Stabilization of Copper(I) by Phosphinoamines

Francesco Tisato,*[a] Fiorenzo Refosco,[a] Giuliano Bandoli,[b] Giuseppe Pilloni[c] and Benedetto Corain[d]

[a] *Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati, C.N.R., corso Stati Uniti 4, 35020 Padova, Italy*

[b] *Dipartimento di Scienze Farmaceutiche, Università di Padova, via Marzolo 5, 35131 Padova, Italy*

[c] *Dipartimento di Chimica Inorganica Metallorganica ed Analitica, Università di Padova, via Marzolo 1, 35131 Padova, Italy*

[d] *Centro per lo Studio della Stabilità e Reattività dei Composti di Coordinazione, C.N.R., via Marzolo 1, 35131 Padova, Italy*

Tetradentate phosphinoamines *N,N′*-bis[2-(diphenylphosphino)phenyl]ethane-1,2-diamine (H_2dpen) and *N,N′*-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine stabilize copper(I) complexes either by ligand-exchange reactions from labile $[Cu^I(MeCN)_4]^+$ or ligand-promoted reduction of a $Cu^{II}Cl_2 \cdot 2H_2O$ precursor; the structure of one of the products, [Cu(H_2dpen)]BF_4, has been determined.

Interest in the co-ordination chemistry of copper(I) stabilized by a variety of carefully designed co-ordination spheres has been particularly high in recent years.[1] We have recently described[2] the synthesis and crystal structure of a heteroleptic copper(I) complex, [Cu(dppf)(odppf)]BF_4 [dppf = 1,1′-bis(diphenylphosphino)ferrocene, odppf = 1,1′-bis(oxodiphenylphosphoranyl)ferrocene], in which the mixed soft–hard co-ordination sphere is particularly suited to stabilizing the metal centre towards valence disproportionation both in the solid state and aprotic solvents. The availability in our laboratories[3] of a variety of soft–hard potentially 'fully aromatic' ligands ranging from phosphinophenol, phosphinocarboxylates, phosphinoaldehyde to phosphinoamines led us to look for a logical confirmation of our findings, upon moving from a P_2O_2 to a P_2N_2 chromophore. While working on this project, the alleged identification of a square-pyramidal copper(II) complex of *N,N′*-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine (H_2dppn)[4] contrasted with our evidence on the capability of this ligand to stabilize copper(I) rather than copper(II),[5] so much so that a class of related aliphatic P_2N_2 chelates was found to co-ordinate copper(I).[6]

We report here on the ability of *N,N′*-bis[2-(diphenylphosphino)phenyl]ethane-1,2-diamine (H_2dpen) and H_2dppn† to stabilize the copper(I) species [Cu(H_2dpen)]BF_4 **1** and [Cu(H_2dppn)]BF_4 **2** both in the solid state and in solution.

Complexes **1** and **2** can be prepared in high yield by ligand-exchange reactions from the labile precursor $[Cu(MeCN)_4]BF_4$ and H_2dpen or H_2dppn in CH_2Cl_2 solution at room temperature.‡ Their FAB mass spectra exhibit molecular ion peaks corresponding to the cationic complexes with the correct copper cluster centred at *m/z* 644 and 658 respectively, with no detectable evidence of fragmentation. The IR spectra confirm the co-ordination of the intact tetradentate ligand, showing bands characteristic of the phosphino moiety and of the BF_4 counter anion together with a sharp band attributable to the symmetric N–H vibration at 3287 (**1**) and 3272 cm^{-1} (**2**) (both bands exhibit the expected bathocromic shift with respect to those in the free ligands). In addition, the crystal structure of complex **1** reveals that the cationic complex contains monomeric units in which the co-ordination sphere around copper, which occupies a crystallographic two-fold axis, is markedly distorted tetrahedral (Fig. 1).§ Thus, the bond angle N(1)–Cu–N(1a) of 85.7(4)° spanned by the N(1)$\cdots$N(1a) bite at 295 pm differs dramatically from the ideal value, as well as the P(1)–Cu–N(1) angle of 87.0(2)°, spanned by the P(1)$\cdots$N(1) bite of 301 pm. As a consequence, the P(1)–Cu–P(1a) angle [132.8(1)°] is rather wide and the P(1)$\cdots$P(1a) separation consequently large (403 pm). The tetradentate co-ordination mode of the ligand leads to a tricyclic (5,5,5) system

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† The ligand H_2dppn was prepared according to the method of Cooper *et al.*[7] The H_2dpen analogue was synthesized in a similar way (yield 30%) (Found: C, 78.90; H, 5.95; N, 4.75. $C_{38}H_{34}N_2P_2$ requires C, 78.60; H, 5.90; N, 4.85%); IR (KBr pellets, $\tilde{\nu}/cm^{-1}$ major bands) 3376w, 1584s, 1503s, 1443s, 1311m, 753s, 697s, 473m; ^1H NMR (200.13 MHz, $CDCl_3$) δ 7.35–6.55 (28 H, Ph), 4.90 (br s, 2 H, NH), 3.25 (s, 4 H, NCH_2); $^{31}P-\{^1H\}$ NMR (81.01 MHz, $CDCl_3$) δ −22.2 (s).

‡ Complexes **1** and **2** were obtained following an identical procedure, detailed here for **1**. The compound H_2dpen (1842 mg, 3.17 mmol) dissolved in CH_2Cl_2 (20 cm^3) was added to a solution of $[Cu(MeCN)_4]BF_4$ (998 mg, 3.17 mmol) in CH_2Cl_2 (50 cm^3) under stirring at room temperature. The pale orange solution was stirred for 60 min until a white solid appeared. It was filtered off, washed with CH_2Cl_2 and dried under vacuum (yield 95%). [Cu(H_2dpen)]BF_4 **1**. Soluble in MeCN, sparingly soluble in chlorinated solvents and insoluble in alcohols (Found: C, 63.25; H, 4.85; N, 4.00. $C_{38}H_{34}BCuF_4N_2P_2$ requires C, 62.45; H, 4.70; N, 3.85%). Crystallization from CH_2Cl_2–propan-2-ol yielded single crystals, one of which was selected and, to prevent its deterioration, sealed in a capillary tube along with the mother-liquor. IR (KBr pellets, $\tilde{\nu}/cm^{-1}$, major bands): 3287s [ν(N–H)], 1444m, 1084vs, 744s, 694s, 500s. FAB mass spectrum (glycerol matrix): *m/z* 644 $[M^+]$. Molar conductivity in MeCN: $\Lambda_M = 190.4$ ohm^{-1} cm^2 mol^{-1} NMR ($CDCl_3$): ^1H (200.13 MHz), δ 7.60–7.20 (28 H, Ph), 5.01 (br s, 2 H, NH), 3.19 (br s, 4 H, NCH_2); $^{31}P-\{^1H\}$ (81.01 MHz) δ −13.14 (s). [Cu(H_2dppn)]BF_4 **2** (Found: C, 63.55; H, 5.00; N, 3.90. $C_{39}H_{36}BCuF_4N_2P_2$ requires C, 62.85; H, 4.85; N, 3.75%): IR 3272s [ν(N–H)], 1445m, 1079vs, 745s, 695s, 502s cm^{-1}; FAB^+ mass spectrum (glycerol matrix) *m/z* 658 $[M^+]$; molar conductivity in MeCN Λ_M = 128.9 ohm^{-1} cm^2 mol^{-1}; ^1H NMR, δ 7.60–7.20 (28 H, Ph), 5.02 (br s, 2 H, NH), 3.00 (m, 4 H, NCH_2), 1.98 (q, 2 H, NCH_2CH_2); $^{31}P-\{^1H\}$ NMR δ −15.14 (s).

§ $C_{38}H_{34}BCuF_4N_2P_2$, $M = 731.0$, monoclinic, space group $C2$, $a = 1185.7(6)$, $b = 1717.8(9)$, $c = 918.7(5)$ pm, $\beta = 94.70(4)°$, $U = 1864.9$ Å^3, $Z = 2$, $F(000) = 752$. Siemens Nicolet R3m/V four-circle diffractometer, Mo-Kα radiation ($\lambda = 0.710\,73$ Å), graphite monochromator, θ–2θ scan mode. 2797 Observed independent reflections up to $\theta = 30°$ of which 1957 had $F_o > 3\sigma(F_o)$. Heavy-atom method with refinement by standard full-matrix least squares. In the last cycles of refinement Cu, P, N and C atoms were allowed to vibrate anisotropically, and H atoms included in calculated positions. The counter anion was affected by a high disorder typical of BF_4 groups. Quantity minimized $\Sigma w(|F_o| - |F_c|)^2$ ($w = 1$), $R = 0.070$. A weighting scheme of the type $w = 1/\sigma^2$ did not improve the refinement. All calculations performed using SHELXTL PLUS.[8] Scattering factors for all the atoms were taken from ref. 9. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

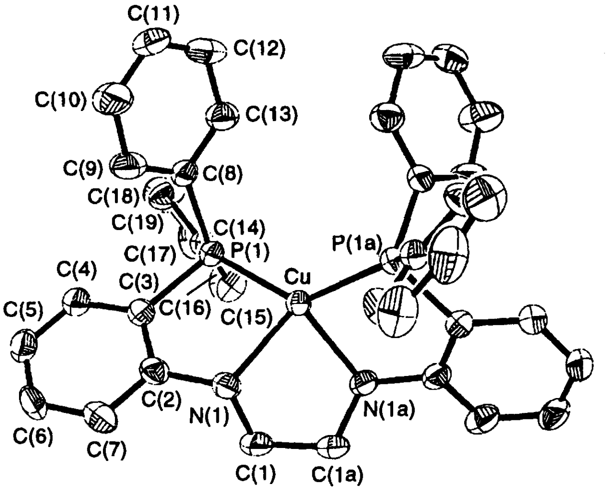

Fig. 1 Crystal structure of the cation $[Cu(H_2dpen)]^+$ of **1**. Selected bond lengths (pm) and angles (°): Cu–P(1) 219.7(2), Cu–N(1) 216.9(8), P(1)–C(3) 184.1(8), P(1)–C(8) 181.4(9), P(1)–C(14) 181.7(9), N(1)–C(1) 150(1), N(1)–C(2) 146(1), C(1)–C(1a) (symmetrically related) 148(2); P(1)–Cu–N(1) 87.0(2), N(1)–Cu–N(1a) 85.7(4), P(1)–Cu–P(1a) 132.8(1), P(1)–Cu–N(1a) 129.7(2), Cu–N(1)–C(1) 101.1(6), Cu–N(1)–C(2) 113.7(5), Cu–P(1)–C(3) 100.8(3), Cu–P(1)–C(8) 113.7(3), Cu–P(1)–C(14) 127.4(3), C(1)–N(1)–C(2) 111.4(7)

around copper, with the middle ring in a twist–envelope conformation and the distal ones making a dihedral angle of 64.3°. An alternative description involves a trigonal pyramid, in which the copper atom is severely out of the basal plane by 39 pm towards the apical N(1a) atom. Among the $Cu^IP_2N_2$ mononuclear four-co-ordinate complexes,[6] a survey of the bond distances reveals a shortening of both the Cu–P [219.7(2) *vs.* a mean value of 227.6 pm] and Cu–N distances [216.9(8) *vs.* a mean value of 219.2 pm]. The cationic nature of the Cu^I complexes is also observed in solution, the conductivity measurements in MeCN being in agreement with those expected for a 1 : 1 electrolyte. Moreover, the four-co-ordinate structure of the diamagnetic Cu^I species appears to be maintained in solution at room temperature, as shown by NMR spectroscopy. The ^{31}P-{^1H} NMR spectra exhibit only one singlet at δ −13.14 (**1**) and −15.14 (**2**), in agreement with the presence of two magnetically equivalent co-ordinated phosphorus atoms, shifted downfield when compared to those of the free ligands (δ −22.2 and −23.0 for H_2dpen and H_2dppn, respectively). Proton NMR resonances include the N–H signal as a relatively broad singlet at δ 5.01 (**1**) and 5.02 (**2**).

The statement that H_2dppn, in the presence of chloride ions, facilitates the transfer of Cu^{II} across a water–1,2-dichloroethane interface through the formation of a 1 : 1 metal to ligand species[4] prompted us to try to synthesize a Cu^{II} phosphinoamino derivative starting from a Cu^{II} precursor. Thus the reaction of $CuCl_2{\cdot}2H_2O$ with H_2dppn in acetone or dichloromethane gives a pale green solution from which a white solid analysing as $[Cu(H_2dppn{\cdot}2HCl)]Cl$ **3*** precipitates. The IR spectrum contains a complex series of bands at 2500–3000 cm^{-1} characteristic of an amine hydrochloride.[10] Suspended in MeCN complex **3** reacts instantaneously with NEt_3 to give a clean colourless solution (whose ^{31}P NMR features are those of **2**), from which **3** can again be precipitated quantitatively upon addition of HCl. The reaction pathway is likely to involve the co-ordination first of the nitrogen donors of the potentially tetradentate ligand to the 'hard' $Cu^{II}Cl_2$ moiety leaving the 'soft' phosphorus donor atoms dangling out of the co-ordination sphere. The intermolecular reduction of Cu^{II} to Cu^I is operated by the unco-ordinated phosphorus atoms present in a fraction of the total original Cu^{II}. As is well known, the ultimate fate of oxidized phosphorus in tertiary phosphines is conversion into phosphine oxide by the nucleophilic attack of water present in the reaction medium. The hydrogen ions released as a consequence are responsible for protonating the nitrogen atoms weakly co-ordinated to Cu^I giving rise to **3**, in which the H_4dppn^{2+} ligand binds linearly to the metal through the P atoms. In accord with the partial involvement of the ligand as reductant, the reaction yield was about 70% and the oxidized ligand was clearly detected in the supernatant by ^{31}P NMR spectroscopy, which identified the P=O group at δ 34.5.

In conclusion, tetradentate phosphinoamines are found to form stable and structurally characterized Cu^I complexes both upon displacement from a Cu^I precursor and upon ligand-promoted reduction of Cu^{II}.

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* Solid H_2dppn (100 mg, 0.17 mmol) was added to a solution of $CuCl_2{\cdot}2H_2O$ (29 mg, 0.17 mmol) dissolved in acetone (10 cm^3) under stirring at room temperature. From the pale green solution a white solid precipitated gradually. After stirring for 30 min the powder was filtered off, washed with acetone and dried under vacuum (yield 69%). $[Cu(H_2dppn{\cdot}2HCl)]Cl$ **3** is practically insoluble in common organic solvents (Found: C, 61.05; H, 4.70; N, 3.45. $C_{39}H_{38}Cl_3CuN_2P_2$ requires C, 61.10; H, 5.00; N, 3.65%); IR (KBr pellets, ν/cm^{-1}, major bands): 3297s, 3000–2500m, 1588m, 1434s, 746s, 695s, 491m. Scanning electron microscopy–energy dispersion X-ray spectroscopy: (Cu : P : Cl) 1 : 2 : 3. ESR silent.