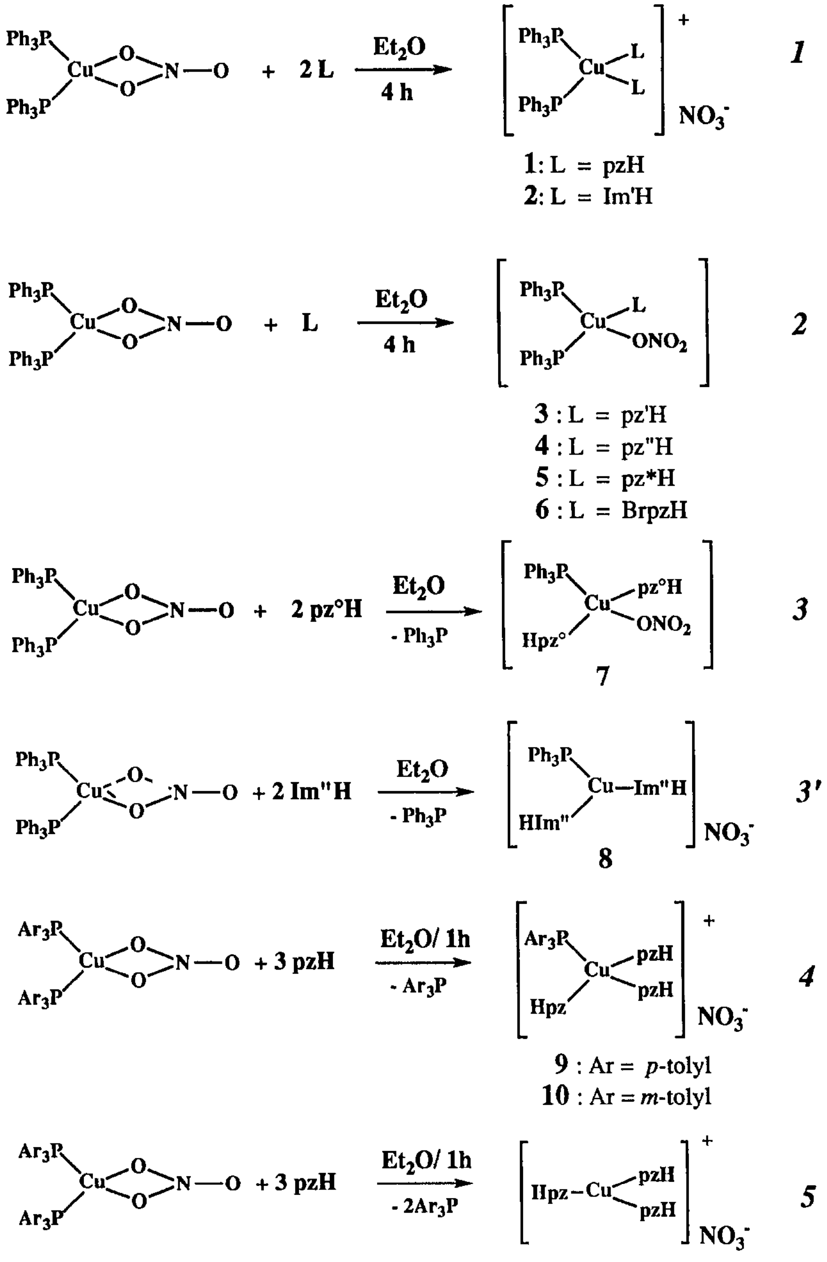
From the reaction of L^1 or L^2 with $CuI(PPh_3)_3$

no adduct was obtained, but the well-described tetrameric CuI(PPh$_3$)[20] was produced.

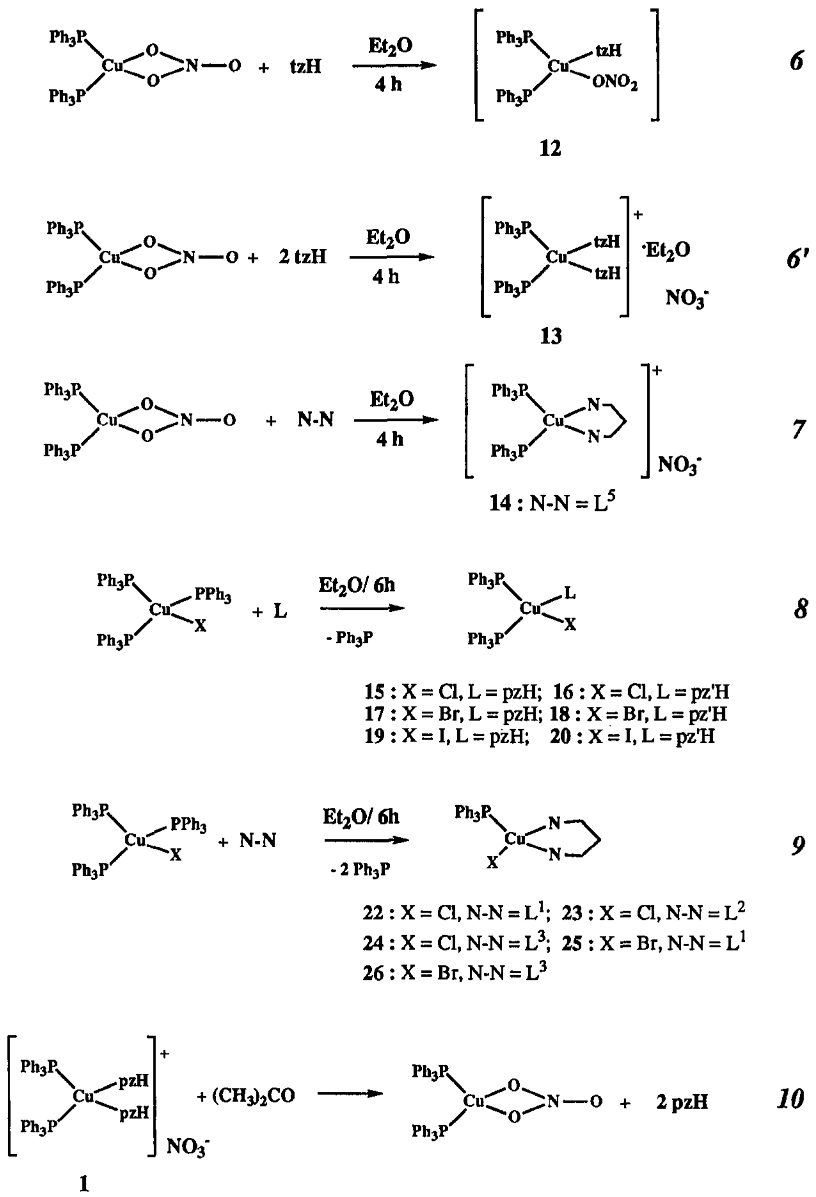
IR spectra

The infrared spectra of the complexes **1–27** showed several peaks characteristic of the organic ligands: a ν(CH) due to the heterocycle was often found at above 3100 cm^{-1}, while at least one band in the 1500–1600 cm^{-1} region is typical of the ring breathing vibration. In the spectra of the compounds **1–13** and **15–21** the presence of (N—H) stretching vibrations at *ca* 3200 cm^{-1} is consistent with a monodentate neutral azole coordinated through the pyridine nitrogen.

The IR spectra of the derivatives **1–14** indicated that the nitrate coordination differed significantly from that found in Cu(NO$_3$)(Ar$_3$P)$_2$[11]: in the complexes **3–7** and **13** the nitrato groups are likely monodentate since their spectra show a separation of 120 cm^{-1} between the ν_1 and ν_4 as opposed to a separation of 200 cm^{-1} in Cu(NO$_3$)(Ph$_3$P)$_2$. Since no copper(I) complexes with a coordination number greater than 4 are known, the presence of ionic nitrate in **1, 2, 9, 10, 12** and **14** seemed likely. The derivatives **8** and **11** also have spectra characteristic



Scheme 1.



Scheme 1 (*continued*).

of the nitrate ion,[21] with a strong broad band at about 1350–1380 cm^{-1}, arising from the doubly degenerate vibration ν_3 and a sharp band of varying intensity at about 800 cm^{-1}, which arises from the out-of-plane bending mode ν_2.

In the far-IR spectra of all the copper(I) derivatives it is not easy to assign the copper–phosphorus stretching bands because both the PPh_3 and the azole exhibit a number of ligand vibrations in the low-frequency region. However, on the basis of previous reports[22] on metal complexes containing triarylphosphines we assigned the strong triplet band near 500 cm^{-1} to Whiffen's y-vibration (out of plane bending of the phenyl ring) of PPh_3, whereas the second group of vibrations which appear near 400 cm^{-1} correspond essentially to Whiffen's t-vibration. In the spectra of some starting copper(I) derivatives and of some adducts, some bands of medium intensity appeared which are not present in the spectrum of the free N- and P-donor: these bands are similar to those recorded for some $(PPh_3)MX$ complexes[23] and could be tentatively assigned to ν(Cu—P) vibrations.

The metal–halide stretching bands in the IR spectra of the $CuX(PPh_3)_n$ derivatives are detected at *ca* 290–280 (X = Cl), 220–200 (X = Br) and 160–140 cm^{-1} (X = I), whereas in the spectra of $CuCl(PPh_3)_n(L)_y$ the ν(Cu—Cl) falls in the range 230–200 cm^{-1}.

Table 2. Physical, analytical and conductivity data of copper(I) derivatives **1–27**

				Elemental analysis (%) Found (Calc.)			Conductivities[a]		
No.	Compound	M.p. °C	Yield %	C	H	N	Solvent	Conc.	Λ
1	$[\{(C_6H_5)_3P\}_2Cu(pzH)_2]NO_3$	167–9	96	64.3	4.9	9.4	Acetone	1.0	13.0
	$C_{42}H_{38}CuN_5O_3P_2$			(64.2)	(4.9)	(8.9)	DMSO	1.0	39.4
2	$[\{(C_6H_5)_3P\}_2Cu(Im'H]_2]NO_3$	180–2	74	64.7	5.4	8.5	Acetone	1.1	82
	$C_{44}H_{42}CuN_5O_3P$			(64.9)	(5.2)	(8.6)	CH_2Cl_2	1.0	1.6
3	$[\{(C_6H_5)_3P\}_2Cu(pz'H)(NO_3)]$	170–3	34	66.3	5.3	5.4	Acetone	0.6	6.0
	$C_{41}H_{38}CuN_3O_3P_2$			(66.0)	(5.1)	(5.6)	CH_2Cl_2	1.0	1.8
4	$[\{(C_6H_5)_3P\}_2Cu(pz''H)(NO_3)]$	186–8	75	65.6	5.1	6.0	Acetone	0.9	1.5
	$C_{40}H_{36}CuN_3O_3P_2$			(65.6)	(5.0)	(5.7)			
5	$[\{(C_6H_5)_3P\}_2Cu(pz^*H)(NO_3)]$	182–6	90	65.5	5.2	5.8	Acetone	1.2	12.3
	$C_{40}H_{36}CuN_3O_3P_2$			(65.6)	(4.9)	(5.7)			
6	$[\{(C_6H_5)_3P\}_2Cu(BrpzH)(NO_3)]$	189–90	63	58.9	4.3	5.1	Acetone	1.0	8.4
	$C_{39}H_{33}BrCuN_3O_3P_2$			(58.8)	(4.2)	(5.3)			
7	$[\{(C_6H_5)_3P\}Cu(pz^{\circ}H)_2]NO_3$	165–6	61	59.4	5.9	11.6	Acetone	1.0	14.9
	$C_{30}H_{35}CuN_5O_3P$			(59.3)	(5.8)	(11.5)	DMSO	1.1	37.2
8	$[\{(C_6H_5)_3P\}Cu(Im''H)_2]NO_3$	98 dec	97	64.2	4.9	10.4	Acetone	0.9	79.2
	$C_{36}H_{31}CuN_5O_3P$			(64.0)	(4.6)	(10.4)			
9	$[\{(p\text{-}C_7H_7)_3P\}Cu(pzH)_3]NO_3$	135	98	57.0	5.6	15.5	Acetone	0.1	29.1
	$C_{30}H_{33}CuN_7O_3P$			(56.8)	(5.3)	(15.5)			
10	$[\{(m\text{-}C_7H_7)_3P\}Cu(pzH)_3]NO_3$	113–6	96	57.2	5.4	15.6	Acetone	0.1	19.3
	$C_{30}H_{33}CuN_7O_3P$			(56.8)	(5.3)	(15.5)			
11	$[Cu(pzH)_3]NO_3$	195 dec	75	32.8	3.6	29.5			
	$C_9H_{12}CuN_7O_3$			(32.8)	(3.7)	(29.7)			
12	$[\{(C_6H_5)_3P\}_2Cu(tzH)_2]NO_3 \cdot Et_2O$	150 dec	90	61.5	5.1	11.0	Acetone	1.1	18.1
	$C_{44}H_{46}CuN_7O_4P_2$			(61.3)	(5.4)	(11.4)			
13	$[\{(C_6H_5)_3P\}_2Cu(tzH)]NO_3$	208–210	98	63.1	4.8	7.6	Acetone	1.0	14.0
	$C_{38}H_{33}CuN_4O_3P_2$			(63.5)	(4.6)	(7.8)			
14	$[\{(C_6H_5)_3P\}_2Cu(L^4)]NO_3$	185–9	98	65.7	5.3	8.7	Acetone	0.9	96.5
	$C_{45}H_{42}CuN_5O_3P_2$			(65.4)	(5.1)	(8.5)	CH_2Cl_2	1.0	13.0
15	$[\{(C_6H_5)_3P\}_2Cu(pzH)]Cl$	179–81	75	67.9	5.2	4.0	Acetone	1.0	2.0
	$C_{39}H_{34}ClCuN_2P_2$			(67.7)	(5.0)	(4.0)	DMSO	0.9	5.8
16	$[\{(C_6H_5)_3P\}_2Cu(pz'H)]Cl$	152–3	78	68.1	5.6	3.8	Acetone	0.9	1.7
	$C_{41}H_{38}ClCuN_2P_2$			(68.4)	(5.3)	(3.9)	CH_2Cl_2	1.0	0.5
17	$[\{(C_6H_5)_3P\}_2Cu(pzH)]Br$	185–7	88	63.5	4.9	3.7	Acetone	0.9	1.2
	$C_{39}H_{34}BrCuN_2P_2$			(63.6)	(4.7)	(3.8)			
18	$[\{(C_6H_5)_3P\}_2Cu(pz'H)]Br$	164–5	61	64.9	5.2	3.3	Acetone	1.0	2.0
	$C_{41}H_{38}BrCuN_2P_2$			(64.4)	(5.0)	(3.7)			
19	$[\{(C_6H_5)_3P\}_2Cu(pzH)]I$	189–91	58	59.3	4.5	2.8	Acetone	1.0	1.4
	$C_{39}H_{34}CuIN_2P_2$			(59.8)	(4.4)	(3.6)			
20	$[\{(C_6H_5)_3P\}_2Cu(pz'H)]I$	150–60	78	60.5	4.9	3.4	Acetone	1.0	1.5
	$C_{41}H_{38}CuIN_2P_2$			(60.7)	(4.7)	(3.9)			
21	$[\{(C_6H_5)_3P\}Cu(pz'H)]I$	199–201	94	50.8	4.4	4.9	Acetone	1.0	4.8
	$C_{23}H_{23}CuIN_2P$			(50.3)	(4.2)	(5.1)	DMSO	1.3	10.9
22	$[(C_6H_5)_3PCu(L^1)Cl]$	185–9	83	59.4	4.6	10.7	Acetone	1.0	44.2
	$C_{25}H_{23}ClCuN_4P$			(58.9)	(4.6)	(11.0)	DMSO	1.0	9.8
23	$[(C_6H_5)_3PCu(L^2)Cl]$	165 dec	87	61.6	5.9	10.0	Acetone	1.0	42.0
	$C_{29}H_{31}ClCuN_4P$			(61.6)	(5.5)	(9.9)			
24	$[(C_6H_5)_3PCu(L^3)Cl]$	176–7	96	54.1	4.3	16.4	Acetone	1.1	10.5
	$C_{23}H_{21}ClCuN_6P$			(54.0)	(4.1)	(16.4)			
25	$[(C_6H_5)_3PCu(L^1)Br]$	186–9	87	54.5	4.2	10.0	Acetone	1.0	36.2
	$C_{25}H_{23}BrCuN_4P$			(54.2)	(4.2)	(10.1)			
26	$[(C_6H_5)_3PCu(L^3)Br]$	208–11	96	49.5	3.9	14.8	Acetone	1.1	8.4
	$C_{23}H_{21}BrCuN_6P$			(49.7)	(3.8)	(15.1)			
27	$[\{(C_6H_5)_3P\}_{1.5}Cu(pz)$	> 170 dec	96	68.3	5.2	5.2	Acetone	1.1	2.0
	$C_{30}H_{25.5}CuN_2P_{1.5}$			(68.6)	(5.1)	(5.3)			

[a] In $\Omega^{-1}cm^2mol^{-1}$ at room temperature; conc. is molar concentration ($\times 10^3$).

Table 3. Selected IR data (cm^{-1})^a for the ligands and for the copper(I) derivatives

Comp.	>3000	1600–1500	<600	other data
$CuNO_3(PPh_3)_2$	3063 w	1588 w, 1579 w	533 m, 521 m, 503 m, 444 w, 430 w, 281 w, 248 w, 227 w	ν(NO_3) : 1470 s, 1280 s
$CuNO_3[(p\text{-}C_7H_7)_3P]_2$	3050 w	1652 w, 1598 m, 1559 w	516 m, 505 m, 495 m, 436 m, 421 m, 356 m, 317 wbr, 237 br	ν(NO_3] : 1460 s, 1288 s
$CuNO_3[(m\text{-}C_7H_7)_3P]_2$	3050 w	1589 m	553 m, 545 m, 455 m	ν(NO_3) : 1470 s, 1286 s
$CuNO_3[(o\text{-}C_7H_7)_3P]_2$	3048 w	1585 w, 1573 w	516 m, 504 m, 496 m, 444 w, 428 w, 411 w	ν(NO_3) : 1470 s, 1284 s
$CuCl(PPh_3)_2$	3047 m	1583 w, 1571 w	530 m, 518 m, 505 m, 495 m, 480 sh, 448 m, 433 m, 225 w, 214 w	ν(Cu—Cl) : 290 s br
$CuBr(PPh_3)_3$	3046 m	1583 w, 1574 w	513 m, 506 m, 490 m, 437 m, 426 m, 411 m, 251 m, 215 m	ν(Cu—Br) : 165 m
$CuI(PPh_3)_3$	3048 w	1585 w, 1573 w	516 m, 504 m, 496 m, 444 w, 428 w, 411 w	ν(Cu—I) : 138 m
$CuCN(PPh_3)_2$	3060 w	1580 w	550 w, 520 s, 510 s, 485 m, 440 w, 415 w	ν(CN) : 2110 m
$CuSCN(PPh_3)_2$	3060 w	1580 w	520 s, 508 s, 485 m	ν(SCN) : 2095 m
pzH	3140 m, 3070 vs	1558 m, 1540 m	285 w	ν(N—H) : 3400–3200 vs, br
Im′H	3173 m, 3137 m, 3109 m	1596 s, 1502 m	378 m, 355 m, 269 m, 164 m, 149 m	ν(N—H) : 3100–2400 br
pz′H	3130 m, 3106 m	1594 s, 1552 w	403 m, 270 m, 230 m	ν(N—H) : 3400–3200 vs
pz″H	3139 w, 3129 m, 3006 w	1583 s	352 m, 282 s	ν(N—H) : 3400–3200 vs
pz*H	3180 s, 2970 s	1577 m, 1500 m	326 m, 284 m	ν(N—H) : 3180 vs
pz°H	3180 m, 3140 m	1594 m, 1520 m	571 m, 474 m, 338 m, 282 s, 175 m	ν(N—H) : 3220 vs, br
BrpzH	3066 m	1590 m, 1560 m	364 m, 225 m	ν(N—H) : 3150 br
Im″H	3129 m, 3113 m	1604 m, 1584 m 1548 m, 1519 m	543 m, 518 m, 447 m, 436 m, 349 m, 301 m	ν(N—H) : 2800–2300 br
tzH	3130 s, 3120 m	1531 m	285 w, 189 w, 152 m	ν(N—H) : 2735 vs br
L^1	3140 w, 3119 w, 3107 m	1520 m, 1515 sh	397 m, 355 m, 280 w, 170 w, 120 w	
L^2	3140 w, 3100 w	1565 sh, 1560 s	465 s, 402 w, 360 m, 310 m, 275 m	
L^3	3120 m, 3115 m	1510 sh, 1505 s	390 m	
L^5	3150 m, 3085 m	1575 m	422 m, 398 w, 346 w, 288 m, 249 m	
1	3150 br, 3070 w	1584 w, 1569 w, 1534 w	527 m, 518 m, 504 m, 495 m, 436 w, 422 w, 284 w, 254 w	ν(N—H) : 3180 m, br ; ν(NO_3) : 1376 s, 1336 s, 827 w
2	3140 w, 3123 w	1586 w, 1569 m	514 w, 508 m, 492 m, 434 w, 417 w, 373 w, 284 w	ν(N—H) : 3170 br ; ν(NO_3) : 1360 s br, 827 w
	3061 w, 3044 w			
3	3135 w, 3110 w, 3046 w	1584 w, 1570 sh	542 w, 527 m, 516 m, 504 m, 495 w, 445 w, 420 w, 285 w	ν(N—H) : 3194 br ; ν(NO_3) : 1430 s br, 1303 s br
4	3140 w, 3130 w, 3051 w	1584 w, 1557 w, 1542 w	526 m, 516 m, 502 m, 443 w, 430 w, 417 w, 369 m, 282 m, 176 m	ν(N—H) : 3200 br ;ν(NO_3) : 1440 s, 1301 s
5	3130 w, 3117 w, 3051 w	1586 w, 1571 w	529 m, 518 s, 508 s, 494 s, 442 w, 432 w, 421 w, 397 w, 284 w	ν(N—H) : 3200 br ; ν(NO_3) : 1435 s, 1301 s
6	3115 w, 3040 w	1584 w, 1571 w, 1539 w	543 w, 516 m, 496 m, 442 w, 430 w, 288 w	ν(N—H) : 3200 br ; ν(NO_3) : 1434 m, 1299 m

7	3186 w, 3159 w, 3106 w 3053 w	1588 w, 1525 w	527 m, 507 m, 494 m, 439 w, 425 w, 292 w	ν(N—H): 3308 br; $\nu(NO_3)$: 1435 m, 1278 s
8	3100 w, br	1607 w, 1586 w, 1516 m	574 w, 521 m, 505 m, 489 m, 438 w, 427 w, 283 w	ν(N—H): 3150 w, br; $\nu(NO_3)$: 1350 br, 829 m
9	3139 w, 3110 w, 3050 w	1598 w, 1560 w, 1543 w 1527 w, 1507 w	589 w, 543 w, 524 m, 508 m, 426 m, 284 w	ν(N—H): 3328 s br, 3180 s br; $\nu(NO_3)$: 1349 s, 1317 s, 829 s
10	3185 sh, 3146 sh, 3047 w	1592 w, 1540 w	551 m, 522 w, 471 m, 455 m, 427 w, 284 w	ν(N—H): 3200 br, $\nu(NO_3)$: 1356 s, 1319 s, 829 w
11	3136 w, 3050 w	1570 w	456 w	ν(N—H): 3300 br, $\nu(NO_3)$: 1360 s br
12	3112 w, 3100 w, 3053 w	1585 w, 1536 w, 1513 w	542 w, 528 m, 515 m, 505 m, 492 m, 442 w, 280 w	ν(N—H): 3200 br; $\nu(NO_3)$: 1378 s, 1324 s, 827 w; ν(C—O): 1470 m
13	3143 w, 3109 w	1586 w, 1535 w, 1520 w	528 m, 513 m, 504 m, 489 m, 441 w, 289 w	ν(N—H): 3200 s br; $\nu(NO_3)$: 1395 s, 1329 s
14	3143 w, 3109 w, 3076 w	1586 w, 1573 w	528 m, 513 m, 504 m, 489 m, 448 vw, 443 w, 285 w	$\nu(NO_3)$: 1374 s, 1329 s
15	3110 w, 3049 w	1585 w, 1571 w, 1518 w	524 m, 513 m, 506 m, 493 m, 437 w, 428 w, 423 w, 284 w	ν(N—H): 3250 s br; ν(Cu—Cl): 220 m br
16	3140 w, 3110 w, 3049 w	1584 w, 1567 m	527 m, 517 m, 505 m, 489 m, 449 w, 437 w, 417 w, 282 vw	ν(N—H): 3212 s br; ν(Cu—Cl): 229 m br
17	3133 m, 3114 w, 3049 m	1585 w, 1571 w, 1520 w	526 m, 516 m, 499 m, 441 m, 417 w, 281 w, 248 w	ν(N—H): 3256 s br
18	3140 w, 3104 w 3053 m, 3031 sh	1586 m, 1570 m	512 s, 493 m, 487 m, 445 w, 429 w, 416 w, 281 w, 252 w	ν(N—H): 3281 s br
19	3140 w, 3100 w, 3050 w	1585 w, 1570 w, 1515 w	516 m, 499 m, 442 w, 415 w	ν(N—H): 3285 s br
20	3140 w, 3100 w, 3045 m	1586 m, 1568 m	597 w, 526 m, 516 m, 504 m, 496 m, 433 m, 415 m, 284 w, 232 w	ν(N—H): 3261 s br
21	3110 w, 3050 w	1586 w, 1568 m	573 m, 524 m, 504 m, 488 m, 448 w, 420 m, 284 m	ν(N—H): 3325 s br
22	3100 w, 3080 m	1580 w, 1520 m br	522 w, 499 m, 402 w, 250 w, 232 w	ν(CuCl): 214 s
23	3117 w, 3071 w, 3051 m	1585 w, 1561 m	526 m, 505 m, 496 m, 488 m, 471 w, 445 w, 421 w, 351 w, 254 w	ν(CuCl): 220 br, 196 m
24	3110 w, 3100 w, 3079 w	1535 w, 1525 w	522 m, 507 m, 500 m, 435 w, 386 w, 304 s	ν(CuCl): 223 s
25	3128 w, 3119 w, 3089 m	1583 w, 1519 w	522 m, 500 m, 434 w, 401 m, 378 w, 215 vw	
26	3076 w	1560 w, 1542 w 1523 w, 1515 w	523 m, 500 m, 436 w, 386 w	
27	3055 w	1585 w, 1571 w, 1559 w 1541 w, 1507 w	542 w, 526 m, 514 m, 497 m, 449 w, 415 w, 283 w	

[a] Nujol mull

Table 4a. Some NMR data[a] of the ligands and of the starting copper(I) derivatives

Compound	Solvent	$\delta(^1H)^b$	$\delta(^{13}C)$	$\delta(^{31}P)$
$CuNO_3(PPh_3)_2$	$CDCl_3$	7.20–7.50 m	128.60 d, 129.5 s, 131.8–132.2 m, 133.7 d	−0.20
	$(CD_3)_2CO$	7.20–7.60 m		
$CuNO_3[(p\text{-}C_7H_7)_3P]_2$	$CDCl_3$	7.00–7.60 m, 2.32 s, 2.39 s	21.40 s, 21.50 s, 129.2 d, 129.5 s, 132.1 d 133.6 br, 140.2 d, 142.2 d	−2.05
$CuNO_3[(m\text{-}C_7H_7)_3P]_2$	$CDCl_3$	7.00–7.70 m, 2.16 s, 2.37 s	21.30 s, 21.40 s, 128.30 d, 128.6 s, 129.2 d 130.6 s, 131.0, 132.5 d, 132.7 s, 134.4 s, 138.5 s	−1.53
$CuNO_3[(o\text{-}C_7H_7)_3P]_2$	$CDCl_3$	6.70–7.50 m, 2.40 s, 2.49 s	21.20 s, 21.50 s, 21.90 s, 22.00 s, 125.5 d, 126.2 d 128.8 s, 130.2 d, 131.8 d, 132.0 d, 132.9 d 133.10 s, 142.51 s, 142.92 s, 143.5 s, 143.6 s	
$CuCl(PPh_3)_2$	$CDCl_3$	7.20 m, 7.40 m	128.64 d, 129.89 s, 132.41 d, 133.91 d	−3.85
$CuBr(PPh_3)_3$	$CDCl_3$	7.15 m, 7.30 m	128.41 d, 129.40 s, 133.77 d, 134.00 d	−4.52
$CuI(PPh_3)_3$	$CDCl_3$	7.20 m, 7.35 m	128.45 d, 129.47 s, 133.74 d, 134.04	−4.76
$CuCN(PPh_3)_2$	$CDCl_3$	7.02 m, 7.22 m	128.28 d, 129.21 s, 133.86 d, 134.35 d, 152.28 s br	
$CuSCN(PPh_3)_2$	$CDCl_3$	7.20–7.40 m		
pzH	$CDCl_3$	6.22 t, 7.35 d, 7.49 d		
Im′H	$CDCl_3$	2.36 s, 6.96 d		
pz′H	$CDCl_3$	2.21 s, 5.75 s		
	CD_2Cl_2	2.28 s, 5.80 s, 10.5 br	12.43 s, 103.76 s, 144.0 br	
pz″H	$CDCl_3$	2.32 s, 6.06 d, 7.48 d		
pz*H	$CDCl_3$	2.09 s, 7.36 s		
pz°H	$CDCl_3$	1.87 s, 2.20 s		
BrpzH	$CDCl_3$	7.65 s		
tzH	$CDCl_3$	7.94 s, 8.09 s		
L^1	$CDCl_3$	6.26 s, 6.29 t, 7.53 d, 7.63 d	65.2 s, 107.2 s, 129.6 s, 140.8 s	
L^2	$CDCl_3$	2.18 s, 2.40 s, 5.78 s, 6.04 s	11.2 s, 13.5 s, 106.4 s, 140.4 s, 148.3 s	
L^3	$(CD_3)_2CO$	6.71 s, 8.10 s, 8.80 s	59.0 s, 145.2 s, 152.4 s	
L^5	$CDCl_3$	2.0 s, 6.23 s, 7.33 s, 7.37 s	9.28 s, 65.79 s, 118.15 s, 128.52 s, 141.80 s	

[a] s = singlet, m = multiplet, d = doublet, br = broad.
[b] δ in ppm.

Table 4b. Some NMR data for the derivatives **1–27**[a]

Compound	Solvent	$\delta(^1H)^a$	$\delta(^{13}C)$	$\delta(^{31}P)$
1	Acetone	6.50 br, 7.20–7.50 m br, 7.80 s br		
	Acetonitrile	6.80 s br, 7.16–7.60 m, 8.30 m		
	$CDCl_3$	6.45 br, 7.05–7.45 br, 7.80 br, 12.40 br		
2	Acetonitrile	2.13 s, 7.20–7.55 m		
	$CDCl_3$	2.10 br, 7.00–7.50 m br		
3	Acetonitrile	2.08 s, 2.12 s, 6.20 br, 7.15–7.70 m	12.26 s, 129.77 d, 131.12 s, 134.30 c, 132.d, 133.65 d	
	$CDCl_3$	1.80–2.40 br, 5.95 s br, 7.0–7.5 m br, 12.4 br		
	Acetone	2.05 br, 2.20 br, 7.20–7.55 m br, 7.60 s		
4	Acetonitrile	2.21 s, 7.20–7.55 m br, 7.70 br	129.81 d, 131.15 s, 134.32 c	−0.281
	$CDCl_3$	2.20 s br, 6.80–7.40 m br, 7.60 br	129.11 d, 130.28 s, 133.20 d, 134.13 c	
5	Acetonitrile	2.21 s, 7.15–7.70 m br	8.96 s, 129.81 d, 131.18 s, 133.50 d, 134.30 d	
	$CDCl_3$	2.28 s br, 7.10–7.80 br	129.10 d, 130.28 s, 133.2 d, 134.13 d	
6	$CDCl_3$	6.16 s, 7.0–7.60 m, 13.5 br		
7	$CDCl_3$	1.90 s, 2.19 s, 7.25–7.45 m br	129.15 d, 130.38 d, 133.32 d, 134.09 d	
8	$CDCl_3$	5.25 sbr, 7.05 s br, 7.20–7.50 m		
9	$CDCl_3$	2.35 s, 7.10–7.35 mbr, 8.20 br	21.85 s, 129.51 d, 129.79 d, 132.56 d, 134.01 d, 140.18 s	
10	$CDCl_3$	2.22 s, 7.10–7.35 br, 7.4–7.8 br		
12	$CDCl_3$	1.22 t, 3.48 q, 7.10–7.40 m br, 7.90 br		
13	$CDCl_3$	7.10–7.45 m br, 7.80 br		
14	$CDCl_3$	2.18 s, 6.20 s br, 6.75 s br, 7.0–7.5 m br, 8.05 s br	13.62, 121.3 s, 128.82 d, 130.14 s, 132.1 d, 133.34 d	+0.87
15	$CDCl_3$	7.15–7.45 m		
16	$CDCl_3$	2.13 s, 5.82 s, 7.20–7.45 m	128.87 d, 129.87 s, 134.35 d, 134.67 s	
17	$CDCl_3$	6.30 s br, 7.15–7.50 m, 11.3 br		
18	$CDCl_3$	2.05 s, 5.80 s, 7.15–7.43 m	12.86 s, 105.44 s, 128.90 d, 129.96 s, 133.93 s, 134.40 d	
	$CD_2Cl_2{}^c$	2.00 s, 5.82 s, 7.30 m, 7.40 m	12.07 s, 104.94, 128.31, 129.44 s, 133.83 d, 144.0 s	
	$CD_2Cl_2{}^d$	1.50 sbr, 2.22 sbr, 5.80 s, 7.20–7.40 m	11.44 s, 13.91 s, 105.33 s, 128.57 d, 129.73 s, 133.8 m, 139.96 s, 148.32 s	
19	$CDCl_3$	6.18 s, 6.30 s, 7.20–7.60 m		
20	$CDCl_3$	2.13 s, 5.00 br, 5.85 s, 7.15–7.45 m	12.87 s, 105.49 s, 128.91 d, 130.04 s, 133.63 s, 134.14 s, 134.47 s	−4.59
21	$CDCl_3$	2.13 s, 5.90 s, 7.25–7.43 m, 7.45–7.60 m		
22	$CDCl_3$	6.28 br, 6.50 br, 7.10–7.50 m br, 7.90 s br	64.01 s, 128.0 br, 128.66 d, 129.92 s, 132.68 d, 133.86 d	
23	$CDCl_3$	2.03 s, 2.38 s, 5.80 s, 6.22 s, 7.20–7.65 m br	12.0 s br, 14.4 br, 129.02 d, 130.15 s, 132.58 d, 134.55 d	−3.43
24	DMSO	6.68 s, 7.35–7.50 br, 8.08 s, 8.90 s	128.61 s, 128.77 s, 130.18 s, 131.41 d, 131.97 d, 133.31 s	
25	$CDCl_3$	6.20 s, 6.49 s br, 7.20–7.50 m br, 7.80 s br	64.05 s, 106.8 s br, 128.60 d, 129.8 s, 130.4 s, 132.83 d, 133.89 d, 141.34 s	
26	DMSO	6.70 s, 7.40–7.50 m br, 8.08 s br, 8.92 s br	128.66 d, 130.0 s, 133.38 d	
27	$CDCl_3$	6.08 s, 7.30–7.50 m		−3.55
	Acetone	7.20–7.30 m		

[a] s = singlet, m = multiple, d = doublet, br = broad.

[b] δ in ppm.

[c] T = 298 K.

[d] T = 200 K.

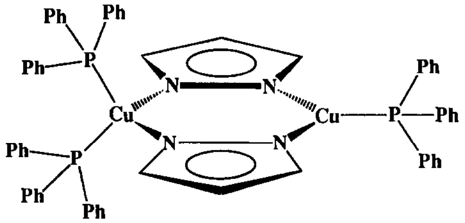


Fig. 2. Structure proposed for the compound **27**.

Conductivities

The conductivity measurements were carried out only on the stable solutions. The complexes **3–7**, **13** and **15–21** are not electrolytes in acetone, thus ruling out ionic structures such as $[Cu(L)(PPh_3)_n]^+[X]^-$, or displacement of the anionic ligands by the solvent. A negligible ionic dissociation is found for the derivatives **9–12** and **22–25** whereas the derivatives **15** and **20–22** are not electrolytes not only in acetone but also in ionizing solvents such as DMSO. Finally, the complexes **2**, **8** and **14** are electrolytes in acetone and the latter also in dichloromethane, thus giving further support to its ionic structure observed also in the solid state. The compound **1**, which is probably ionic in the solid state, is a non-electrolyte in acetone, in accordance with a dissociation according to eq. 10. This is also supported by its IR spectrum recorded in acetone solution: the $\nu(NO_3)$ absorptions are similar to those indicated for the $Cu(NO_3)(Ph_3P)_2$.[11]

NMR spectra

^1H and ^{13}C NMR spectra (for a comparison in Table 4A the NMR data of some ligands and of the starting copper(I) derivatives are reported) were carried out only when the compounds were sufficiently soluble and the solutions sufficiently stable. For the derivatives of bis(pyrazol-1-yl)alkanes the pattern of chemical shifts on going from the free to the coordinated ligand is the same as that previously observed:[24] the signals due to ring and methylene protons are shifted downfield upon coordination, whereas the carbons of the methylene bridges undergo an upfield displacement. Indeed the Δ, difference in chemical shift of a given carbon in the complex and in the free ligand, is negligible for the methyl carbons and positive for the azole ring carbons.

On the other hand, in the ^1H and ^{13}C NMR spectra of most of the complexes containing monodentate azole ligands, the resonances due to protons or carbons of the azole ring cannot be detected because they are often overlapped with the resonances due to aromatic protons of the phosphine ligands, or because the solutions are not sufficiently stable. For example, most of the compounds when dissolved in chloroform or in acetone, were oxidized by air, giving a blue solution in a very short time. A comparison between the ^1H spectra of the complexes **1**, **3–5** and **15–21** and of the ligands in the same solvents reveals that, upon complex formation, the signals of protons of the azole ring are generally shifted downfield, as required by a diminution of the electron density on the ligand owing to the existence of the N—Cu donor bond. The presence of only one signal in the ^{31}P NMR spectrum of compound **27** is not in accordance with the structure proposed, but that is probably due to some rapid exchange process and/or to dissociation.

The ^1H and ^{13}C NMR spectra of the derivatives **15–21** exhibit only one resonance instead of the two expected for the protons and carbons in 3 and 5 positions. This is due to a fluxional behaviour of these compounds, which probably requires a concomitant prototropy and metallotropy of the ligand.[25] On cooling the CD_2Cl_2 solutions of these complexes, changes in the NMR spectra occur: at *ca* 250 K the resonance due to 3 and 5 positions broadens and at *ca* 223 K collapses. At temperatures below 200 K the metal/proton "shuttling" between the two nitrogen sites is slow enough to allow the observations of two well-separated signals (Fig. 3) (for example the signals of C3 and C5 in the ^{13}C spectrum of **18** fall at *ca* 140.0 and 148.3 ppm respectively).

*Description of the molecular structure of nitrato bis(tri-*p*-tolyphosphine)copper(I)*

The crystal structure consists of discrete molecules of nitratobis(tri-*p*-tolyphosphine)copper(I) separated by van der Waals distances.

The molecular structure of the title compound is shown in Fig. 4. The relevant bond distances and angles are reported in Table 5. This compound is monomeric with four-coordinated copper in the solid state. The copper atom is in a strongly distorted tetrahedral environment [O1—Cu—O2 and P1—Cu—P2 are 56.2(4) and 128.0(1)° respectively]. The nitrate anion acts as bidentate ligand with Cu—O distances [Cu—O2: 2.184(9) Å and Cu—O1: 2.217(9) Å] longer than the sum (*ca* 1.83 Å) of the covalent radii of O and copper(I), suggesting poor coordination of the nitrate, whereas the Cu—P distances [2.254(3) and 2.252(3)] are normal. The long Cu—N distance [2.61(2) Å] precludes any bonding interaction between these two atoms. There are two different sets of Cu—P—C bond angles [116.8(4), 116.4(3), 116.7(3), 117.9(4)

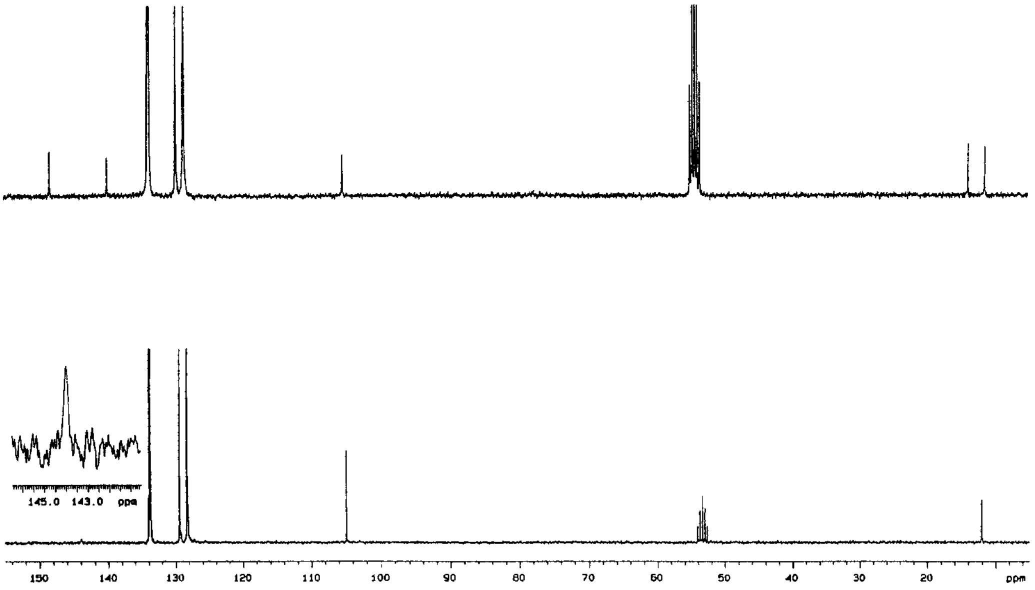


Fig. 3. ^{13}C NMR spectra of $CuCl(PPh_3)_2(pz'H)$, 18, at 298 and 193 K.

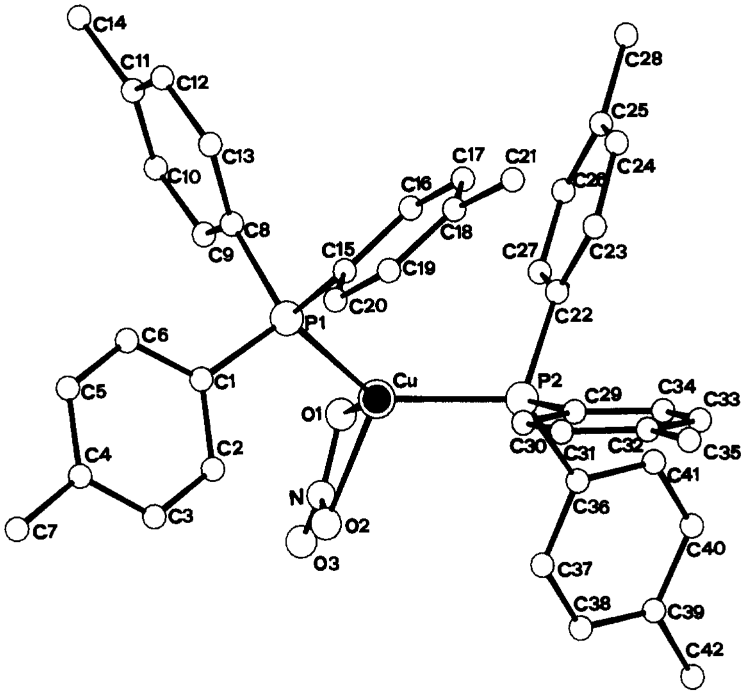


Fig. 4. Molecular structure and labelling scheme for $CuNO_3[P(p\text{-tolyl})_3]_2$.

and 108.0(3) and 110.2(3)°] in accordance with the non-equivalence of the phenyl rings found also in the ^{1}H and ^{13}C NMR spectra in $CDCl_3$ solution where two sets of aromatic methyls are observed.

The small differences with respect to the similar $Cu(NO_3)(Ph_3P)_2$,[26] [for example in this compound the P—Cu—P angle is 131.2(1) and both the Cu—O distances are 2.22(1) Å] are probably of electronic origin caused by the presence in the phenyl ring of an electron-releasing group such as the methyl, which makes the phosphine ligand more basic, whereas the differences are more evident with respect to other pseudotetrahedral copper(I) derivatives as $Cu(NO_3)(Cy_3P)_2$[27] and Cu(hfac) $(Cy_3P)_2$[28] (hfac = hexafluoroacetylacetonate), containing sterically hindered groups as Cy_3P and

Table 5. Selected bond distances (Å) and bond angles (°) with e.s.d.s in parentheses

Cu—P (1)	2.254 (3)	P (1)—C (1)	1.786 (12)
Cu—P (2)	2.252 (3)	P (1)—C (8)	1.799 (14)
Cu—O (1)	2.217 (9)	P (1)—C (15)	1.798 (13)
Cu—O (2)	2.184 (9)	P (2)—C (22)	1.788 (12)
N—O (1)	1.238 (23)	P (2)—C (29)	1.807 (9)
N—O (2)	1.228 (14)	P (2)—C(36)	1.819 (9)
N—O (3)	1.161 (20)		
Cu—P (1)—C (1)	116.8 (4)	P (1)—Cu—P (2)	128.0 (1)
Cu—P (1)—C (8)	116.4 (3)	C (1)—P (1)—C (8)	103.5 (5)
Cu—P (1)—C (15)	110.2 (3)	C (1)—P (1)—C (15)	103.8 (5)
Cu—P (2)—C (22)	108.0 (3)	C (8)—P (1)—C (15)	104.7 (6)
Cu—P (2)—C (29)	116.7 (3)	C (22)—P (2)—C (29)	104.9 (6)
Cu—P (2)—C (36)	117.9 (4)	C (22)—P (2)—C (36)	103.7 (5)
P (1)—Cu—O (1)	117.2 (3)	C (29)—P (2)—C (36)	104.2 (4)
P (2)—Cu—O (1)	104.9 (3)	O (1)—N—O (2)	114 (1)
P (1)—Cu—O (2)	116.4 (2)	O (1)—N—O (3)	125 (1)
P (2)—Cu—O (2)	111.9 (2)	O (2)—N—O (3)	121 (1)
O (1)—Cu—O (2)	56.2 (4)		

hfac, or with respect to $Cu(BH_4)(Ph_3P)_2$[29] where probably a delocalized bonding between the copper atom and the borohydride group is present.

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Supplementary material available

Tables of observed and calculated structure factors, anisotropic thermal parameters for non-hydrogen atoms, tables of atomic coordinates and isotropic thermal parameters, as well as hydrogen parameters, are available as supplementary material.

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