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# Copper(I) and copper(II) complexes of polydentate phosphinoamines

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#### Abstract

Bidentate {PN} and tetradentate { $P_2N_2$ } ligands stabilize copper(1) and copper(11) inside tetrahedral ( $Cu^1$ ) and square planar ( $Cu^1$ ) coordination spheres, to give [ $Cu(PN_2$ ]<sup>+,2+</sup> and [ $Cu(P_2N_2$ )]<sup>+,2+</sup> complexes, which were characterized by various spectroscopies. The crystal structure of [ $Cu(H_2dppd)$ ]BF<sub>4</sub>·MeCN (H<sub>2</sub>dppd = *N*,*N*'-bis[2-(diphenylphosphino)phenyl]-propane-1,3-diamine) was determined: monoclinic, space group *P*2<sub>1</sub>/*n*, *Z*=4, *a*=11.483(4), *b*=13.516(6), *c*=24.224(9) Å, *β*=97.53(3)°, *R*=0.064 using 1897 observed reflections; Cu-P(1) 2.205(5), Cu-P(2) 2.213(4), Cu-N(1) 2.16(1), Cu-N(2) 2.14(1) Å; P(1)-Cu-P(2) 125.1(2)°, N(1)-Cu-N(2) 95.9(4)°, P(1)-Cu-N(1) 87.4(3)°, P(2)-Cu-N(2) 87.8(3)°. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Phosphinoamine complexes; Copper complexes; Crystal structures

## 1. Introduction

The coordination chemistry of copper(1) and copper(11) has received much attention in recent years, see for example Ref. [1]. In fact, beyond its obvious appeal attributable to the widespread awareness of the manifold biological role of the metal centre, we believe that the design of synthetic oxygen carriers or of bio-mimicking catalysts is now the real spring pushing so much scientific effort.

Recently we reported preliminarily on the preparation of a few tetracoordinated Cu<sup>1</sup> and Cu<sup>11</sup> complexes with bidentate {PN} and tetradentate {P<sub>2</sub>N<sub>2</sub>} ligands in which tricovalent phosphorus and nitrogen donor sites offer a balanced availability of  $\sigma$ -donating and  $\pi$ -accepting electronic effects [2–4] (Scheme 1). We feel that this feature of the coordination sphere made possible the formation of an X-ray authenticated example of a Cu<sup>11</sup> phosphino complex [4], the preparation of which species had been an elusive goal for decades [5].

We give in this paper a full description of the synthesis and thorough characterization of a number of  $Cu^{1}$  and  $Cu^{11}$ 

complexes featuring a  $\{P_2N_2\}$  chromophore (Table 1) and we provide a thermodynamic evaluation of the  $Cu^1 \rightarrow Cu^0$ conversion as a function of geometric features of this mixed soft-hard coordination sphere.

## 2. Experimental

## 2.1. Materials

Anhydrous 1,2-dichloroethane, DCE, succinyl and glutaryl dichlorides were purchased from Aldrich and used as received. Electrochemical grade tetrabutylammonium perchlorate, TBAP, was obtained from Fluka and used without further purification after drying in vacuo at 60°C. Commercially available copper(11) tetrafluoroborate (Aldrich) was crystallized twice from dilute aqueous HBF<sub>4</sub> by cooling from room temperature in polyethylene vessels. All other reagents and starting materials were of reagent-grade quality and were used as supplied. High purity argon, further purified from oxygen by passage over reduced copper at 450°C, was used in the electrochemical experiments.

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	diamine
H <sub>2</sub> dpbd	N,N'-bis[2-(diphenylphosphino)phenyl]butane-1,4-diamine
H-dpped	N,N'-bis[2-(diphenylphosphino)phenyl]pentane-1,5- diamine
PNH <sub>2</sub>	2-(diphenylphosphino)benzeneamine
PNHMe	N-methyl-2-(diphenylphosphino)aniline
PNMe2	N,N'-dimethyl-2-(diphenylphosphino)aniline

Table 1

The copper(1)	ana cobhei ( n	) complexes
New York Contraction of Contraction		

[Cu <sup>1</sup> (H <sub>2</sub> dped)]BF <sub>4</sub> (1)	$[Cu''(H_2dped)](BF_4)_2(8)$
${Cu1(H2dppd)}BF_4(2)$	[Cuii(H2dppd)](ClO4)2(9)
(Cu <sup>1</sup> (H <sub>2</sub> dpbd)]BF <sub>4</sub> (3)	$[Cu^{II}(H_2dpbd)](ClO_4)_2(10)$
${Cu1(H2dpped)]BF4(4)}$	
$[Cu^{1}(PNH_{2})_{2}]BF_{4}(5)$	$[Cu^{II}(PNH_2)_2](BF_4)_2(11)$
[Cu <sup>1</sup> (PNHMe) <sub>2</sub> ]BF <sub>4</sub> (6)	$[Cu^{II}(PNHMe)_2](BF_4)_2(12)$
[Cu <sup>1</sup> (PNMe <sub>2</sub> ) <sub>2</sub> ]BF <sub>4</sub> (7)	

## 2.2. Apparatus

Microanalyses were carried out with a Fisons EA1108 elemental analyser. The IR spectra were recorded in KBr pellets with a Mattson 3030 Fourier-transform spectrometer (400.0-400 cm<sup>-1</sup>). Ion positive fast atom bombardment (FAB<sup>+</sup>) mass spectra were recorded on a VG ZAB-2F instrument (8 keV Xe atoms bombarding 3-nitrobenzyl alcohol solutions of samples). The solution 'H and "P NMR experiments were performed with a Bruker AC-200 spectrometer. Chemical shifts are quoted relative to internal SiMe. (<sup>1</sup>H) or to external 85% w/w H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Solid state <sup>31</sup>P CP-MAS NMR spectra at 80.13 MHz were recorded on a Bruker AC-200 spectrometer equipped with an HP amplifier <sup>1</sup>H 200 MHz, 120 W cw and with a pulse amplifier M3205. The spin rate of the sample was 10 kHz. The  $\pi/2$  pulse width was 3.2 µs, the contact time for the cross polarization experiment was 2 ms and the relaxation delay was 10 s. <sup>31</sup>P NMR spectra were obtained with 1 K in the time domain, zero filled and Fourier transformed with a size of 2 K. Related chemical shifts were referenced to solid ammonium phosphate. X-band electron spin resonance (ESR) experiments were carried out using a computer-controlled Bruker ER 200 D spectrometer equipped with a variable-temperature apparatus. ESR computer simulations were performed using a home written program running on a PC. All electrochemical experiments were performed in anhydrous deoxygenated DCE solutions with  $0.2 \text{ mol dm}^{-3}$  TBAP as the supporting electrolyte, using a conventional three-electrode liquic \_\_\_\_\_ keted cell. Cyclic voltammetry (CV) measurements were performed with an Amel 551 potentiostat modulated by an Amel 566 function generator, and the recording device was an Amel model 863 X-Y recorder. The working electrode was either a planar platinum microelectrode ( $\sim 0.3 \text{ mm}^2$ ) or a glassy-carbon electrode  $(\sim 2 \text{ mm}^2)$  surrounded by a platinum spiral counter electrode. Controlled potential electrolyses were performed with an Amel 552 potentiostat linked to an Amel 731 digital integrator. The working electrode was a platinum gauze (  $\sim 100$ cm<sup>2</sup>), and the counter electrode was external, the connection being made through an appropriate salt bridge. In all cases silver/0.1 mol dm<sup>-3</sup> silver perchlorate in MeCN, separated from the test solution by 0.2 mol dm<sup>-3</sup> TBAP in DCE solution sandwiched between two fritted disks, was used as the reference electrode. Compensation for iR drop was achieved by positive feedback. Ferrocene was added at the end of each experiment as the internal reference. All potentials are referred to the ferrocenium/ferrocene redox couple ( $E_{1/2}$ = +0.120 V relative to the actual Ag/AgClO<sub>4</sub> reference electrode and +0.420 V versus aqueous SCE under the present experimental conditions). Conductivity measurements were carried out in MeCN at 293 K with a model E518 Metrohm Herison conductimeter.

## 2.3. Preparation of the ligands

The tetradentate ligand  $H_2$ dped was synthesized as reported previously [2] whereas  $H_2$ dppd [6] and the bidentate ligands PNH<sub>2</sub> [7], PNHMe [8] and PNMe<sub>2</sub> [9] were prepared according to the methods published in the literature. The homologous ligands  $H_2$ dpbd and  $H_3$ dpped were obtained through the procedure below detailed for  $H_3$ dpbd.

H<sub>2</sub>dpbdCO. In a three-necked flask equipped with a refrigerator, succinyl dichloride (2.085 cm<sup>3</sup>, 18 mmol) was added, under a nitrogen atmosphere, to a stirred solution containing  $PNH_2$  (10 g, 36 mmol) and py (6 cm<sup>3</sup>, 114 mmol) dissolved in anhydrous THF (40 cm<sup>3</sup>). The deep-red reaction mixture deposited a white precipitate  $(py \cdot HCl)$  which was filtered off. The filtrate was concentrated by a rotavapor and treated with water (50 cm<sup>3</sup>) and  $CH_2Cl_2$  (200 cm<sup>3</sup>). The organic phase was then desiccated with MgSO<sub>4</sub>, reduced in volume and treated with *n*-hexane ( $150 \text{ cm}^3$ ). Standing in the freezer overnight the solution deposited a white precipitate which was filtered off and recrystallized from THF (yield 37.7%). Anal. Found: C, 76.1; H, 5.7; N, 4.2. Calc. for C<sub>40</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C, 75.5; H, 5.4; N, 4.4%. IR (cm<sup>-1</sup>): 3241,  $\nu$ (N–H); 1680 v(C=O). <sup>1</sup>H NMR (CDCl<sub>1</sub>):  $\delta$  8.05 (m, 2H, N-H), 7.40-6.80 (28H, aromatic H), 2.28 (s, 4H,  $CH_2$ ). <sup>31</sup>P{<sup>1</sup>H}:  $\delta$ -21.0 (s).

 $H_2$ dpbd. In a three-necked flask equipped with a refrigerator and a dropping funnel, an excess of LiAlH<sub>4</sub> (1.5 g, 39.5 mmol) was suspended in Et<sub>2</sub>O (50 cm<sup>3</sup>). To this mixture at reflux, H<sub>2</sub>dppdCO (2 g, 3.14 mmol) dissolved in benzene (300 c. $\sigma^3$ ) was added dropwise within 4 h giving a green coloured solution which was cooled at room temperature and treated with water and then with a 20%  $H_2SO_4$  solution. The organic phase was desiccated with MgSO<sub>4</sub>, reduced in volume and treated under stirring with EtOH until the precipitation of a white solid, which was collected by filtration and washed with Et<sub>2</sub>O (yield 45.2%). Anal. Found: C, 79.9; H, 6.1; N, 4.8. Calc. for C<sub>40</sub>H<sub>38</sub>N<sub>2</sub>P<sub>2</sub>: C, 78.9; H, 6.3; N, 4.6%. IR (cm<sup>-1</sup>): 3354,  $\nu$ (N-H); 2944, 2870  $\nu$ (C-H)<sub>aliph</sub>; 1585, 1503  $\nu$ (C-C)<sub>arom</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.45–6.50 (28H, aromatic H), 4.51 (bs, 2H, N-H), 2.98 (t, 4H, N-CH<sub>2</sub>), 1.37 (t, 4H, central CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H}:  $\delta$  – 22.0 (s).

H<sub>2</sub>dppedCO. A similar procedure was adopted to that for H<sub>2</sub>dpbdCO using glutaryl dichloride instead of succinyl dichloride (yield 38.9%). *Anal.* Found: C, 75.9; H, 5.7; N, 4.5. Calc. for C<sub>41</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C, 75.6; H, 5.6; N, 4.3%. IR (cm<sup>-1</sup>): 3368,  $\nu$ (N-H); 1692  $\nu$ (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 8.10–7.80 (2H, N–H), 7.35–6.80 (28H, aromatic H), 2.10 (t, 4H, N–CH<sub>2</sub>), 1.82 (q, 2H, central CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H}:  $\delta$ – 21.2 (s).

H<sub>2</sub>dpped. A similar procedure was adopted to that for H<sub>2</sub>dpbd using H<sub>2</sub>dppedCO as the substrate (yield 35.8%). Anal. Found: C, 79.9; H, 6.1; N, 4.8. Calc. for C<sub>41</sub>H<sub>40</sub>N<sub>2</sub>P<sub>2</sub>: C, 79.1; H, 6.5; N, 4.5%. IR (cm<sup>-1</sup>): 3385,  $\nu$ (N-H); 2933, 2850  $\nu$ (C-H)<sub>aliph</sub>; 1588, 1503  $\nu$ (C-C)<sub>arom</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.40-6.50 (28H, aromatic H), 4.50 (bs, 2H, N-H), 2.96 (t, 4H, N-CH<sub>2</sub>), 1.41 (q, 4H, N-CH<sub>2</sub>-CH<sub>2</sub>), 1.08 (q, 2H, central CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H}:  $\delta$  - 22.0 (s).

#### 2.4. Preparation of the complexes

The labile Cu<sup>1</sup> complex  $[Cu(MeCN)_{4}]BF_{4}$  was prepared according to the method published in the literature [10].  $[Cu(H_{2}dped)]BF_{4}$  (1),  $[Cu(H_{2}dppd)]BF_{4}$  (2) [2],  $[Cu(H_{2}dped)](BF_{4})_{2}$  (8) [3] and  $[Cu(H_{2}dppd)](ClO_{4})_{2}$ (9) [4] were synthesized as previously reported. Crystals of 2 · MeCN were grown from a CH<sub>2</sub>Cl<sub>2</sub>-MeCN solution.

[Cu(H<sub>2</sub>dpbd)]BF<sub>4</sub> (3). Solid H<sub>2</sub>dpbd (0.400 g, 0.66 mmol) was added to a solution of [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> (0.207 g, 0.66 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 cm<sup>3</sup>) The reaction mixture was left to stir at room temperature for approximately 2 h until a white precipitate appeared. The white solid was collected by filtration, washed with CH<sub>2</sub>Cl<sub>2</sub> and dried under a vacuum pump (yield 81%). *Anal*. Found: C, 64.0; H, 5.3; N, 4.0. Calc. for C<sub>40</sub>H<sub>38</sub>BCuF<sub>4</sub>N<sub>2</sub>P<sub>2</sub>: C, 63.3; H, 5.0; N, 3.7%.

[Cu(H<sub>2</sub>dpped)]BF<sub>4</sub> (4). This compound was prepared as 3 by using H<sub>2</sub>dpped as ligand (yield 77%). Anal. Found: C, 62.7; H, 5.3; N, 3.7. Calc. for  $C_{41}H_{40}BCuF_4N_2P_2$ : C, 63.7; H, 5.2; N, 3.6%.

 $[Cu(PNH_2)_2]BF_4$  (5). Solid PNH<sub>2</sub> (0.28 g, 1.01 mmol) was added under stirring to a solution of  $[Cu(MeCN)_4]BF_4$  (0.159 g, 0.5 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>). After 2 h the solvent was removed using a gentle stream of nitrogen and the residue was treated with MeOH (10 cm<sup>3</sup>). A white solid was collected by filtration, washed with few drops of Et<sub>2</sub>O and dried under a vacuum pump (yield 79%). Anal.

Found: C, 60.4; H, 4.5; N, 3.8. Calc. for  $C_{36}H_{32}BCuF_4N_2P_2$ : C, 61.3; H, 4.6; N, 3.9%.

[Cu(PNHMc)<sub>2</sub>]BF<sub>4</sub> (6). This was prepared as detailed above for 5 (yield 80%). Anal. Found: C, 61.8; H, 5.1; N, 3.9. Calc. for  $C_{38}H_{36}BCuF_4N_2P_2$ : C, 62.3; H, 4.9; N, 3.8%.

 $[Cu(PNMe_2)_2]BF_4$  (7). This was prepared as detailed above for 5 (yield 74%). Anal. Found: C, 64.1; H, 5.3; N, 3.7. Calc. for C<sub>40</sub>H<sub>40</sub>BCuF<sub>4</sub>N<sub>2</sub>P<sub>2</sub>: C, 63.1; H, 5.3; N, 3.7%.

[Cu(H<sub>2</sub>dpbd)](ClO<sub>4</sub>)<sub>2</sub> (**10**). A slurry of **3** (0.91 g, 1.20 mmol) in DCE (25 cm<sup>3</sup>) containing 0.2 mol dm<sup>-3</sup> TBAP, was exhaustively (1 F mol<sup>-1</sup>) oxidized at a platinum gauze electrode at +0.90 V versus SCE. During the electrolysis a deep-red solid began to precipitate. Upon completion, toluene (25 cm<sup>3</sup>) was added to induce precipitation, and the mixture was cooled at 0°C. The product was isolated by filtration, rinsed with two 5 cm<sup>3</sup> portions of cold DCE-toluene, and dried in vacuo. Yield 0.85 g (81%). Anal. Found: C, 56.0; H, 4.5; N, 3.2. Calc. for C<sub>40</sub>H<sub>38</sub>Cl<sub>2</sub>CuN<sub>2</sub>O<sub>8</sub>P<sub>2</sub>: C, 55.1; H, 4.4; N, 3.2%.

[Cu(PNH<sub>2</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (11). Solid PNH<sub>2</sub> (0.20 g, 0.72 mmol) was added to a light-blue solution of [Cu(H<sub>2</sub>O)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> (0.124 g, 0.36 mmol) dissolved in the minimum volume of acetone (6 cm<sup>3</sup>) with stirring at ro- $\gamma$  temperature. The solution immediately turned dark-red and was stirred for a few additional minutes until complete ligand dissolution. Addition of diethyl ether (20 cm<sup>3</sup>) led to the precipitation of a dark-red microcrystalline powder, which was collected upon filtration and dried in vacuo. Yield 0.19 g (67%). Anal. Found: C, 54.4; H, 4.0; N, 3.5. Calc. for C<sub>30</sub>H<sub>32</sub>B<sub>2</sub>CuF<sub>8</sub>N<sub>2</sub>P<sub>2</sub>: C, 54.6; H, 4.1; N, 3.5%.

 $[Cu(PNHMe)_2](BF_4)_2$  (12). A similar procedure was adopted to that for 11 using  $[Cu(H_2O)_6](BF_4)_2$  (0.178 g, 0.51 mmol) and PNHMe (0.30 g, 1.03 mmol) as the substrates in acetone. Yield 0.27 g (65%). Anal. Found: C, 54.9; H, 4.2; N, 3.3. Calc. for  $C_{38}H_{36}B_2CuF_8N_2P_2$ : C, 55.7; H, 4.4; N, 3.4%.

**Caution!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Particular caution must be exercised when they are dried under vacuum.

#### 2.5. X-ray crystallography

A colourless transparent crystal, formed by slow evaporation of a  $CH_2Cl_2$ -MeCN solution, of dimensions  $0.20 \times 0.08 \times 0.24$  mm was used.

Crystal data for 2 · MeCN. Formula C<sub>41</sub>H<sub>30</sub>BCuF<sub>4</sub>N<sub>3</sub>P<sub>2</sub>. M = 786.0, monoclinic, Z = 4, a = 11.483(4), b = 13.516(6), c = 24.224(9) Å,  $\beta = 97.53(3)^\circ$ , V = 3727(3) Å<sup>3</sup>, space group  $P2_1/n$ , Z = 4,  $D_c = 1.400$  g cm<sup>-3</sup>,  $\mu = 7.3$  cm<sup>-1</sup>. The lattice parameters were obtained from least-squares analysis of 50 reflections with  $2\theta > 20^\circ$ , from graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Siemens Nicolet R3m/V diffractometer. Intensity data of 3619 unique reflections were collected at room temperature by the  $\omega - 2\theta$ scan technique with  $2\theta$  between 4 and  $40^\circ$ , since a preliminary data collection showed paucity of observed reflections at

 $2\theta > 40^\circ$ . The intensity and orientation of two standard reflections were measured again every 150 reflections; no significant decomposition or movement of the crystal was observed. Corrections were made for Lorentz and polarization and

Table 2 Atomic fractional coordinates  $(\times 10^4)$  and equivalent isotropic displacement coefficients  $(\times 10^3)$  for 2·MeCN

Atom	x	у	z	U <sub>eq</sub>
Cu	1410(2)	223(1)	1758(1)	33(1)
P(1)	2436(3)	-608(3)	1205(2)	31(1)
P(2)	-451(3)	-60(3)	1852(2)	33(1)
N(1)	2273(10)	1547(9)	1515(5)	33(4)
N(2)	1712(9)	504(8)	2633(5)	34(4)
C(1)	3262(13)	1687(12)	1992(6)	42(4)
C(2)	2827(12)	2066(11)	2493(7)	42(4)
C(3)	1691(13)	1629(11)	2649(7)	45(4)
C(4)	2915(11)	416(10)	809(6)	28(4)
C(5)	3419(12)	288(14)	322(6)	47(4)
C(6)	3751(15)	1073(13)	23(8)	61(5)
C(7)	3625(14)	2018(14)	219(7)	55(5)
C(8)	3143(13)	2164(12)	692(7)	42(4)
C(9)	2767(11)	1370(10)	1003(6)	24(3)
C(10)	- 345(12)	-5(11)	2606(6)	35(4)
C(11)	-1314(14)	-205(13)	2871(7)	51(4)
C(12)	-1159(15)	-286(14)	3450(7)	59(5)
C(13)	-63(16)	183(15)	3740(8)	74(6)
C(14)	885(14)	85(12)	3480(7)	53(5)
C(15)	723(12)	173(11)	2914(6)	34(4)
C(16)	3788(12)	- 1274(11)	1437(6)	31(4)
C(17)	4309(13)	= 1109(11)	1970(6)	40(4)
C(18)	5350(14)	= 1561(12)	2186(8)	55(5)
C(19)	5841(15)	= 2203(12)	1836(7)	53(5)
C(20)	5363(14)	= 2377(13)	1316(7)	55(5)
C(21)	4322(13)	= 1906(12)	1099(7)	47(4)
C(22)	1626(13)	= 1417(11)	688(6)	39(4)
C(23)	1510(14)	= 2416(13)	809(7)	49(5)
C(24)	811(15)	= 3003(15)	425(8)	67(6)
C(25)	294(16)	- 2634(15)	- 56(9)	71(6)
C(26)	347(16)	= 1651(14)	182(8)	69(6)
C(27)	1043(15)	-1013(14)	202(7)	61(5)
C(28)	= 1717(12)	687(11)	16(14(6)	31(4)
C(29)	- 1505(16)	1655(14)	1497(7)	60(5)
C(30)	= 2413(18)	2294(16)	1311(8)	80(6)
C(31)	= 3560(1B)	1947(16)	1219(8)	79(6)
C(32)	3754(16)	986(13)	1319/7)	57(5)
C(33)	~ 2845(12)	359(13)	1304(6)	45(4)
C(34)	=914(12)		1705(6)	33(4)
C(35)	- 785(14)	- 2053(12)	2109(7)	53(4)
C(36)	- 1030(14)	- 1037(13)	1087(7)	S4(S)
C(37)	- 1383(14)		1463/9)	54(5) 80(8)
C(38)	- 1565(14)	- 3201(14)	1071(8)	67(3)
C(39)	-1303(13)		1156(7)	38681
B	4351(22)	= 674/201	1120(7) 3614(11)	40(3) 77171
- Fr1)	40197181	(U#)#\U ((1)A&L	3100201	74(7) 16.1+4 -
+ \ + / Fr?\	4418(13) 4418(13)		**************************************	104(()) 134/61
- 16/ F(3)	3084101	- (3114) 3465	3330. RV	1.34(3) 90.cas
F(4)	30331131	6(7) 	3467(3) 3490/k/	(4) (99/4)
1 (4/ N(3)	40001161 40001101	*** 1391(11) 3939/19/	347U(0)	148(3)
(1) (3) (1) (3)	50701171 86344331	3131(17)	- 34(7) 842 101	120(7)
5140) C(A))	いいづねし <u>どどり</u> うまいうょうつい	469U(19) 2010-20-	38(1U)	Y8(8)
6(41)	1392(22)	2019(20)	141(10)	119(9)

Equivalent isotropic U defined as one-third of the trace of the orthogonalized  $U_0$  rensor.

Ladie 3			
Selected bond lengths (Å)	and angles	(°)	for 2 · MeCN

			and the second se
Cu-P(1)	2.205(5)	N(1)-C(9)	1.45(2)
Cu-P(2)	2.213(4)	N(2)-C(15)	1.47(2)
Cu-N(1)	2.16(1)	N(1)-C(1)	1.52(2)
Cu-N(2)	2.14(1)	C(1)-C(2)	1.46(2)
P(1)-C(4)	1.81(1)	C(2)-C(3)	1.52(2)
P(2)-C(10)	1.82(1)	C(3)-N(2)	1.52(2)
P(1)-Cu-P(2)	125.1(2)	Cu-N(1)-C(9)	110(1)
P(1)-Cu-N(1)	87.4(3)	Cu-N(2)-C(15)	112(1)
P(2)-Cu-N(2)	87.8(3)	Cu-N(1)-C(1)	102.6(8)
N(1)-Cu-N(2)	95.9(4)	Cu-N(2)-C(3)	101.7(8)
P(1)-Cu-N(2)	131.6(3)	N(1)-C(1)-C(2)	112(1)
P(2)-Cu-N(1)	130.9(3)	C(1)-C(2)-C(3)	<b>L18(1)</b>
Cu-P(1)-C(4)	99.1(4)	N(2)-C(3)-C(2)	$\mathbf{III}(1)$
Cu-P(2)-C(10)	99.1(4)		
and the second se			

absorption effects, via  $\Psi$  scans. The structure was solved by heavy-atom methods and refined by full-matrix least-square method, using 1897 ( $F_0 > 3\sigma(F_0)$ ) reflections. The final *R* value was 0.064. In the refinement procedure the quantity minimized was  $\sum w(|F_0| - |F_c|)^2$  with unit weight to each observation and all hydrogen atoms fixed at calculated positions. In the final  $\Delta F$  map the largest peak was 0.72 e Å<sup>-3</sup>, 0.88 Å far from F(1), along with some other peaks of comparable height in the BF<sub>4</sub> vicinity. Final fractional atomic coordinates are reported in Table 2, while selected bond distances and angles are listed in Table 3. All calculations were performed using the SHELXTL-PLUS package [11] and scattering factors for all the atoms were taken from Ref. [12].

## 3. Results and discussion

### 3.1. The ligands

The  $\{P_2N_2\}$  ligands were prepared by joining the nitrogen atoms of two molecules of the parent bidentate ligand PNH<sub>2</sub> using two different reaction procedures. The tetradentate ligands which incorporate the ethane or propane chain between the nitrogen donors (i.e. H<sub>2</sub>dped and H<sub>2</sub>dppd) were obtained by reacting 1,3-bis(toluene-p-sulfonyloxy) propane with cis-[Ni(PNH)<sub>2</sub>], as reported in the literature [6]. The sequential nucleophilic attack on the toluene-p-sulfonate substituted carbon atoms of the ethane (or propane) by the activated amido nitrogen atoms of cis-[Ni(PNH)2] does not work with longer (toluene-p-sulfonyloxy)aikanes. Consequently, H<sub>2</sub>dpbd and H<sub>2</sub>dpped were synthesized by reacting succinyl dichloride (and glutaryl dichloride) with PNH<sub>2</sub> in anhydrous THF in the presence of pyridine, followed by reduction with LiAlH<sub>4</sub> of the phosphinoamides to the corresponding phosphinoamines. This latter approach was found to be of general application for obtaining all the tetradentate phosphinoamines utilized in this work except for H<sub>2</sub>dppd.

 Table 4

 Relevant physicochemical data for Cu<sup>1</sup>-phosphinoamine complexes 1–7

Compound	IR(cm <sup>~1</sup> )		'H NMR " (ppm)		<sup>31</sup> P NMR <sup>a,b</sup>	FAB <sup>+</sup> m/z	-A <sub>M</sub> <sup>c</sup>	
	v(N-H)	v(BF4)	Hann	Haliph	N–H *	(ppm)	[fragment,%]	$(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$
$[Cu(H_2dped)]BF_4(1)$	3287	1084	7.2-7.6	3.19(s)	5.02(s)	- 13.1(s)	643[ <i>M</i> <sup>+</sup> ,100] 566[ <i>M</i> <sup>+</sup> -Ph.12]	150.4
$[Cu(H_2dppd)]BF_4(2)$	3272	1069	7.2–7.6	2.99(m) 1.98(m)	5.03(s)	- 15.1(s)	657[ <i>M</i> <sup>+</sup> ,100]	128.9
$Cu(H_2dpbd)BF_4(3)$	3280	1075	7.0–7.6	2.83(m) 1.66(m)	4.88(m)	- 15.4(s)	671[ <i>M</i> <sup>+</sup> ,100]	135.6
{Cu(H <sub>2</sub> dpped)]BF <sub>4</sub> (4)	3260	1080	6.9 <b>-7.6</b>	2.99(m) 1.29(m) 1.13(m)	<b>4.97(</b> s)	- 13.2(s)	685[ <i>M</i> <sup>+</sup> ,100]	120.2
$[Cu(PNH_2)_2]BF_4(5)$	3342 3264	1095	7.1-7.4		4.82(s)	- 13.4(s)	617[ <i>M</i> <sup>+</sup> ,41] 340[ <i>M</i> <sup>+</sup> -PNH <sub>2</sub> ,100]	160.4
$[Cu(PNHMe)_2]BF_4(6)$	3278	1068	7.07.5	2.52(d)	5.15(s)	- 16.0(s)	645[M <sup>+</sup> ,80] 354[M <sup>+</sup> -PNHMe,100]	151.7
$[Cu(PNMe_2)_2]BF_4(7)$		1058	7.2–7.6	2.52(d)		- 18.8(s)	673[ <i>M</i> <sup>+</sup> ,55] 368[ <i>M</i> <sup>+</sup> -PNMe <sub>2</sub> ,100]	127.1

" In chloroform-d.

<sup>b</sup> broad singlet.

<sup>c</sup> acetonitrile solutions.

#### 3.2, The copper(1) complexes

Complexes 1-7 can be prepared in high yields ( $\sim 80\%$ ) by ligand exchange reaction with the convenient already tested [2] reagent [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>, comploying the stoichiometric amount of the required ligand:

 $[Cu(MeCN)_{4}]^{+} + 2\{PN\}$  ligand

$$\rightarrow$$
 [Cu(PN)<sub>2</sub>]<sup>+</sup> + 4MeCN (1)

 $[Cu(MeCN)_{4}]^{+} + \{P_2N_2\}$  ligand

$$\rightarrow [Cu(P_2N_2)]' + 4MeCN = (2)$$

Analytical results, reported in Section 2, are in good agreement with the proposed formulae. Selected IR, NMR, FAB data and conductivity measurements (Table 4) reveal that the complexes are also tetracoordinated cationic species (Scheme 2).

The IR data for complexes 1-6 show the expected bathochromic shift of the  $\nu$ (N-H) band upon ligand coordina-



Scheme 2. Sketch of the molecular structure of complexes 1-7.

tion. Similarly, the solution state <sup>1</sup>H and <sup>31</sup>P NMR spectra reveal an appreciable downfield shift of both phosphorus and proton resonances when compared with those exhibited in uncoordinated ligands, thus confirming the involvement of the nitrogen and phosphorus bites in metal coordination. However, room temperature <sup>31</sup>P spectra of the Cu<sup>1</sup> complexes in each case consist of singlets without any evidence for unresolved fine structure. Lowering the temperature to 223 K (in chloroform-*d*) has no influence on the spectra. The absence of  $^{63/65}$ Cu- $^{31}$ P spin-spin coupling implies the occurrence of a chemical exchange process on the NMR timescale. Only the solid state CPMAS <sup>31</sup>P NMR spectra, depicted in Fig. 1 for 1 and 2, show clearly the metal-phosphorus coupling, which consists of unequally spaced quartets.

The multiplicity is due to spin-spin coupling of the copper nuclei ( $^{63}$ Cu,  $^{65}$ Cu, I = 3/2) with phosphorus. The line spacings in the quartet are unequal, as a result of the presence of a nuclear quadrupole coupling interaction between the copper nucleus and its surroundings owing to the lack of a spherically symmetrical charge distribution [13-17]. This is consistent also with the distorted coordination environments of 1 and 2 established by crystallographic analyses. In addition, the average line spacing of the quartet (1.248 and 1.188 kHz for 1 and 2 respectively) compares well with copper complexes which contain two coordinated phosphines [16]. Positive FAB and conductivity data confirm the monomeric and 1:1 electrolytic nature of these complexes. As to the geometrical nature of all complexes 1-7, a tetrahedral structure appears to be the most likely, as suggested by the known coordination chemistry of copper(1) and by the X-ray molecular structure of complex 1 [2]. We report here also on the X-ray molecular structure of complex 2, which confirms the expected tendency to the tetrahedral geometry of copper(1) complexes and pro-



Fig. 1. Solid-state CPMAS <sup>31</sup>P spectra of 1 (a) and 2 (b). The chemical shifts are relative to NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> ( $\delta = 0.0$  ppm), and centred at  $\delta = -13.2$  and = 14.0 ppm respectively.

vides further comparative information on this family of  $\{P_2N_2\}$  copper(I) species.

The molecular structure of complex 2, obtained as monoacetonitrile solvate, is depicted in Fig. 2.

The coordination sphere around copper is markedly distorted tetrahedral, major distortions arising from P(1)-Cu-N(1) and P(1)-Cu-N(2) angles (87.4 and 131.6° respectively). The tetradentate coordination mode of H<sub>2</sub>dppn leads to a tricyclic (5,6.5) system around copper, with the middle ring in a 'twist-boat' conformation (torsion angles in the range  $-76.1 - +48.2^{\circ}$ ) and making dihedral angles of 43.2 and 36.7° with the adjacent five-membered rings. These two rings are coughly perpendicular to each other, the dihedral angle being 100.4°. N(1) and N(2) donor atoms are located symmetrically above and below the P(1), Cu, P(2) plane by 1.35 Å. The BF<sub>4</sub><sup>-</sup> counter anion interacts via hydrogen bonding with N(1) and N(2) atoms; in particular, an intramolecular contact N(2)...F(3) of 2.89 Å, along with an intermolecular interaction N(1)...F(4) (at 1/2 - x, 1/2 + y, 1/2 - z) of 2.93 Å were found, and the geometry looks appropriate (pertinent angles at the hydrogen atoms both of 167°, with  $H(2)\cdots F(3)$  and  $H(1)\cdots F(4)$  separations of 2.01 and 2.05 Å respectively). The structures of  $[Cu(H_2dped)]^+(1)$ 



Fig. 2. Crystal structure of the cation in  $2 \cdot MeCN$ . The atom numbering scheme is shown and the thermal ellipsoids are drawn at 40% probability.  $BF_4^-$  and MeCN have been omitted for clarity.



Fig. 3. Superimposition of 1 and 2 (---).

and  $[Cu(H_2dppd)]^+$  (2) are roughly superimposable (Fig. 3), the weighted root mean square deviation derived by the BMFIT program [18] being 0.09 Å when the fitting is performed using the tetrahedral atoms and the only differences are shown by N(1)-Cu-N(2) angles (85.7 and 95.9° in 1 and 2 respectively) and P(1)-Cu-P(2) angles (132.8 and 125.1° in 1 and 2 respectively).

#### 3.3. The copper(II) complexes

The complexes  $|Cu(H_2dped)|^{2+}$  (8) and  $[Cu(H_2dppd)]^{2+}$  (9) were characterized previously in these laboratories by ESR (8) [3] and X-ray structural analysis (9); the last species was isolated as perchlorate salt [4]. The actual coordination sphere of the metal centre in the solid state is  $\{P_2N_2O\}$  in that an  $n^1$ -OClO<sub>3</sub> anion acts as a fifth ligand (vide infra) in a square-pyramidal geometrical array around Cu<sup>II</sup> and one ClO<sub>4</sub><sup>-</sup> unit acts as the counter anion. The two Cu<sup>II</sup>-P bond lengths are seen to be remarkably longer (2.325(4) Å) than the corresponding lengths in the related

Cu<sup>1</sup> complex (2.208(5) Å). Concomitantly, the Cu-N bonds are 2.06(1) versus 2.16(1) Å observed for the copper(I) precursor.

We report here on the synthesis and ESR characterization of  $Cu^{II}$  complexes derived from bidentate {PN} and tetradentate {P<sub>2</sub>N<sub>2</sub>} ligands, and on the redox behaviour of complexes **8–12**.

Complexes 8, 11 and 12 are obtained as dark-red microcrystalline products at ambient conditions upon reacting  $[Cu(H_2O)_6](BF_4)_2$  with the appropriate ligand under stoichiometric conditions in acetone with 65% yield. Complexes 9 and 10 are prepared by controlled potential one-electron oxidation of their corresponding Cu<sup>1</sup> species. The 1070 or 1095 cm<sup>-1</sup> single band due to BF<sub>4</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup> respectively is well apparent in both cases in DCE solution, while splitting of the  $\nu$ (Cl-O) in solid 9 and 10 is observed. The magnetic moments,  $\mu = 1.8$  BM, fit the expected values (1.75-2.20 BM) for square-planar, octahedral and pentacoordinate Cu<sup>11</sup> species.

The remarkably facile synthesis and apparent thermal stability of these and the other reported  $Cu^{11}$  phosphine complexes [3,4] suggested a cyclovoltammetric investigation upon starting from the relevant  $Cu^{1}$  analogues. The aim was to evaluate the relevance of the geometric features and hapticity of the {PN} ligands to the apparent stability of  $Cu^{11}$ complexes. The data are collected in Table 5 and depicted graphically in Figs. 4 and 5.

From the data reported in Table 5 it is apparent that the oxidation process

$$[\mathbf{Cu}^{\mathsf{I}}(\mathbf{P}_{2}\mathbf{N}_{2})]^{+} \rightarrow [\mathbf{Cu}^{\mathsf{II}}(\mathbf{P}_{2}\mathbf{N}_{2})]^{2+} + \mathrm{Ie}^{-1}$$
(3)

is not quite electrochemically reversible under the employed conditions. However, a reversible chemical character is shown by the perfect detectability of the cathodic peak associated with the anodic peak, even at lower scan rates. The remarkable thermal stability of the  $Cu^{II}$  species is shown by the substantial identity of the cyclovoltammetric patterns exhibited both by authentic (vide infra)  $Cu^{II}$  solutions and by  $Cu^{II}$  solutions obtained upon controlled potential oxidation of the relevant  $Cu^{I}$  species. The electrochemical irreversibility is seen to increase consistently with the length of the

**Tuble 5** 

Essential voltammetric data referring to the oxidation of Cu<sup>1</sup>-phosphino-amine species in 1,2-dichloroethane, 0.2 mol dm<sup>-1</sup> TBAP, at  $25^{\circ}C$ 

n-CH <sub>2</sub>	<i>Ε</i> <sub>1/2</sub> (V)	$\Delta E_{\rm p}$ (mV)			
2	0.080	132			
3	0.145	170			
4	0.170	220			
5	0.315	400			
	0.130	150			
	0.235	240			
	<i>n-</i> CH, 2 3 4 5	<i>n</i> -CH <sub>2</sub> $E_{1/2}$ (V)           2         0.080           3         0.145           4         0.170           5         0.315           0.130         0.235			

Platinum or glassy-carbon electrode. Scan rate 50 mV s<sup>-1</sup>. Potentials are referred to the ferrocenium/ferrocene redox couple ( $E_{1/2}$  = +0.420 V vs. aqueous SCE).

polymethylene tether featuring the  $\{P_2N_2\}$  ligands. Electrochemical irreversibility has often been interpreted as the consequence of significant geometric changes occurring in the depolarizer, associated with electron loss or uptake. In this case, the results can be interpreted as reflecting the increasing reluctance of the  $\{P_2N_2\}$  tetrahedral coordination sphere surrounding Cu<sup>1</sup> to 'accept' a square-planar geometry in the Cu<sup>11</sup> oxidation products. Indeed, this resistance parallels the reluctance of the metal centre to accept the removal of one electron  $(E_{1/2}$  increases from + 80 to + 315 mV). Consequently, Cu<sup>11</sup> appears to be best stabilized by shorter polymethylene tethers.

The data referring to complexes 11 and 12 cannot be easily interpreted in the light of the data discussed so far. The bidentate ligands appear to be only moderately suitable to stabilize Cu<sup>II</sup>, but still effective in this connection.

The copper(II) complexes were investigated by ESR spectroscopy in DCE solutions at room temperature. The spectrum of complex 8 has been reported and discussed in Ref. [3] and the spectra of complexes 11 and 12 are depicted in Figs. 6 and 7.

The ESR spectra of the copper(II) compounds consist of eight main lines of different widths. They arise from the



Fig. 4. Plot of  $E_{1/2}$ , expressed as the mean value of the potentials for the anodic and cathodic peak currents, as a function of the number *n* of the methylenes bridging the two nitrogen atoms in [Cu(P<sub>2</sub>N<sub>2</sub>)]<sup>+</sup> derivatives.



Fig. 5. Electrochemically reversible character of the Cu<sup>1</sup>  $\Leftrightarrow$  Cu<sup>1</sup> interconversion, expressed as the value of the anodic to cathodic peak separation  $\Delta E_p$  as a function of the number *n* of the methylenes bridging the two nitrogen atoms in [Cu(P<sub>2</sub>N<sub>2</sub>)]<sup>+</sup> derivatives.



Fig. 6. ESR spectrum of 11 in 1,2-dichloroethane at room temperature.



Fig. 7. ESR spectrum of 12 in 1.2. lichloroethane at = 30°C.

hyperfine interaction of the unpaired electron with a spin 3/2 nucleus (either <sup>63</sup>Cu or <sup>53</sup>Cu) and with two equivalent spin I = 1/2 nuclei (<sup>31</sup>P). Since the coupling constant for <sup>31</sup>P is about twice that for Cu, some of the expected 12 lines overlap partially. The high field components of the copper multiplet are much narrower than the other components and they show further splitting into a five line multiplet with approximate intensity ratios 1:2:3:2:1. This is expected for the hyperfine interaction of two equivalent nuclear spins I = 1 (<sup>14</sup>N). The latter is very well resolved in the high field line of the copper multiplet. The spectra were computer simulated by taking into account the presence of two copper isotopes in the natural isotopic abundance and also second order effects caused by the large value of the hyperfine couplings. Moreover, the linewidth was assumed to change with the Cu and clear spin quantum number  $m_{t}$ , according to the equation

$$(1/T_2)m_i = A + Bm_i + Cm_i^2$$
 (4)

The coefficients A, B and C depend on the anisotropies of the g tensor and of the Cu hyperfine dipolar coupling tensor. Other terms involving the  ${}^{31}$ P nuclear spin component were

l aoic o				
Hyperfine	constants	for Cu <sup>11</sup>	complexes	8-13

Cu <sup>11</sup> complex	A <sup>Cu</sup> ISO	A <sup>P</sup> ISO	A <sup>N</sup> ISO
	(G)	(G)	(G)
$[Cu(H_2dped)]^{2+}(8)$	84	169	10
$[Cu(H_{3}dppd)]^{2+}(9)$	80	179	10
$[Cu(H,dpped)]^{2+}$ (10)	79	178	10
$[Cu(PNH_2)_2]^{2+}(11)$	82	180	10
${Cu(PNHMe)_2}^{2+}$ (12) *	80	184	10

<sup>a</sup> The spectrum of 12 has been recorded at  $-30^{\circ}$ C owing to the instability of the complex at ambient temperature.

not necessary. This fact indicates that the anisotropy of the  ${}^{31}$ P coupling is negligible.

The Cu, P and N splitting constants are collected in Table 6. Inspection of Table 6 shows that the Cu and <sup>31</sup>P hyperfine splittings are very similar for the series of compounds which have been investigated. However, it is to be pointed out that complex 8, which in the series exhibits the highest Cu hyperfine coupling, also features the smallest P constant. This observation clearly indicates a shift of the unpaired electron density towards the metal centre. It is tempting to relate this observed increase in electron density on the metal atom with the lower oxidation potential of 8 compared with those of the other complexes. The differences between 9 and 10 are too small to be significant; remarkably, their oxidation potentials are also very similar. Unfortunately, the complex  $[Cu(dpped)]^{2+}$  was not sufficiently stable in solution for ESR measurements and complexes 11 and 12, although featuring a molecular structure related to that of compounds 8-10, cannot be considered sufficiently similar to them to be discussed reliably in this context.

The ESR spectra of frozen solutions of the copper(11) complexes 8 and 9 were also recorded. Unfortunately, computer simulation does not allow extraction of the g and hyperfine tensor components, owing to the complicated structure of the spectra. This complexity is due to the simultaneous contribution of the anisotropies of the g tensor and of the  ${}^{05}Cu_{-}{}^{03}Cu$  and <sup>31</sup>P hyperfine tensors having non-coincident principal axes.

Spectra were also recorded with a high field/high frequency (95 GHz) spectrometer (courtesy of Professor K. Möbius, Freie Universität Berlin) in order to increase the spectral resolution, in view of the g tensor anisotropy. However, again only poorly resolved spectra were obtained.

In view of the above, only the isotropic g factor could be obtained, i.e.  $g_{(x)} = 2.057$ , with no appreciable variations related to the nature of the coordinated ligands.

#### 4. Conclusions

The data presented in this paper clearly confirm the remarkable suitability of a  $\{P_2N_2\}$  chromophore to stabilize copper(II), and the voltammetric and ESR results start to shed light on the electronic and geometric features of the ligands apparently suitable to allow general access to this so far elusive class of copper(II) compounds.

### 5. Supplementary material

Additional material, available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, comprises full listing of bond lengths (Table A) and angles (Table B), anisotropic thermal parameters (Table C), H-atom coordinates (Table D) and observed/calculated structure factors (Table E). A packing diagram of the unit cell (Fig. A) has been deposited.

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#### References

[1] (a) A. Sobkowiak, A. Qui, X. Liu, A. Llobet and D.T. Sawyer, J. Am. Chem. Soc., 115 (1993) 609; (b) Z. Tyeklar, R.R. Jacobson, N. Wei, N.M. Murthy, J. Zubieta and K.D. Karlin, J. Am. Chem. Soc., 115 (1993) 2677; (c) K.D. Karlin, N. Wei, B. Jung, S. Kaderli, P. Niklaus and A.D. Zuberbuhler, J. Am. Chem. Soc., 115 (1993) 9506; (d) I. Sanyal, N.M. Murthy and K.D. Karlin, Inorg. Chem., 32 (1993) 5330; (e) S.P. Abraham, A.G. Samuelson and J. Chandrasekhar, Inorg. Chem., 32 (1993) 6107; (f) H. Okawa, M. Tadokoro, Y. Arakate, M. Ohba, K. Shindo, M. Mitsumi, M. Koikawa, M. Tomono and D.E. Fenton, J. Chem. Soc., Dalton Trans., (1993) 253; (g) G. Pilloni, B. Corain, M. Degano, B. Longato and G. Zanotti, J. Chem. Soc., Dalton Trans., (1993) 1777; (h) N. Kitajima and Y. Moro-oka, Chem. Rev., 94 (1994) 737; (1) K.D. Karlin, M.S. Nasir, B.I. Cohen, R.W. Cruse, S. Kaderli and A.D. Zuberbuhler, J. Am. Chem. Soc., 116 (1994) 1324; (j) N. Wei, N.M. Murthy, Z. Tyeklar and K.D. Karlin, Inorg. Chem., 33 (1994) 1177; (k) K.D. Karlin, S. Fox, A. Nanthakumar, N.N. Murthy, N. Wei, H.V. Obias and C.F. Martens, Pure Appl. Chem., 67 (1995) 289; (1) G. Pilloni, G. Valle, C. Corvaja, B. Longato and B. Corain, Inorg. Chem., 34 (1995) 5910; (m) G. Pilloni, B. Longato, G. Bandoli and B. Corain, J. Chem. Soc., Dalton Trans., (1997) 819.

- [2] F. Tisato, F. Refosco, G. Bandoli, G. Pilloni and B. Corain, J. Chem. Soc., Dalton Trans., (1994) 2471.
- [3] F. Tisato, F. Vallotto, G. Pilloni, F. Refosco, C. Corvaja and B. Corain, J. Chem. Soc., Chem. Commun., (1994) 2397.
- [4] G. Pilloni, F. Tisato, G. Bandoli and B. Corain, J. Chem. Soc., Chem. Commun., (1996) 433.
- [5] W. Levason, in F.R. Hartley (ed.), The Chemistry of Organophosphorous Compounds, Wiley-Interscience, New York, 1990, Vol. 1, Ch. 15.
- [6] M.K. Cooper, P.A. Duckworth, T.H. Hambley, G.J. Organ, K. Hendrick, M. McPartlin and A. Parekh, J. Chem. Soc., Dalton Trans., (1989) 1067.
- [7] M.K. Cooper, J.M. Downes, P.A. Duckworth, M.C. Kerby, R.J. Powell and M.D. Soucek, Inorg. Synth., 25 (1989) 129.
- [8] M.K. Cooper, J.M. Downes, P.A. Duckworth and E.R. Tiekink, Aust. J. Chem., 45 (1992) 595.
- [9] T.B. Rauchfuss and D.M. Roundhill, J. Am. Chem. Soc., 96 (1974) 3098.
- [10] B.J. Hathaway, D.G. Holah and J.D. Postlethwaite, J. Chem. Soc., (1961) 3215.
- [11] G.M. Sheldrick, SHELXTL-PLUS program for crystal structure determination, University of Cambridge, Cambridge, 1990.
- [12] International Tables for X-Ray Crystallography, Vol. 4, Kynoch, Birmingham, 1974.
- [13] A. Marker and M.J. Gunther, J. Magn. Reson., 47 (1983) 118.
- [14] E.M. Menger and W.S. Veeman, J. Magn. Reson., 46 (1982) 257.
- [15] J. Bacon, R.J. Gillespie and J.W. Quail, Can. J. Chem., 41 (1963) 3063.
- [16] G.A. Bowmaker, J.D. Cotton, P.C. Healy, J.D. Kildea, S.B. Silong, B.W. Skelton and A.H. White, Inorg. Chem., 28 (1989) 1462.
- [17] (a) G.A. Bowmaker, A. Camus, P.C. Healy, B.W. Skelton and A.H. White, Inorg. Chem., 28 (1989) 3883; (b) B. Mohr. J. Schimdt, E.E. Brooks, M.J. Heeg, D.M. Ho and E. Deutsch, Inorg. Chem., 32 (1993) 3236.
- [18] S.C. Nyburg, Acta Crystallogr., Sect. B, 30 (1974) 251