PERGAMON

Polyhedron 18 (1999) 1941–1951

POLYHEDRON

Synthesis and characterization of derivatives of copper(I) with *N*- and *S*-donor ligands

V. Imidazole and imidazoline-2(3*H*)-thione derivatives

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Received 5 February 1999; accepted 15 March 1999

Abstract

New copper(I) complexes of the type $[(PBz_3)L_3Cu]X$, $(PBz_3)L_2CuX$, $[(PBz_3)_2L_2Cu]X$, $[(PBz_3)_3LCu]X$ (L=monodentate *N*-donor imidazole- or pyrazole-type ligand, Bz=benzyl, $X=NO_3$ or ClO_4), $(PBz_3)_y(N\text{-}N)_xCuNO_3$ (N-N=bis(pyrazol-1-yl)methane, $x=y=1$; N-N=bis(1,2,4-triazol-1-yl)methane, $x=y=2$), $(PPh_3)L'_2CuX$, $(PPh_3)_2L'CuX$, $[(PPh_3)L'_3Cu]X$ and $(PPh_3)L'CuX$, (L′=monodentate *S*-donor 1-methyl-imidazoline-2(3*H*)-thione or imidazoline-2(1,3*H*)-thione) were obtained from the reaction of $(PR_3)_nCuX$ with the appropriate *N*- or *S*-donor ligand. Reaction between $[(PPh_3)_nCu(L)_m]X$ with PBz_3 often resulted in the formation of new $[(PBz_3)_zL_{m-1}Cu]X$ ($z=n$ or $n+1$) complexes upon displacement of one molecule of L and two or three molecules of PPh_3, whereas reaction of $[(N\text{-}N)_2Cu]ClO_4$ with PBz_3 and 1,10-phenanthroline (Phen) yielded $[(PBz_3)_2CuClO_4]$ and $[(Phen)_2Cu]ClO_4$, respectively, upon displacement of both molecules of bidentate chelating ligands. No reaction occurred between $(PPh_3)L'_2CuX$, $(PPh_3)_2L'CuX$ or $[(PPh_3)L'_3Cu]X$ and PBz_3. All the derivatives obtained were characterized by IR spectroscopy, ^1H NMR, and conductance studies, and in some cases also by molecular weight measurements.

Keywords: Copper(I); *N*-donor ligand; *S*-donor ligand; IR spectroscopy

1. Introduction

Coordination compounds of copper(I) containing mono- or bi-dentate *N*-donor ligands have been extensively investigated in recent years [1–7]. This class of derivatives is often very interesting due to their relevant structural features [8–13] and their potential application in catalysis, [14–16] CVD techniques, [17–19] and also in the study of redox-active copper containing proteins [20–23].

In a series of studies [24–26] involving the reactivity of the triorganophosphinocopper(I)-nitrato, -halide and -perchlorato complexes of *N*-donor ligands, we found that from the interaction of $(PR_3)_nCuX$ (R=phenyl or cyclohexyl, $n=1$–4, X=Cl, Br, I, NO_3 or ClO_4) with azole ligands L, complexes with different nuclearity, stoichiometry and geometry could be obtained depending on the steric hindrance and pK_a of phosphorus donor PR_3, basicity and steric requirements of the azole type *N*-donor ligand L, and finally on the nature of the counter-ion. For example, we found that compounds of empirical formula PR_3(imidazole)CuX are often dinuclear when X is halide, whereas all the perchlorato derivatives are in general ionic, the ClO_4 group often being strongly hydrogen bonded to the azole ligand [26].

Along this line of research, many dimeric, tetrameric and polymeric adducts with heterocyclic thione as ligands have been synthesized and structurally characterized [27–33]. In fact heterocyclic thiones represent more accurately the thioamido moieties present in the proximity of copper within biological media, but no systematic studies on mononuclear [34] copper(I) complexes of heterocyclic thiones has been reported. The present study marks the completion of our research on the vast series of the above-mentioned azole-phosphino copper(I) compounds, we report on the synthesis and characterization of new triphenylphosphino copper(I) complexes of imidazoline-2(3*H*)-thiones.

In addition, until now the data reported in the literature has been limited to triphenyl- (PPh_3) and tricyclohexylphosphine (PCy_3) derivatives, no study has been reported on the interaction of azole with tribenzylphosphinecop-

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0277-5387/99/$ – see front matter

PII: S0277-5387(99)00089-3

per(I) acceptors. The tribenzylphosphine ligand (PBz_3) is more basic and more hindered than PPh_3, and less basic and less hindered than PCy_3, therefore we decided to extend our study to the interaction of PBz_3 with Cu(I) and different classes of azoles, with the aim to obtain complexes with new stoichiometries, nuclearity, and spectroscopic and structural properties.

2. Experimental section

All solvents were dried by standard techniques. All operations were carried out under an atmosphere of dinitrogen. 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 CHNSO-elemental analyser. IR spectra from 4000 to 150 cm^{-1} were recorded with a Perkin-Elmer System 2000 FT-IR instrument. ^1H and ^{31}P NMR spectra were recorded on a VXR-300 Varian Spectrometer operating at room temperature (300 for ^1H and 121.4 MHz for ^{31}P, respectively). Melting points were taken on an IA 8100 Electrothermal instrument. The electrical resistance of solutions were measured with a Crison CDTM conductimeter at room temperature. Molecular weight determinations were performed with a Knauer membrane osmometer. (Caution. The perchlorato derivatives reported in this paper may explode by shock or heating when dry. Small quantities (≤0.5 g) of the dry products should be handled with all possible precaution).

2.1. Synthesis of the ligands

The donors bis(pyrazol-1-yl)methane, bis(1,2,4-triazol-1-yl)methane and bis(3,5-dimethylpyrazol-1-yl)methane were prepared according to previously published methods [35,36]. Imidazole (ImH), 1-methylimidazole (1-Meim), 2-methylimidazole (2-MeimH), 1-benzylimidazole (1-Bzim), 4-phenylimidazole (4-PhimH), benzoimidazole (BzimH), pyrazole (pzH), 1-methyl-imidazoline-2(3*H*)-thione (Hmimt) or imidazoline-2(1,3*H*)-thione) (Himt), triphenylphosphine (PPh_3), tricyclohexylphosphine (PCy_3), tribenzylphosphine (PBz_3), 1,10-phenanthroline (Phen) were purchased from Aldrich.

2.2. Synthesis of the copper(I) complexes

2.2.1. Nitratobis(tribenzylphosphine)copper(I)

PBz_3 (5.0 g, 16.6 mmol) in warm methanol (30 ml) was treated with $Cu(NO_3)_2 \cdot 2.5H_2O$ (1.0 g, 4.3 mmol) in methanol. The copper salt dissolved immediately and the blue color of the solution was discharged within 5 min. The solution was heated at reflux for 24 h and then stirred at room temperature for 3 h. A colorless precipitate was formed which was filtered off and washed with methanol (2×5 ml) and diethyl ether (2×5 ml) (95% yield). M.p. 177–180°C dec. Found: C, 68.3; H, 6.1; N, 2.1. Calc. for $C_{42}H_{42}CuNO_3P_2$, C, 68.7; H, 5.8; N, 1.9. IR (nujol, cm^{-1}): 1956w, 1882w, 1816w, 1756w, 1694w, 1417s, 1317s, 849s, 717s, 699s $\nu_{(NO_3)}$, 481m (Ph), 360m, 352vw, 308m, 280w. ^1H NMR ($CDCl_3$): δ, 3.0 (d, 12H, PCH_2), 7.0–7.4 (m br, 30H, C_6H_5).

2.2.2. Perchloratobis(tribenzylphosphine)copper(I)

$(PBz_3)_2CuClO_4$ was prepared by the same procedure as $(PBz_3)_2CuNO_3$ by using 5.0 g of PBz_3 and 2.07 g of $Cu(ClO_4)_2 \cdot 6H_2O$; and re-crystallized from methanol (2×10 ml) (80% yield). M.p. 244–248°C dec. Found: C, 65.6; H, 6.0. Calc. for $C_{42}H_{42}CuClO_4P_2$, C, 65.4; H, 5.5. IR (nujol, cm^{-1}): 3110w, 3060w $\nu_{(CH)}$, 1599w, 1581w $\nu_{(C\cdots C)}$, 1089s br, 622s (ClO_4), 484s (Ph) 382w, 346w, 309w, 284w. ^1H NMR ($CDCl_3$): δ, 2.9 (br, 12H, PCH_2), 7.0–7.3 (m br, 30H, C_6H_5).

2.2.3. Tetrafluoroboratetetrakis(triphenylphosphine)copper(I)

$(PPh_3)_4CuBF_4$ was prepared by the same procedure as $(PBz_3)_2CuNO_3$ by using 21.0 g of PPh_3 and 2.9 g of $Cu(BF_4)_2 \cdot xH_2O$; and re-crystallized from ethanol (2×10 ml) (90% yield). M.p. 143–144°C dec. Found: C, 71.9; H, 4.8. Calc. for $C_{72}H_{60}CuBF_4P_4$, C, 72.1; H, 5.0. IR (nujol, cm^{-1}): 3054w $\nu_{(CH)}$, 1964w, 1888w, 1812w, 1759w $\nu_{(BF_4)}$, 1583w $\nu_{(C\cdots C)}$, 1052s $\nu_{(BF_4)}$, 523m, 499m (Ph), 429w, 398w. ^1H NMR ($CDCl_3$): δ, 7.0–7.4 (m br, 60H, C_6H_5).

2.2.4. Thiocyanatebis(triphenylphosphine)copper(I), nitratebis(triphenylphosphine)copper(I), nitratebis(tricyclohexylphosphine)copper(I), perchloratetetrakis(triphenylphosphine)copper(I), bromotris-(triphenyl-phosphine)copper(I)

The above compounds were prepared according to previously published studies [37–42].

*[$(PBz_3)(ImH)_3Cu]NO_3 \cdot Et_2O$, **1**.* Imidazole (ImH) (0.27 g, 4.0 mmol) was added to a diethyl ether suspension (30 ml) of [$(PBz_3)_2CuNO_3$] (0.734 g, 1.0 mmol). After 3 h stirring, the solid was filtered and washed with diethyl ether, affording compound **1** (0.616 g, 0.87 mmol) (87% yield). M.p. 165–168°C dec. Found: C, 57.7; H, 5.8; N, 13.4. Calc. for $C_{34}H_{43}CuN_7PO_4$, C, 57.7; H, 6.1; N, 13.8. IR (nujol, cm^{-1}): 3250–2800 br $\nu_{(NH)}$, 1950w, 1881w, 1759w, 1694w, 1350s (br), 835m, 703s $\nu_{(NO_3)}$, 480m (Ph), 385vw, 352vw, 305vw, 292w. ^1H NMR (CD_3CN): δ, 2.99 (d, 6H, PCH_2), 5.2 (br, 3H, NH_{ImH}), 6.9 (br, 3H, CH_{ImH}), 7.0–7.3 (m, 15H, C_6H_5), 7.6 (br, 6H, CH_{ImH}). Λ_m (CH_3CN, $c=0.94\times10^{-3}$ M): 129.4 $\Omega^{-1}cm^2\ mol^{-1}$.

*[$(PBz_3)_2(2\text{-}MeimH)_2Cu]NO_3$, **2**.* Complex **2** was prepared by the same procedure as **1** by using 2.0 mmol of 2-methylimidazole (2-MeimH) and 1.0 mmol of [$(PBz_3)_2CuNO_3$] (82% yield). M.p. 137°C dec. Found: C, 66.3; H, 6.0; N, 7.6. Calc. for $C_{50}H_{54}CuN_5O_3P_2$, C, 66.8; H, 6.1; N, 7.8. IR (nujol, cm^{-1}): 3200br $\nu_{(NH)}$ 1957w,

1886w, 1815w, 1716w, 1690w, 1350s (br), 850s, 841s, 699s $\nu_{(NO_3)}$, 482m (Ph), 386vw, 351vw, 305vw, 309w. ^{1}H NMR (CD_3CN): δ, 2.1 (s, 6H, CH_3), 3.0 (d, 12H, PCH_2), 7.0–7.2 (m br 12H, C_6H_5), 7.4 (m, 22H, $C_6H_5+CH_{2\text{-MeimH}}$). ^{1}H NMR ($CDCl_3$): δ, 2.0 (br, 6H, CH_3), 2.9 (s br, 12H, PCH_2) 6.6 (br, 2H, $CH_{2\text{-MeimH}}$), 6.9–7.4 (m, 34H, $C_6H_5+CH_{2\text{-MeimH}}$). Λ_m (CH_3CN, $c=0.98\times10^{-3}$ M): 161.7 $\Omega^{-1}cm^2\ mol^{-1}$. M.W. ($CHCl_3$, $c=0.5\times10^{-3}$ M): 341.

[(PBz$_3$)$_2$(1-Meim)$_2$Cu]NO$_3$, ***3***. Complex **3** was prepared by the same procedure as **1** by using 4.0 mmol of 1-methylimidazole (1-Meim) and 1.0 mmol of [(PBz_3)$_2$$CuNO_3$] (82% yield). M.p. 170–175°C. Found: C, 66.5; H, 6.1; N, 7.4. Calc. for $C_{50}H_{54}CuN_5O_3P_2$, C, 66.8; H, 6.1; N, 7.8. IR (nujol, cm^{-1}): 3114w $\nu_{(CH)}$, 1950w, 1890w, 1820w, 1738w, 1682w, 1330br, 850sh, 844br, 701s $\nu_{(NO_3)}$, 1598, 1532 ($C\overset{\cdots}{—}C$, $C\overset{\cdots}{—}N$), 482m (Ph), 392w, 351w, 308w. ^{1}H NMR (CD_3CN): δ, 2.9 (s br, 12H, PCH_2), 3.6 (br, 6H, N-CH_3), 6.6 (br, 2H, $CH_{1\text{-Meim}}$) 6.8 (br, 2H, $CH_{1\text{-Meim}}$), 6.8 (m, 12H, C_6H_5), 7.3 (m, 18H, C_6H_5), 7.6 (br, 2H, $CH_{1\text{-Meim}}$). Λ_m (CH_3CN, $c=1.09\times10^{-3}$ M): 175.2 $\Omega^{-1}cm^2\ mol^{-1}$. M.W. ($CHCl_3$, $c=0.9\times10^{-3}$ M): 448.

(PBz$_3$)(4-PhimH)$_2$CuNO$_3$, ***4***. Complex **4** was obtained by the same procedure as **1** by using 2.0 mmol of 4-phenylimidazole (4-PhimH) and 1.0 mmol of [(PBz_3)$_2$$CuNO_3$] (56% yield). M.p. 117–119°C. Found: C, 64.7; H, 5.4; N, 9.4. Calc. for $C_{39}H_{37}CuN_5O_3P$, C, 65.2; H, 5.2; N, 9.7. IR (nujol, cm^{-1}): 3120 br $\nu_{(NH)}$, 1946w, 1883w, 1812w, 1750w, 1409s, 1377s, 1317s, 860m, 834d br, 701s, 690sh $\nu_{(NO_3)}$, 1599m, 1587m $\nu_{(C\cdots C)}$, 482m (Ph), 439m ($Ph_{4\text{-PhimH}}$), 352w, 309w. ^{1}H NMR (CD_3CN): δ, 3.0 (d, 6H, PCH_2), 7.0 (m, 6H, C_6H_5), 7.2 (m, 6H, C_6H_5), 7.4 (br, 9H, $CH_{4\text{-PhimH}}+C_6H_{5_{4\text{-PhimH}}}$), 7.7 (br, 8H, $CH_{4\text{-PhimH}}+C_6H_{5_{4\text{-PhimH}}}$). Λ_m (CH_3CN, $c=0.91\times10^{-3}$ M): 136.3 $\Omega^{-1}cm^2\ mol^{-1}$.

(PBz$_3$)(BzimH)$_2$CuNO$_3$, ***5***. Complex **5** was prepared by the same procedure as **1** by using 2.0 mmol of benzimidazole (BzimH) and 1.0 mmol of [(PBz_3)$_2$$CuNO_3$] (99% yield). M.p. 160°C dec. Found: C, 63.6; H, 5.4; N, 10.6. Calc. for $C_{35}H_{33}CuN_5O_3P$, C, 63.1; H, 5.0; N, 10.5. IR (nujol, cm^{-1}): 3184br $\nu_{(NH)}$, 1940w br, 1890w br, 1779w, 1734w, 1418m, 1374br, 1350br, 839m, 826w, 705s, 698s $\nu_{(NO_3)}$ 1622m, 1597m $\nu_{(C\cdots C)}$, 477m (Ph), 389w, 358w, 311w, 279w. ^{1}H NMR (CD_3CN): δ, 3.0 (d, 6H, PCH_2), 4.7 (br, 2H, NH_{BzimH}), 7.0–7.1 (m, 8H, C_6H_5), 7.2–7.4m (m, 12H, $C_6H_5+C_6H_{5_{BzimH}}$), 7.6 (br, 3H, CH_{BzimH}), 8.0 (br, 2H, CH_{BzimH}). Λ_m (CH_3CN, $c=0.86\times10^{-3}$ M): 112.6 $\Omega^{-1}cm^2\ mol^{-1}$.

(PBz$_3$)(1-Bzim)$_2$CuNO$_3$·H$_2$O, ***6***. Complex **6** was prepared by the same procedure as **1** by using 4.0 mmol of 1-benzylimidazole (1-Bzim) and 1.0 mmol of [(PBz_3)$_2$$CuNO_3$] (94% yield). M.p. 149–152°C. Found: C, 63.8; H, 5.7; N, 9.5. Calc. for $C_{41}H_{43}CuN_5O_4P$, C, 64.4; H, 5.7; N, 9.2. IR (nujol, cm^{-1}): 3400br $\nu_{(O-H)}$, 3137w $\nu_{(NH)}$, 1944w, 1890w, 1810w, 1750w, 1684w, 1417m, 1350br, 840m, 823m, 705sh, 696s $\nu_{(NO_3)}$, 1599m, 1581m, 1559w $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 478s (Ph), 386w, 359w, 319w, 305w. ^{1}H NMR (CD_3CN): δ, 2.3 (br, 2H, OH), 3.0 (d, 6H, PCH_2), 5.18 (s, 4H, N–CH_2), 7.11 (m, 6H, $CH_{1\text{-Bzim}}+C_6H_5$), 7.2 (m, 12H, C_6H_5), 7.3 (m, 8H, $CH_{1\text{-Bzim}}+C_6H_5$). Λ_m (CH_3CN, $c=1.03\times10^{-3}$ M): 115.6 $\Omega^{-1}cm^2\ mol^{-1}$.

[(PBz$_3$){bis(pyrazol-1-yl)methane}Cu]NO$_3$, ***7***. Complex **7** was prepared by the same procedure as **1** by using 5.0 mmol of bis(pyrazol-1-yl)methane and 1.0 mmol of [(PBz_3)$_2$$CuNO_3$] (58% yield). M.p. 172–177.°C dec. Found: C, 58.7; H, 5.3; N, 11.8. Calc. for $C_{28}H_{29}CuN_5O_3P$, C, 58.2; H, 5.1; N, 12.1. IR (nujol, cm^{-1}): 3126w $\nu_{(NH)}$, 1948w, 1887w, 1815w, 1760w, 1317br, 868m, 823m, 702s $\nu_{(NO_3)}$, 1599m, 1581w, 1557w, 1514w $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 483s (Ph), 414w, 386m, 361w, 305w, 288w. ^{1}H NMR (CD_3CN): δ, 2.99 (br, 6H, PCH_2), 6.60 (br, 2H, $CH_{2_{N\text{-}N}}$), 6.80 (br, 2H, $CH_{N\text{-}N}$), 7.00 (m, 6H, C_6H_5), 7.3 (m, 11H, $C_6H_5+CH_{N\text{-}N}$), 7.6 (br, 2H, $CH_{N\text{-}N}$). Λ_m (CH_3CN, $c=0.98\times10^{-3}$ M): 182.6 $\Omega^{-1}cm^2\ mol^{-1}$.

[(PBz$_3$)$_2${bis(1,2,4-triazol-1-yl)methane}$_2$Cu]NO$_3$, ***8***. Complex **8** was prepared by the same procedure as **1** by using 3.0 mmol of bis(1,2,4-triazol-1-yl)methane and 1.0 mmol of [(PBz_3)$_2$$CuNO_3$] (34% yield). M.p. 170°C dec. Found: C, 60.5; H, 5.4; N, 17.8. Calc. for $C_{52}H_{54}CuN_{13}O_3P_2$, C, 60.4; H, 5.3; N, 17.6. IR (nujol, cm^{-1}): 3111w $\nu_{(CH)}$, 1950w, 1883w, 1812w, 1748w, 1345m, 1320m, 850m, 700m $\nu_{(NO_3)}$, 1597m, 1580w, 1557w, 1506w $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 483m (Ph), 392w, 385w, 351w, 309m. ^{1}H NMR (CD_3CN): δ, 2.9 (br, 12H, PCH_2), 6.5 (s, 4H, $CH_{2_{N\text{-}N}}$), 7.0 (m, 12H, C_6H_5), 7.2–7.3 (m, 18H, C_6H_5), 7.8 (s, 4H, $CH_{N\text{-}N}$), 8.49 (s, 4H, $CH_{N\text{-}N}$). Λ_m (CH_3CN, $c=1.96\times10^{-3}$ M): 109 $\Omega^{-1}cm^2\ mol^{-1}$.

[(PBz$_3$)$_2$(pzH)Cu]NO$_3$·H$_2$O, ***9***. Complex **9** was prepared by the same procedure as **1** by using 4.0 mmol of pyrazole (pzH) and 1.0 mmol of [(PBz_3)$_2$$CuNO_3$] (98% yield). M.p. 180–184°C. Found: C, 65.8; H, 5.8; N, 4.7. Calc. for $C_{45}H_{48}CuN_3O_4P_2$, C, 65.9; H, 5.4; N, 5.1. IR (nujol, cm^{-1}): 3200–2800br $\nu_{(NH)}$, 3053w $\nu_{(C-H)}$, 1955w, 1890w, 1807w, 1738w, 1308br, 850m, 701m $\nu_{(NO_3)}$, 1633 (O–H), 1598m, 1580w, 1577w $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 483s, 351w, 308m. ^{1}H NMR (CD_3CN): δ, 2.9 (br, 12H, PCH_2), 3.2 (br, 2H, H_2O), 6.6 (br, 1H, CH_{pzH}), 7.0 (m, 12H, C_6H_5), 7.2 (m, 18H, C_6H_5), 7.7 (br, 2H, CH_{pzH}). ^{1}H NMR ($CDCl_3$): δ, 3.0 (d, 12H, PCH_2), 6.0–7.0 (br, 1H, CH_{pzH}), 7.0–7.4 (br, 32H, $C_6H_5+CH_{pzH}$). Λ_m (CH_3CN, $c=0.99\times10^{-3}$ M): 130.4 $\Omega^{-1}cm^2\ mol^{-1}$.

[(PBz$_3$)$_2$(ImH)$_2$Cu]ClO$_4$, ***10***. Complex **10** was prepared by the same procedure as **1** by using 4.0 mmol of ImH and 1.0 mmol of (PBz_3)$_2$$CuClO_4$ (40% yield). M.p. 160–165°C. Found: C, 62.3; H, 5.6; N, 6.1. Calc. for

$C_{48}H_{50}ClCuN_4O_5P_2$, C, 62.3; H, 5.7; N, 6.1. IR (nujol, cm^{-1}): 3258 $\nu_{(NH)}$, 3128w, 3098w, 3028w $\nu_{(CH)}$, 1955mbr, 1884w, 1812w, 1762w, 1160–1050br, 623s $\nu_{(ClO_4)}$, 1600m, 1584w, 1538w $\nu_{(C\overset{\cdots}{-}C)}$ and $\nu_{(C\overset{\cdots}{-}N)}$, 482s (Ph), 389m, 352w, 337w, 305m, 297sh, 256w. ^{1}H NMR (CD_3CN): compound **10** is completely dissociated in CD_3CN solution and for this reason we observed in this solvent only the signal of $Bz_3P{=}O$ and PBz_3. ^{1}H NMR ($CDCl_3$): δ, 3.1 (d, 12H, PCH_2), 6.9 (s, 2H, CH_{ImH}), 7.0 (br, 4H, CH_{ImH}), 7.1–7.3 (br, 30H, C_6H_5). Λ_m (CH_3CN, $c=0.88\times10^{-3}$ M): 172.7 $\Omega^{-1}cm^2\ mol^{-1}$.

*$[(PBz_3)_2(2\text{-}MeimH)_2Cu]ClO_4\cdot 2H_2O$, **11**.* Complex **11** was prepared by the same procedure as **1** by using 2.0 mmol of 2-MeimH and 1.0 mmol of $(PBz_3)_2CuClO_4$ (90% yield). M.p. 180°C dec. Found: C, 61.6; H, 6.0; N, 5.4. Calc. for $C_{50}H_{58}ClCuN_4O_6P_2$, C, 61.8; H, 6.0; N, 5.8. IR (nujol, cm^{-1}): 3500–3000br (N–H), 1958m (br), 1887m, 1810m, 1776m, 1150–1050br, 621s (ClO_4), 1626br OH, 1599m, 1581w, 1567m $\nu_{(C\overset{\cdots}{-}C)}$ and $\nu_{(C\overset{\cdots}{-}N)}$, 482s (Ph), 387m, 348w, 304m, 282w, 272w. ^{1}H and ^{31}P NMR (CD_3CN): compound **11** is completely dissociated in CD_3CN solution and it is possible only to observe the signal of $Bz_3P{=}O$ (δ $^{31}P=41.3$) and PBz_3 (δ $^{31}P=-11.8$). Λ_m (CH_3CN, $c=0.87\times10^{-3}$ M): 196.5 $\Omega^{-1}cm^2\ mol^{-1}$. M.W. ($CHCl_3$, $c=0.8\times10^{-3}$ M): 658.

*$[(PBz_3)(1\text{-}Meim)_3Cu]ClO_4\cdot Et_2O$, **12**.* Complex **12** was prepared by the same procedure as **1** by using 6.0 mmol of 1-Meim and 1.0 mmol of $(PBz_3)_2CuClO_4$ (81% yield). M.p. 185°C dec. Found: C, 56.0; H, 5.7; N, 10.3. Calc. for $C_{37}H_{49}ClCuN_6O_5P$, C, 56.4; H, 6.3; N, 10.7. IR (nujol, cm^{-1}): 3120w (N–H), 1950w, 1890w, 1815w, 1774w, 1150–1050br, 618s $\nu_{(ClO_4)}$, 1599m, 1581w, 1534m, 1518m $\nu_{(C\overset{\cdots}{-}C)}$ and $\nu_{(C\overset{\cdots}{-}N)}$, 482s (Ph), 385m, 352w, 304w, 268w, 230w. ^{1}H NMR (CD_3CN): δ, 3.0 (br, 6H, PCH_2), 3.6 (br, 9H, N–CH_3), 7.0 (m, 6H, C_6H_5), 7.2 (m, 9H, C_6H_5). Λ_m (CH_3CN, $c=0.98\times10^{-3}$ M): 168.9 $\Omega^{-1}cm^2\ mol^{-1}$. M.W. ($CHCl_3$, $c=0.6\times10^{-3}$ M): 388.

*$[(PBz_3)_3(4\text{-}PhimH)Cu]ClO_4\cdot Et_2O$, **13**.* Tribenzylphosphine (0.6 g, 2.0 mmol) in diethyl ether was added to a diethyl ether suspension of $[(PPh_3)_2Cu(4\text{-}PhimH)_2]ClO_4$ (0.90 g, ~1.0 mmol) as previously prepared according to the literature [26]. The suspension was stirred for 2 days, and then filtered off, washed with diethyl ether, affording compound **13** (90% yield). M.p. 158–160°C dec. Found: C, 70.9; H, 6.1; N, 2.1. Calc. for $C_{76}H_{81}ClCuN_2O_4P_3$, C, 71.4; H, 6.4; N, 2.2. IR (nujol, cm^{-1}): 3277br $\nu_{(N-H)}$, 3040w $\nu_{(C-H)}$, 1966w, 1888w, 1823w, 1772w, 1121br, 1091br, 1065br, 623s $\nu_{(ClO_4)}$, 1611w, 1601m, 1584w, 1558w, 1540w $\nu_{(C\overset{\cdots}{-}C)}$ and $\nu_{(C\overset{\cdots}{-}N)}$, 485s, 438w, 414w, 386m, 348w, 310w. ^{1}H NMR ($CDCl_3$): δ, 3.1 (d, 18H, PCH_2), 7.1 (s, 2H, $CH_{4\text{-}PhimH}$), 7.2–7.5 (m, 45H, C_6H_5), 7.5–8.0 (m, 4H, $CH_{4\text{-}PhimH}$), 8.3 (br, 4H, $CH_{4\text{-}PhimH}$). Λ_m (CH_3CN, $c=0.96\times10^{-3}$ M): 64.7 $\Omega^{-1}cm^2\ mol^{-1}$.

*$[(PBz_3)_2(1\text{-}Bzim)_2Cu]ClO_4\cdot 2H_2O$, **14**.* Complex **14** was prepared by the same procedure as **13** by using 2 mmol of tribenzylphosphine and 1 mmol of $[(PPh_3)Cu(1\text{-}Bzim)_3]ClO_4$ as previously prepared according to the literature [26] (90% yield). M.p. 169–170°C dec. Found: C, 66.6; H, 5.9; N, 4.8. Calc. for $C_{62}H_{66}ClCuN_4O_5P_2$, C, 66.2; H, 5.9; N, 5.0. IR (nujol, cm^{-1}): 3500br $\nu_{(O-H)}$, 3040w $\nu_{(C-H)}$, 1952w, 1888w, 1819w, 1772w, 1130–1050br, 621s $\nu_{(ClO_4)}$, 1598m, 1580w, 1558w, 1517m, 1512m $\nu_{(C\overset{\cdots}{-}C)}$ and $\nu_{(C\overset{\cdots}{-}N)}$, 479m, 392w, 316w, 301w. ^{1}H NMR ($CDCl_3$): δ, 1.9 (br, 4H, OH), 2.9 (s (br) 12H, PCH_2), 5.2 (br, 4H, NCH_2), 6.9 (m, 12H, $CH_{1\text{-}Bzim}+C_6H_5$), 7.2 (m, 22H, $CH_{1\text{-}Bzim}+C_6H_5$), 7.3 (m, 12H, $CH_{1\text{-}Bzim}+C_6H_5$). Λ_m (CH_3CN, $c=1.03\times10^{-3}$ M): 139.4 $\Omega^{-1}cm^2\ mol^{-1}$.

*$[(PBz_3)_2(BzimH)Cu]ClO_4\cdot Et_2O$, **15*** Complex **15** was prepared by the same procedure as **13** by using 2 mmol of tribenzylphosphine and 1 mmol of $[(PPh_3)_2\text{-}Cu(BzimH)_2]ClO_4$ as previously prepared according to the literature [26] (88% yield). M.p. 240–250°C dec. Found: C, 65.8; H, 5.8; N, 2.4. Calc. for $C_{53}H_{58}ClCuN_2O_5P_2$, C, 66.0; H, 6.0; N, 2.9. IR (nujol, cm^{-1}): 3200–2800br $\nu_{(N-H)}$, 3050w $\nu_{(C-H)}$, 1960w, 1888w, 1817w, 1765w, 1621w, 1599m, 1581w, 1557w $\nu_{(C\overset{\cdots}{-}C)}$ and $\nu_{(C\overset{\cdots}{-}N)}$, 1140–1050br $\nu_{(ClO_4)}$, 621s $\nu_{(ClO_4)}$, 484m, 431w, 427w, 395w, 384w, 346w, 309w, 280w. ^{1}H NMR ($CDCl_3$): δ, 3.0 (d, 12H, PCH_2), 7.0 (m, 2H, CH_{BzimH}), 7.2–7.3 (m, 30H, C_6H_5), 7.4–7.7 (m, 4H, CH_{BzimH}). Λ_m (CH_3CN, $c=1.06\times10^{-3}$ M): 106.7 $\Omega^{-1}cm^2\ mol^{-1}$.

*$[(PPh_3)(Himt)_2Cu]ClO_4$, **16**.* Complex **16** was prepared the same procedure as **1** by using 2 mmol of Himt and 1 mmol of $[(PPh_3)_4Cu]ClO_4$ (48% yield). M.p. 216–218°C. Found: C, 45.7; H, 3.8; N, 8.8; S, 9.8. Calc. for $C_{24}H_{23}ClCuN_4O_4PS_2$, C, 46.1; H, 3.7; N, 9.0; S, 10.2. IR (nujol, cm^{-1}): 3400br $\nu_{(NH)}$, 1582m $\nu_{(C\overset{\cdots}{-}C)}$ and $\nu_{(C\overset{\cdots}{-}N)}$, 1094s, 623m $\nu_{(ClO_4)}$, 521m, 498m (Ph), 434w, 314w, 280w. ^{1}H NMR ($CDCl_3$): δ, 6.8 (s, 4H, 4-CH_{Himt} and 5-CH_{Himt}), 7.4–7.7 (m, 15H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ, -1.7 br. Λ_m (acetone, $c=1.03\times10^{-3}$ M): 73.4 $\Omega^{-1}cm^2\ mol^{-1}$.

*$[(PPh_3)(Himt)_2Cu]NO_3$, **17**.* Complex **17** was prepared by the same procedure as **1** by using 2 mmol of Himt and 1 mmol of $[(PPh_3)_2CuNO_3]$ (68% yield). Compound **17** is insoluble in acetone and CH_2Cl_2. M.p. 182–185°C. Found C, 49.0; H, 3.7; N, 11.8; S, 10.6. Calc. for $C_{24}H_{23}CuN_5O_3PS_2$, C, 49.0; H, 3.9; N, 11.9; S, 10.9. IR (nujol, cm^{-1}): 3100–2800br $\nu_{(NH)}$, 1581m $\nu_{(C\overset{\cdots}{-}C)}$ and $\nu_{(C\overset{\cdots}{-}N)}$, 1330 br, 693m $\nu_{(NO_3)}$. ^{1}H NMR ($CDCl_3$): δ, 6.6 (s, 4H, 4-CH_{Himt} and 5-CH_{Himt}), 7.2–7.6 (m, 15H, C_6H_5).

*$[(PPh_3)(Himt)_2Cu]BF_4$, **18**.* Complex **18** was prepared by the same procedure as **1** by using 4 mmol of Himt and 1 mmol of $[(PPh_3)_4Cu]BF_4$ (55% yield). M.p. 151–156°C. Found C, 46.7; H, 3.5; N, 9.1; S, 10.3. Calc. for $C_{24}H_{23}BCuF_4N_4PS_2$, C, 47.0; H, 3.8; N, 9.1; S, 10.5. IR (nujol, cm^{-1}): 3300br $\nu_{(NH)}$, 3100w $\nu_{(CH)}$, 1583s $\nu_{(C\overset{\cdots}{-}C)}$ and $\nu_{(C\overset{\cdots}{-}N)}$, 1132s br, 1094s br, 1037s br $\nu_{(BF_4)}$, 521m,

499m (Ph), 436w, 397w, 353w, 327w, 314w, 280w. ^{1}H NMR (acetone): δ, 6.9 (s, 4H, 4-CH_{Himt} and 5-CH_{Himt}), 7.3–7.5 (m, 15H, C_6H_5), 11.1 (br, 2H, NH). Λ_m (acetone, $c=0.99\times10^{-3}$ M): 75.1 Ω^{-1}cm^2 mol^{-1}.

[(PPh$_3$)(Himt)$_2$(SCN)Cu], ***19****.* Complex **19** was prepared by the same procedure as **1** by using 2 mmol of Himt and 1 mmol of [(PPh$_3$)$_2$CuSCN] (74% yield). M.p.178–182°C. Found: C, 51.8; H, 3.7; N, 12.3; S, 16.9. Calc. for $C_{25}H_{23}CuN_5PS_3$, C, 51.4; H, 4.0; N, 12.0; S, 16.5. IR (nujol, cm^{-1}): 3250br $\nu_{(NH)}$, 2094m $\nu_{(CN)}$ 1584s $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 519s, 503s (Ph), 440w, 425w, 420w, 415w, 380w, 348m, 340m. ^{1}H NMR (DMSO-d$_6$): δ, 6.8 (s, 4H, 4-CH_{Himt} and 5-CH_{Himt}), 7.2–7.5 (m, 15H, C_6H_5), 12.0 (br, 2H, NH). Λ_m (acetone, $c=1.02\times10^{-3}$ M): 7.0 Ω^{-1}cm^2 mol^{-1}.

[(PPh$_3$)$_2$(Himt)BrCu], ***20****.* Complex **20** was prepared by the same procedure as **1** by using 2 mmol of Himt and 1 mmol of [(PPh$_3$)$_3$CuBr] (71% yield). M.p. 170–172°C. Found: C, 60.5; H, 4.6; N, 4.0; S, 4.3. Calc. for $C_{39}H_{34}BrCuN_2P_2S$, C, 61.0; H, 4.5; N, 3.6; S, 4.2. IR (nujol, cm^{-1}): 3200br $\nu_{(NH)}$, 1581s $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 524s, 516s, 503s, 491s (Ph), 442w, 426w, 419w, 334w, 340m. ^{1}H NMR (CDCl$_3$): δ, 6.6 (s, 2H, 4-CH_{Himt} and 5-CH_{Himt}), 7.2–7.5 (m, 15H, C_6H_5), 11.0 (br, 2H, NH). Λ_m (acetone, $c=1.08\times10^{-3}$ M): 0.3 Ω^{-1}cm^2 mol^{-1}.

[(PPh$_3$)(Hmimt)$_3$Cu]ClO$_4$, ***21****.* Complex **21** was prepared by the same procedure as **1** by using 2 mmol of Hmimt and 1 mmol of [(PPh$_3$)$_4$Cu]ClO$_4$ (40% yield). M.p. 125–128°C. Found: C, 46.9; H, 4.0; N, 10.9; S, 12.4. Calc. for $C_{30}H_{33}ClCuN_6O_4PS_3$, C, 46.9; H, 4.3; N, 10.9; S, 12.5. IR (nujol, cm^{-1}): 3400br $\nu_{(NH)}$, 3133w $\nu_{(CH)}$, 1569w, 1559w, 1503w $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 1090sh, 1076s, 622m $\nu_{(ClO_4)}$, 518m, 493m (Ph), 437w. ^{1}H NMR (CDCl$_3$): δ, 3.5 (s, 9H, NCH_3), 6.6 (d br, 3H, 4-CH_{Hmimt} or 5-CH_{Hmimt}), 6.8 (d br, 3H, 4-CH_{Hmimt} or 5-CH_{Hmimt}), 7.3–7.7 (m, 15H, C_6H_5), 11.0 (br, 3H, NH). Λ_m (acetone, $c=0.89\times 10^{-3}$ M): 121.3 Ω^{-1}cm^2 mol^{-1}.

[(PPh$_3$)(Hmimt)$_2$NO$_3$Cu], ***22****.* Complex **22** was prepared by the same procedure as **1** by using 2 mmol of Hmimt and 1 mmol of [(PPh$_3$)$_2$CuNO$_3$] (73% yield). M.p. 100–110°C dec. Found: C, 51.0; H, 4.3; N, 11.6; S, 10.6. Calc. for $C_{26}H_{27}CuN_5O_3PS_2$, C, 50.7; H, 4.4; N, 11.4; S, 10.4. IR (nujol, cm^{-1}): 3100–2800br $\nu_{(NH)}$, 1575w $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 1320s, 696m $\nu_{(NO_3)}$, 518m, 506m, 489m (Ph), 418w. ^{1}H NMR (CDCl$_3$): δ, 3.8 (br, 6H, NCH_3), 6.6–6.7 (d br, 2H, 4-CH_{Hmimt} or 5-CH_{Hmimt}), 7.1 (s, 2H, 4-CH_{Hmimt} or 5-CH_{Hmimt}), 7.5–8.0 (m, 15H, C_6H_5), 12.4 (br, 2H, NH). Λ_m (acetone, $c=1.0\times10^{-3}$ M): 19.3 Ω^{-1}cm^2 mol^{-1}.

[(PPh$_3$)(Hmimt)$_3$Cu]BF$_4$, ***23****.* Complex **23** was prepared by the same procedure as **1** by using 4 mmol of Hmimt and 1 mmol of [(PPh$_3$)$_4$Cu]BF$_4$ (37% yield). M.p. 130–131°C. Found: C, 47.2; H, 4.0; N, 10.8; S, 12.4. Calc. for $C_{30}H_{33}BCuF_4N_6PS_3$, C, 47.7; H, 4.4; N, 11.1; S, 12.7. IR (nujol, cm^{-1}): 3100–2700br $\nu_{(NH)}$, 1571m $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 1051s br $\nu_{(BF_4)}$, 518m, 497m (Ph), 437w, 414w. ^{1}H NMR (CDCl$_3$): δ, 3.6 (br, 9H, NCH_3), 6.7 (br, 3H, 4-CH_{Hmimt} or 5-CH_{Hmimt}), 6.8 (br, 3H, 4-CH_{Hmimt} or 5-CH_{Hmimt}), 7.2–7.8 (m, 15H, C_6H_5), 11.4 (br, 3H, NH). Λ_m (acetone, $c=0.60\times10^{-3}$ M): 124.3 Ω^{-1}cm^2 mol^{-1}.

[(PPh$_3$)(Hmimt)$_2$(SCN)Cu], ***24****.* Complex **24** was prepared by the same procedure as **1** by using 6 mmol of Hmimt and 1 mmol of [(PPh$_3$)$_2$CuSCN] (60% yield). M.p. 178–182°C. Found: C, 53.4; H, 4.3; N, 11.6; S, 15.9. Calc. for $C_{27}H_{27}CuN_5PS_3$, C, 53.0; H, 4.4; N, 11.4; S, 15.7. IR (nujol, cm^{-1}): 3200–2700br $\nu_{(NH)}$, 2095m $\nu_{(CN)}$, 1570m $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 505s (Ph), 429w, 417w, 348w. ^{1}H NMR (CDCl$_3$): δ, 3.6 (br, 6H, NCH_3), 6.7 (br, 2H, 4-CH_{Hmimt} or 5-CH_{Hmimt}), 6.8 (br, 2H, 4-CH_{Hmimt} or 5-CH_{Hmimt}), 7.3–7.8 (m, 15H, C_6H_5). Λ_m (acetone, $c=1.0\times10^{-3}$ M): 6.2 Ω^{-1}cm^2 mol^{-1}.

(PPh$_3$)(Hmimt)BrCu, ***25****.* Complex **25** was prepared by the same procedure as **1** by using 2 mmol of Hmimt and 1 mmol of [(PPh$_3$)$_3$CuBr] (38% yield). M.p. 215–216°C. Found: C, 51.1; H, 3.9; N, 5.4; S, 6.0. Calc. for $C_{22}H_{21}BrCuN_2PS$, C, 50.8; H, 4.1; N, 5.4; S, 6.2. IR (nujol, cm^{-1}): 3200–2800br $\nu_{(NH)}$, 1572w $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 523m, 508m, 494m (Ph), 440w, 428w, 412w. ^{1}H NMR (CDCl$_3$): δ, 3.6 (br, 3H, NCH_3), 6.8 (br, 1H, 4-CH_{Hmimt} or 5-CH_{Hmimt}), 6.9 (br, 1H, 4-CH_{Hmimt} or 5-CH_{Hmimt}), 7.1–7.8 (m br, 15H, C_6H_5), 12.6 (br, 1H, NH). Λ_m (acetone, $c=0.73\times10^{-3}$ M): 1.03 Ω^{-1}cm^2 mol^{-1}.

[(PPh$_3$)$_2$(Himt)Cu]BF$_4$, ***26****.* Complex **26** was obtained when a diethyl ether solution of compound **18** reacted with an excess of PBz$_3$; and re-crystallized from methanol (45% yield). M.p. 165–168°C. Found: C, 60.0; H, 4.5; N, 3.6; S, 3.9. Calc. for $C_{39}H_{34}BCuF_4N_2P_2S$, C, 60.4; H, 4.4; N, 3.6; S, 4.1. IR (nujol, cm^{-1}): 3200–2800br $\nu_{(NH)}$, 1577w $\nu_{(C\cdots C)}$ and $\nu_{(C\cdots N)}$, 516s, 502s, 486s (Ph), 441m, 418m, 333w. ^{1}H NMR (CDCl$_3$): δ, 6.6 (br, 2H, 4-CH_{Himt} and 5-CH_{Himt}), 7.2–7.5 (m br, 30H, C_6H_5), 11.0 (br, 2H, NH). Λ_m (acetone, $c=0.3\times10^{-3}$ M): 31.0 Ω^{-1}cm^2 mol^{-1}.

2.3.1. Reaction between [(PPh$_3$)$_2$bis(pyrazol-1-yl)methaneCu]ClO$_4$ and PBz$_3$

The reaction between [(PPh$_3$)$_2$bis(pyrazol-1-yl)methaneCu]ClO$_4$ and PBz$_3$ was carried out following the procedure indicated above for compound **13**. A colorless precipitate was obtained and identified as a compound of empirical formula (PBz$_3$)$_4$(L^1)(CuClO$_4$)$_2$. The ^{1}H, ^{31}P NMR and IR spectra are in accordance with a mixture of two different compounds [(PBz$_3$)$_2$CuClO$_4$] and [(PBz$_3$)$_2$bis(pyrazol-1-yl)methaneCu]ClO$_4$ that is impossible to separate due to the very fast oxidation of Cu$^{\mathrm{I}}$ to Cu$^{\mathrm{II}}$.

2.3.2. Reaction between [(PPh$_3$)$_2$bis(3,5-dimethylpyrazol-1-yl)methaneCu]ClO$_4$ and PBz$_3$

This reaction was carried out following the procedure indicated above for compound **13** by using 1 mmol of

$[(PPh_3)_2$bis(3, 5 - dimethylpyrazol - 1 - yl)methaneCu]ClO_4 and 2 mmol of PBz_3. A colorless precipitate was obtained and identified as $[(PBz_3)_2CuClO_4]$ by analysis, IR and ^1H NMR spectra.

2.3.3. Reaction between [bis{bis(3,5-dimethylpyrazol-1-yl)methane}Cu]ClO$_4$ and PBz$_3$

This reaction was carried out following the procedure indicated above for compound **13** by using 1 mmol of [bis{bis(3,5-dimethylpyrazol-1-yl)methane}Cu]ClO_4 and 5 mmol of PBz_3. A colorless precipitate was obtained and identified as $[(PBz_3)_2CuClO_4]$ by analysis, IR and ^1H NMR spectra.

2.3.4. Reaction between [(PBz$_3$)$_2$CuClO$_4$] and 1,10-phenanthroline (Phen)

This reaction was carried out following the procedure indicated above for compound **13** by using 1 mmol of $[(PBz_3)_2CuClO_4]$ and 2 mmol of Phen. The colorless precipitate obtained was identified as $[(Phen)_2Cu]ClO_4$ by analysis, IR and ^1H NMR spectra.

2.3.5. Reaction between [bis{bis(3,5-dimethylpyrazol-1-yl)methane}Cu]ClO$_4$ and Phen

This reaction was carried out following the procedure indicated above for compound **13** by using 1 mmol of [bis{bis(3,5-dimethylpyrazol-1-yl)methane}Cu]ClO_4 and 2 mmol of Phen. A colorless precipitate was obtained and identified as $[(Phen)_2Cu]ClO_4$ by analysis, IR and ^1H NMR spectra.

3. Results and discussion

The copper complexes **1–12** and **16–25** (see Section 2) were prepared by reacting an excess of the corresponding heterocyclic *N*-, N_2-, or *S*-donor ligand as in Fig. 1 with a diethyl ether suspension of $[(PR_3)_nCuX]$ previously synthesized.

$$[(PBz_3)_2CuX] + xL \rightarrow (PBz_3)_{2-n}(L)_xCuX + nPBz_3 \quad (1)$$

1–12

1: L = ImH, X = NO_3, $x = 3$, $n = 1$
2: L = 2-MeimH, X = NO_3, $x = 2$, $n = 0$
3: L = 1-Meim, X = NO_3, $x = 2$, $n = 0$
4: L = 4-PhimH, X = NO_3, $x = 2$, $n = 1$
5: L = BzimH, X = NO_3, $x = 2$, $n = 1$
6: L = 1-Bzim, X = NO_3, $x = 2$, $n = 1$
7: L = bis(pyrazol-1-yl) methane, X = NO_3, $x = n = 1$
8: L = bis(triazol-1-yl)methane, X = NO_3, $x = 2$, $n = 0$
9: L = pzH, X = NO_3, $x = 1$, $n = 0$
10: L = ImH, X = ClO_4, $x = 2$, $n = 0$
11: L = 2-MeimH, X = ClO_4, $x = 2$, $n = 0$
12: L = 1-Meim, X = ClO_4, $x = 3$, $n = 1$

$$[(PPh_3)_yCuX] + xL' \rightarrow (PPh_3)_{y-n}(L')_xCuX + nPPh_3 \quad (2)$$

16–25

16: L′ = Himt, X = ClO_4, $y = 4$, $x = 2$, $n = 3$
17: L′ = Himt, X = NO_3, $y = x = 2$, $n = 0$
18: L′ = Himt, X = BF_4, $y = 4$, $x = 2$, $n = 1$
19: L′ = Himt, X = SCN, $y = x = 2$, $n = 1$
20: L′ = Himt, X = Br, $y = 3$, $x = n = 1$
21: L′ = Hmimt, X = ClO_4, $y = 4$, $x = 3$, $n = 3$
22: L′ = Hmimt, X = NO_3, $y = x = 2$, $n = 1$
23: L′ = Hmimt, X = BF_4, $y = 4$, $x = n = 3$
24: L′ = Hmimt, X = SCN, $y = x = 2$, $n = 1$
25: L′ = Hmimt, X = Br, $y = 3$, $x = 1$, $n = 2$

When less than two equivalents of the azole were used, unreacted starting material was recovered from the reaction. No reaction took place from the reaction of $[(PBz_3)_2CuClO_4]$ with 4-PhimH, BzimH and 1-Bzim, even when the reaction was carried out under forcing conditions, i.e. strong excess of ligand and refluxing solvent. However, it is possible to obtain tribenzylphosphinecopper(I)perchlorate derivatives containing the ligand indicated above (4-PhimH, BzimH and 1-Bzim) by reaction of their triphenylphosphinecopper(I)perchlorato derivatives with tribenzylphosphine in accordance with Eq. 3, or also by reduction of the 4:1 copper(I) complexes $[(L)_4Cu(II)](ClO_4)_2$ (L = 4-PhimH, BzimH or 1-Bzim) with PBz_3, which again yielded compounds **13–15**

$$[(PPh_3)_x(L)_yCu]ClO_4 + nPBz_3 \rightarrow (PBz_3)_n(L)_{y-1}CuClO_4 + xPPh_3 + L \quad (3)$$

13: L = 4-PhimH, $x = y = 2$, $n = 3$
14: L = 1-Bzim, $x = 1$, $y = 3$, $n = 2$
15: L = BzimH, $x = y = n = 2$

No reaction took place between the copper(I) derivatives of 1-methyl-imidazoline-2(3*H*)-thione or imidazoline-2(1,3*H*)-thione **16–25** and PBz_3. In this case no displacement of the PPh_3 by PBz_3 was observed. However, in some cases when compounds **16–25** were stored for a long time in diethyl ether suspension, a dissociation occurred which yielded a derivative different from the starting reagent: for example, compound $[(PPh_3)_2(Himt)Cu]BF_4$**26** was obtained when $[(PPh_3)(Himt)\ _2Cu]BF_4$**18** reacted for 2 days with PBz_3 in diethyl ether.

From the reaction of [bis{bis(3,5-dimethylpyrazol-1-yl)methane}Cu]ClO_4 or $[(PPh_3)_2$bis(3,5-dimethylpyrazol-1-yl)methaneCu]ClO_4 with PBz_3, $[(PBz_3)_2CuClO_4]$ was always obtained, suggesting that the bond between Cu and the chelating N_2-donor {bis(3,5-dimethylpyrazol-1-yl)methane is weaker than that between Cu and imidazoles. We also observed that the bond between Cu(I) and 1,10-phenanthroline is stronger than that between Cu and triorganophosphines and that between Cu and bis(3,5-dimethylpyrazol-1-yl)methane; in fact, from the reaction of

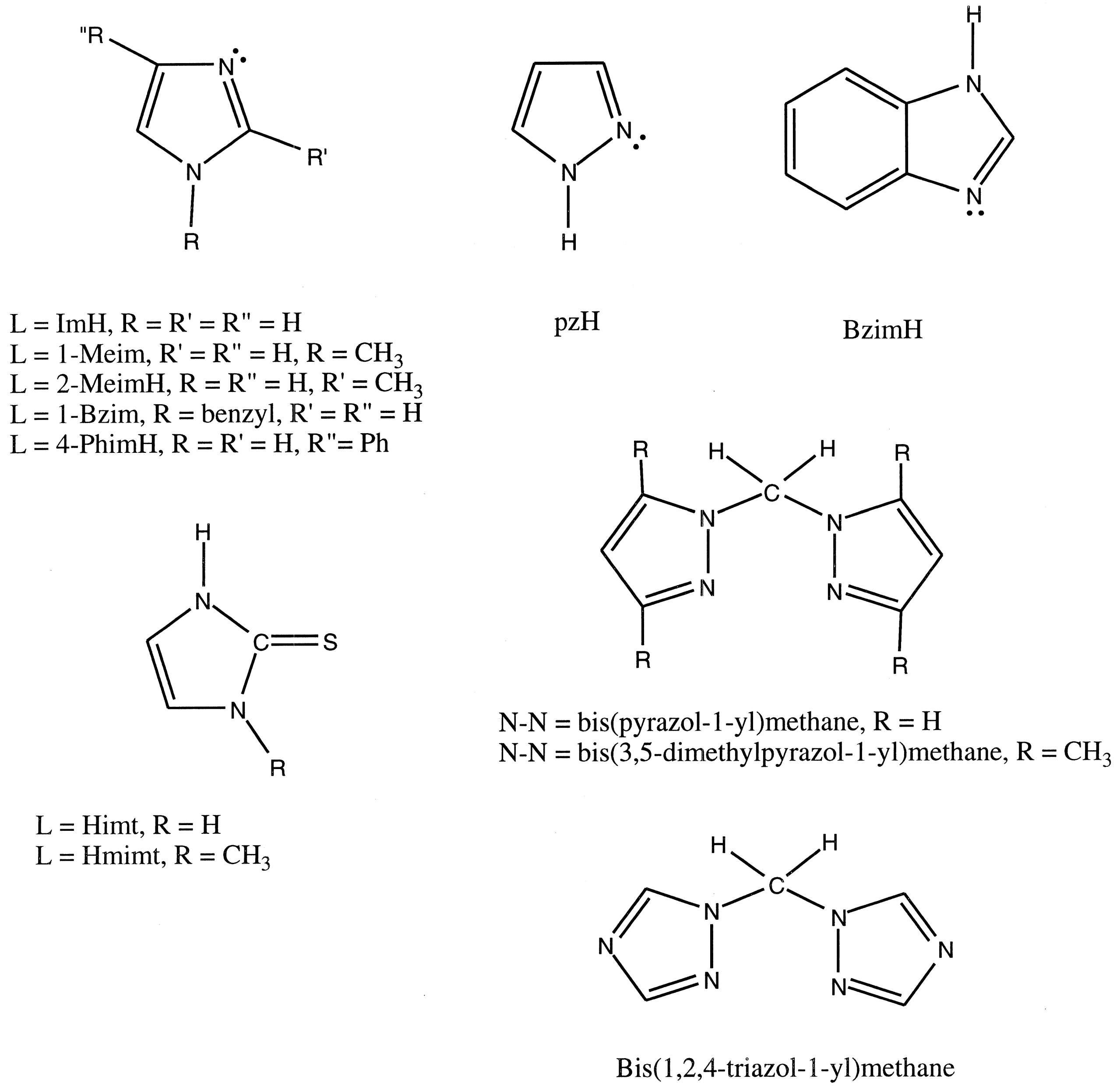


Fig. 1. Structures of the ligands employed.

$[(PBz_3)_2CuClO_4]$ or [bis{bis(3,5-dimethylpyrazol-1-yl)methane}Cu]ClO_4 with Phen the derivative $[(Phen)_2Cu]ClO_4$ was always obtained.

It was found that the steric effects and the basicity of the heterocyclic donor determine, to a great extent, the coordination environment on the copper center and also the stoichiometry of the complexes obtained. Adducts 1:3:1 of $[PBz_3(L)_3Cu]X$ can be obtained only when the azole donor is ImH or 1-Meim, which are less sterically hindered and also more basic than the other imidazole-type ligands employed here, whereas 1:2:1 $[PBz_3(L)_2Cu]X$ and 2:1:1 $[(PBz_3)_2(L)Cu]X$ adducts are generally afforded when L is BzimH, 4-PhimH or 1-Bzim.

As previously observed, the ligand pzH which is less basic with respect to ImH, yielded only the 2:1:1 adduct $(PBz_3)_2(pzH)CuNO_3 \cdot H_2O$ **9**. No adduct can be prepared from the reaction of pzH with $(PBz_3)_2CuClO_4$, and the reaction of **9** with excess PBz_3 also yielded untractable material. If the reaction was carried out in the presence of a strong excess, no displacement of PBz_3 occurred, in accordance with the behavior previously observed with other triorganophosphinecopper(I) acceptors [24–26].

Instead the stoichiometry of the imidazoline-2(3*H*)-thione derivatives **16**–**26** is strongly dependent on the nature of the counter ion: the ligands Himt and Hmimt are able to displace not only the PPh_3 ligand but also the NO_3, BF_4 and ClO_4 groups from the coordinations sphere of Cu(I) yielding 1:2:1 or 1:3:1 adducts, but are generally unable to displace strongly coordinating groups such as SCN or Br.

We also found that in the same conditions it is more easy to displace the PBz_3 ligand ($pK_a = 6.0$) from Cu(I), not only than PCy_3 ($pK_a = 9.70$) but also than the less basic PPh_3 ($pK_a = 2.73$) [43,44]. This is due to the greater Tolman cone angle of PBz_3 (165°) with respect to PPh_3 (145°) [45].

All the compounds are generally insoluble in diethyl ether and ethanol, and soluble in acetone, DMSO, chlorinated solvents, and acetonitrile. They may be crystallized by slow diffusion of diethyl ether into an acetonitrile solution in which they are stable; however it was impossible to obtain crystals suitable for X-ray analysis. Instead, they are generally unstable in $CHCl_3$ and in acetone solution where they are readily oxidized by air, rapidly giving a blue solution. However, none of the tribenzylphosphine complexes synthesized are very stable in solution. We observed that the substitution of triphenylphosphine with tribenzylphosphine increases the dissociation of the copper(I) complexes, and then also of the oxidation of Cu(I) to Cu(II). The oxidation is strongly dependent on the number of PBz_3 groups coordinated to Cu: the $[(PBz_3)_3LCu]X$ complexes are stable in chloroform solution also for several hours, the $[(PBz_3)_2L_2Cu]X$ derivatives for a time which can vary from 15 min to 2 h, and finally the $[(PBz_3)L_3Cu]X$ ones are completely oxidized within 20 min.

On the other hand, all the imidazoline-2(3*H*)-thione derivatives **16**–**26** are stable in solution for a very long time, suggesting that the formation of the Cu–S bond can allow Cu(I) derivatives to be obtained, which are sufficiently stable to be spectroscopically characterized.

The conductivity measurements carried out only on the sufficiently stable compounds in dichloromethane or in acetonitrile (the choice is determined only by the solubility of compounds) show that the nitrato, perchlorato and tetrafluoroborato derivatives (**1**–**3**, **10**–**16**, **18**, **21**, **23** and **26**) are electrolytes also in non-ionizing solvents such as dichloromethane, which is in reasonable agreement with their ionic structure proposed in Fig. 2. In a few cases (compounds **19**, **22**, **24** and **25**) the conductivity values are considerably lower than those expected for a 1:1 electrolyte: this is likely due to the little amount of non-ionic dissociation such as **4**, which likely yields non-ionic compounds.

$$[(PBz_3)_yL_xCu]X \leftrightarrow [(PBz_3)_yCuX] + xL \qquad (4)$$

The compounds **4**–**9**, which are not ionic in the solid state, are 1:1 electrolytes in dichloromethane, in accordance with an ionic dissociation in this solvent. Molecular weight measurements were also performed in chloroform on selected sufficiently stable derivatives. The ratio *r* between the vaporimetric molecular weight and the formula weight lies in the range 0.38–0.75 and indicates that, as previously reported for triphenylphosphine derivatives, our tribenzylphosphine complexes **1**–**15** presumably dissociate partly in these solvents, in accordance with their ionic nature or partial ligand loss in solution (Eqs. 4 and 5).

$$[(PBz_3)_yL_xCu]X \leftrightarrow [(PBz_3)_{y-n}L_xCuX] + nPBz_3 \qquad (5)$$

The dissociation is strongly dependent on the concentration of the solutions and also on the Tolman cone angle: [45] *r* generally decreases with decreasing concentration, and decreases with increasing cone angle value.

3.1. Spectroscopy

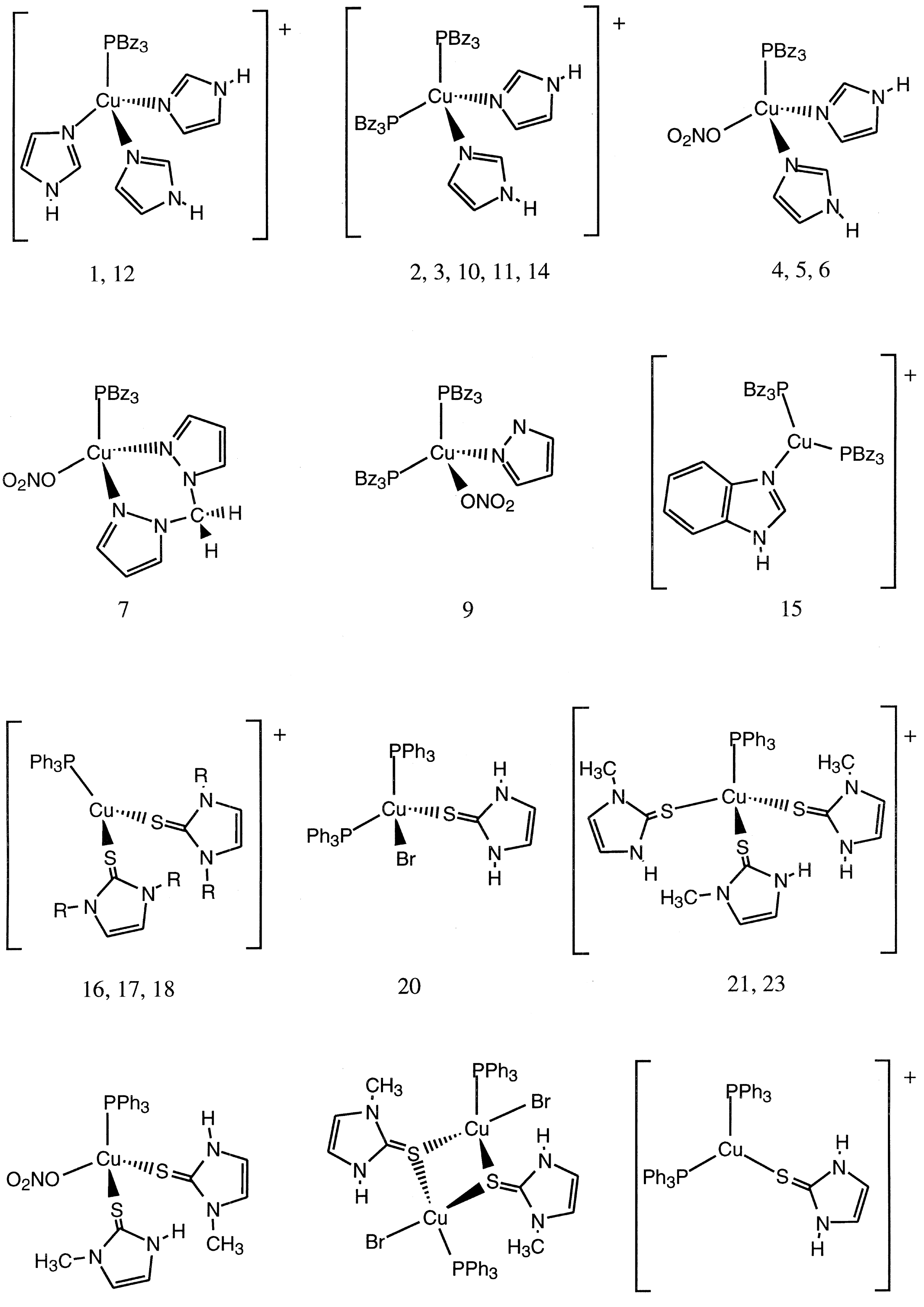
3.1.1. IR spectra

The main vibrational bands of the starting copper(I) phosphino and their azole adducts are given Section 2. The $\nu_{(NH)}$ bands of the imidazoles, pyrazole and imidazoline-2-thiones are observed as medium to strong broad bands in the 3300–2600 cm^{-1} region. The slight shift and the broadening and also the appearance of new medium absorptions in the 3300–3000 cm^{-1} region, suggest the participation of the NH groups in hydrogen bonding.

The copper(I) nitrato derivatives **1**–**9**, **17** and **22** show spectra in the regions 2000–1600, 1400–1100 and 1000–700 cm^{-1}; these are considerably different from the spectra of their starting $[(PBz_3)_2CuNO_3]$ and $[(PPh_3)_2CuNO_3]$ which contain bidentate nitrato groups. Compounds **1**–**3** show four absorptions at approximately 1350, 1040, 830 and 700 cm^{-1} characteristic of an ionic nitrato group [46]. In the spectra of compounds **4**–**6**, **9**, **17** and **22**, the ν_1 and ν_4 differ in frequency by approximately 60–90 cm^{-1}. This suggests for these compounds, in the solid state, the presence of a monodentate nitrato group [47,48]. This hypothesis is also confirmed by the splitting of the combination band ($\nu_1 + \nu_4$) which appears in the 1800–1700 cm^{-1} region, and also by the splitting of the ν_4 (near 700 cm^{-1}) in two bands, as expected for unidentate nitrato groups [49]. In the other nitrato complexes, the bands are often hidden under some ligand absorption, so that it is not possible to distinguish between unidentate or ionic nitrato groups.

The IR spectra of the perchlorato and tetrafluoroborato derivatives **10**–**16**, **18**, **21**, **23** and **26** all show two absorptions characteristic of ClO_4 and BF_4 groups: a strong absorption between 1100 and 1000 cm^{-1} and a strong sharp band at approximates 625 cm^{-1}: these absorptions, similar to those found in the ionic compounds $[(PPh_3)_4Cu]XY_4$ ($XY_4 = ClO_4$ or BF_4), are indicative of the presence of ionic uncomplexed XY_4 group [50], in accordance with the structures proposed in Fig. 2. The absorptions are very similar to those observed in tricyclohexylphosphinecopper(I)perchlorato derivatives of imidazoles in which the perchlorato group is strongly hydrogen bonded [26].

The NCS group may be bonded to a metal through the N



1, 12

2, 3, 10, 11, 14

4, 5, 6

7

9

15

16, 17, 18

20

21, 23

22, 24

25

26

Fig. 2. Selected structures of the complexes obtained.

or S atom or may form a bridge between the two metals by using both atoms. In our complexes **19** and **24**, we found $\nu_{(CN)}$ near 2100 cm^{-1}, several bands of low intensity near 420 cm^{-1} due to δ(NCS), and finally a medium absorption near 700 cm^{-1} due to $\nu_{(CS)}$, all typical of *S*-bonded complexes [51–54]. A neutral structure as in that in Fig. 2 is likely. In derivatives **16**–**26**, the $\nu_{(C=S)}$ vibrations, found in the free ligands at approximately 770 and 740 cm^{-1}, respectively, exhibit a slight shift by ±15 cm^{-1}. Slight changes (±10 cm^{-1}) also occur in the δ(CS) (670 cm^{-1}) and π(CS) (530 cm^{-1}) bands, and finally some absorptions having $\nu_{(CS)}$ character appear at approximately 700 cm^{-1}, which suggests coordination of the imidazolinethiones to the copper(I) atom throughout the thiocarbonyl sulfur as previously observed [55]. This observation is supported by the presence of weak absorptions at approximately 300 cm^{-1}, absent in the spectrum of the free *S*-donors and of the starting copper(I) derivative, due to $\nu_{(Cu-S)}$ stretching vibration [28].

The two bromide complexes **20** and **25** exhibit a very different far IR spectrum, as expected on the basis of their stoichiometry: compound **20** exhibits a band at ca. 200 cm^{-1}, characteristic of a terminal Cu–Br bond and in accordance with a tetrahedral structure, whereas the spectrum of **25** is very similar to those reported for dinuclear complexes synthesized by Raper and Clegg [31] The thioamide IV bands in the free ligand at 770 and 740 cm^{-1} are replaced with a sharp but split band in the complex. Slight shift and band splitting have also been found for δ(CS) at 670 cm^{-1} and π(CS) at 525 cm^{-1}. On the basis of these similarities, the dinuclear structure in Fig. 2 is likely.

3.1.2. ^{1}H NMR spectra

The ^{1}H NMR spectra recorded in chloroform or in acetonitrile only when the compounds were sufficiently soluble and the solution sufficiently stable, support the formulae proposed and show that our *N*- and *S*-donors have not undergone any structural changes upon coordination.

As previously observed for the tricyclohexylphosphine and the triphenylphosphino derivatives [24–26], a small coordination shift is generally found which is due to a partial dissociation of complexes in solution. The observed resonances are averaged between those of the complex and free ligand owing to a rapid exchange reaction between both (Eq. 4). The dissociation is often larger in the complexes containing sterically hindered imidazoles, i.e compounds **2**, **4**–**6**, **11**, and **13**–**15**. The small coordination shifts are therefore assignable to the small fraction of the complex present in solution and are caused by a change in the electron density of the donor owing to the formation of the Cu–N or Cu–S bond. The coordination chemical shifts are generally greater in complexes containing imidazolinethiones than in those containing *N*-donor azoles, in accordance with the relative strength of the Cu–N and Cu–S bonds.

The presence of a broad resonance at approximately 7.4 ppm in the ^{1}H NMR spectrum of compound **1** and at approximately 6.6 ppm in the ^{1}H NMR spectrum of derivatives **16**–**20**, instead of the two expected signals for the two H4 and H5 hydrogens, may be due to a rapid interchange of the azole in a dissociative process, a ‘shuttling’ of the H and the copper(I) atom between the pair of N atoms [56,57].

In the ^{1}H NMR spectra in $CDCl_3$ of tribenzylphosphino compounds **1**–**15**, a broad signal at approximately 3.0 ppm and a complex multiplet between 7.0 and 7.30 ppm often appear, which are due to the formation of $Bz_3P{=}O$ in accordance with the previously described fast oxidation of free PBz_3 in $CHCl_3$.

4. Conclusions

The conclusions of our study on the interaction between monodentate *N*- or *S*-donor, or bidentate N_2-donor ligands and triorganophosphinecopper(I)X acceptors showed that different compounds can be obtained depending on:

1. steric hindrance, basicity, and atom donor of the azole-type ligand;
2. steric hindrance (Tolman cone angle) and basicity (pK_a) of the phosphorus donor;
3. reaction conditions (solvent, temperature, ligand to metal ratio employed . . . .);
4. nature of the counter-ion.

While it is generally very simple to obtain triphenylphosphino derivatives by direct interaction of the starting $[(PR_3)_nCuX]$ with the azole ligand, the tribenzyl- and tricyclohexyl-phosphino derivatives can be more efficiently prepared by substitution reaction of the phosphorus donor ligand.

The complexes containing *S*-donor ligands are generally more stable than complexes containing *N*-donor ligands; complexes containing three triorganophosphines are more stable than those containing two triorganophosphines, which, however, are more stable than those containing only one triorganophosphine ligand. Stability generally decreases with increasing Tolman cone angle and with decreasing pK_a of the triorganophosphine, so that it is not possible to indicate which triorganophosphine is the better ligand.

Acknowledgements

We would like to thank the Italian Ministry of the University (MURST) and the University of Camerino for financial help.

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