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Binuclear copper(I) complexes containing bis(diphenylphosphino)ethane bridges: the crystal structure of bis[{μ-bis(diphenylphosphino)ethane}(pyridine-2-thione)copper(I) bromide]

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Abstract

Treatment of copper(I) bromide with one equivalent of 1,2-bis(diphenylphosphino)ethane (dppe), followed by the addition of one equivalent of heterocyclic thione L {L = pyridine-2-thione (py2SH), pyrimidine-2-thione (pymtH), imidazole-2-thione (imtH), benz-1,3-imidazoline-2-thione (bzimtH$_2$), benz-1,3-thiazoline-2-thione (bztztH), 2-mercapto-1-methylimidazole (meimtH), 4,6-dimethylpyrimidine-2-thione (dmpymtH), and 6-ethoxybenz-1,3-thiazoline-2-thione (etObztztH) in dry acetone affords the dinuclear complexes [CuBr(dppe)(L)]$_2$ in ca. 60–80% yield. These compounds have been characterized by their IR, far-IR, UV–Vis and ^{1}H NMR spectroscopic data. The crystal structure of [CuBr(dppe)(py2SH)]$_2$ has been determined by single-crystal X-ray diffraction methods. In the dinuclear complex in which the two monomers are related by inversion, each Cu(I) centre exhibits a tetrahedral coordination sphere involving, besides the bromine, the exocyclic sulfur of one thione molecule and two phosphor atoms from two different diphosphine units. Vibrational, electronic and ^{1}H NMR spectral data of the complexes are discussed in relation to the structure. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Copper(I) bromide complexes; Heterocyclic thione complexes; Diphosphine complexes; Dinuclear complexes; Crystal structures

1. Introduction

Owing to their relevance in biological systems, heterocyclic thiones have attracted considerable attention as ligands in metal complexes [1]. Because of their application in catalytic functions, transition metal complexes with phosphine ligands have also been studied extensively [2]. In recent years, we have explored the group IB metal complexes blending both heterocyclic thione and tertiary arylphosphine ligands. In the course of our investigations, whose major target was the study of the factors that govern the coordination geometry of the metal atom, a large set of compounds with an interesting and in some cases unpredictable structural variety has been observed [3]. Although the interplay of several parameters like the geometrical flexibility of the coinage metals and electronic properties or bulkiness on the part of the ligands make structural prediction of these complexes virtually impossible, steric demands of the phosphine ligands seems to be of major importance causing significant changes on the coordination geometry of the metal atom [4]. To obtain further insight into this very interesting field of research we, therefore, decided to initiate a comparative investigation on substituting the unidentate triarylphosphines with acyclic multidentate phosphine ligands.

Recent interest in copper(I) bis(diphosphine) complexes, which are mostly polynuclear species containing bridging diphosphines, stems from their potential biological significance [5]. In this work, we report on the reaction of copper(I) bromide with 1,2-bis(diphenylphosphino)ethane (dppe) and several heterocyclic thione ligands, as well as the structure of [CuBr(dppe)(py2SH)]$_2$.

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2. Experimental

2.1. Materials and instruments

Copper(I) bromide, 1,2-bis(diphenylphosphino)-ethane and all solvents are commercially available and were used as obtained, while the thiones (E. Merck or Aldrich) were recrystallized from hot ethanol prior to their use. IR, UV, Vis and NMR spectra, conductivities, melting points and elemental analyses of carbon, nitrogen and hydrogen were performed as described previously [6].

2.2. Preparation of the complexes

The complexes of the formula $[CuBr(dppe)(L)]_2$ were prepared according to the following general procedure. A solution of 1,2-bis(diphenylphosphino)ethane (99.6 mg, 0.25 mmol) in dry acetone (20 ml) was added to a stirred suspension of CuBr (35.3 g, 0.25 mmol) in 15 ml of the same solvent and the mixture was stirred and moderately heated. After the formation of a complete clear solution, 0.25 mmol of the appropriate thione, dissolved in dry acetone (30 ml), was added slowly and the stirring was continued for 2 h. The resulting solution was filtered off and allowed to cool. Slow evaporation of the solvent at room temperature (r.t.) gave the microcrystalline solid, which was filtered off and dried in vacuo.

2.2.1. $[CuBr(dppe)(py2SH)]_2$

Yellow crystals. Yield: 80%, m.p. 220°C. *Anal.* Calc. for $C_{62}H_{58}Br_2Cu_2N_2P_4S_2$: C, 57.0; H, 4.5; N, 2.1. Found: C, 56.3; H, 4.5; N, 2.1%. UV–Vis (λ, log ε): 295 (4.46); 244 (4.52). IR (cm^{-1}): 3048 m, 2960 m, 2897 s, 1610 s, 1577 vs, 1500 s, 1433 vs, 1366 s, 1132 vs, 1097 s, 882 m, 745 vs, 695 vs, 518 s, 479 s, 448 s, 336 m. ^{1}H NMR: δ 14.25 (s, >NH), 7.60–7.10 (m, aromatic), 2.17 (s, P–CH_2CH_2–P).

2.2.2. $[CuBr(dppe)(pymtH)]_2$

Orange–red crystals. Yield: 80%, m.p. 148°C. *Anal.* Calc. for $C_{60}H_{56}Br_2Cu_2N_4P_4S_2$: C, 55.1; H, 4.3; N, 4.2. Found: C, 55.9; H, 4.4; N, 4.2%. UV–Vis (λ, log ε): 290 (4.69); 247 (4.66). IR (cm^{-1}): 3066 m, 2923 w, 1606 m, 1564 vs, 1480 s, 1432 vs, 1324 s, 1175 vs, 1091 s, 1025 m, 744 vs, 697 vs, 511 s, 481 m, 448. ^{1}H NMR: δ 14.80 (s, >NH), 7.50–7.20 (m, aromatic), 2.17 (s, P–CH_2CH_2–P).

2.2.3. $[CuBr(dppe)(bzimtH_2)]_2$

Pale-yellow crystals. Yield: 60%, m.p. 146°C. *Anal.* Calc. for $C_{66}H_{60}Br_2Cu_2N_4P_4S_2$: C, 57.3; H, 4.4; N, 4.1. Found: C, 57.8; H, 4.2; N, 4.1%. UV–Vis (λ, log ε): 309 (4.95); 248 (5.09). IR (cm^{-1}): 3049 s, 2925 m, 1618 m, 1500 vs, 1463 s, 1434 vs, 1359 s, 1172 s, 1099 s, 1026 m, 740 vs, 694 vs, 512 s, 478 m, 418 m. ^{1}H NMR: δ 12.43 (s, >NH), 7.65–7.15 (m, aromatic), 2.17–2.50 (m, P–CH_2CH_2–P).

2.2.4. $[CuBr(dppe)(bztzH)]_2$

Yellow crystals. Yield: 66%, m.p. 177°C. *Anal.* Calc. for $C_{66}H_{58}Br_2Cu_2N_2P_4S_4$: C, 55.9; H, 4.5; N, 2.0. Found: C, 54.8; H, 4.1; N, 2.1%. UV–Vis (λ, log ε): 328 (4.38); 244 (4.58). IR (cm^{-1}): 3057 m, 2953 m, 1597 m, 1490 vs, 1458 s, 1428 vs, 1321 vs, 1170 s, 1099 s, 1076 m, 1031 vs, 1013 s, 745 vs, 693 s, 512 s, 423 m. ^{1}H NMR: δ 12.90 (s, >NH), 7.70–7.26 (m, aromatic), 2.03–2.59 (m, P–CH_2CH_2–P).

2.2.5. $[CuBr(dppe)(meimtH)]_2$

Pale-yellow crystals. Yield: 75%, m.p. 225°C. *Anal.* Calc. for $C_{60}H_{60}Br_2Cu_2P_4N_4S_2$: C, 54.9; H, 4.6; N, 4.3. Found: C, 55.3; H, 4.9; N, 4.1%. UV–Vis (λ, log ε): 266 (4.31); 245 (4.25). IR (cm^{-1}): 3131 m, 3046 m, 2940 w, 1572 vs, 1478 vs, 1433 vs, 1281 vs, 1254 m, 1153 s, 1095 s, 1025 m, 998 m, 883 m, 756 vs, 670 vs, 514 vs, 487 s, 416 m, 341 m. ^{1}H NMR: δ 12.50 (s, >NH), 7.80–7.26 (m, aromatic), 6.80–6.75 (m, –CH=CH–), 3.67 (s, >N–CH_3), 2.03–2.17 (m, P–CH_2CH_2–P).

2.2.6. $[CuBr(dppe)(imtH)]_2$

Red–brown crystals. Yield: 65%, m.p. 171°C. *Anal.* Calc. for $C_{58}H_{60}Br_2Cu_2N_4P_4S_2$: C, 54.1; H, 4.7; N, 4.3. Found: C, 53.7; H, 4.4; N, 4.9%. UV–Vis (λ, log ε): 290 (4.54); 243 (4.42). IR (cm^{-1}): 3138 m, 3055 m, 2950 w, 1582 vs, 1480 s, 1438 vs, 1306 m, 1169 vs, 1115 vs, 989 m, 738 vs, 730 vs, 697 vs, 618 s, 535 vs, 511 vs, 406 m, 340 m. ^{1}H NMR: δ 13.10 (s, >NH), 7.76–7.26 (m, aromatic), 2.52 (s, N–CH_2CH_2–N), 2.09–2.17 (m, P–CH_2CH_2–P).

2.2.7. $[CuBr(dppe)(dmpymtH)]_2$

Yellow crystals. Yield: 76%, m.p. 246°C. *Anal.* Calc. for $C_{64}H_{64}Br_2Cu_2N_4P_4S_2$: C, 56.3; H, 4.7; N, 4.1. Found: C, 55.8; H, 4.5; N, 4.0%. UV–Vis (λ, log ε): 294 (4.80); 247 (4.74). IR (cm^{-1}): 3148 m, 2910 w, 1614 vs, 1560 vs, 1483 s, 1433 vs, 1320 m, 1227 vs, 1189 s, 1098 s, 1027 m, 982 m, 885 m, 741 vs, 694 vs, 512 vs, 484 s, 416 m, 341 m. ^{1}H NMR: δ 13.95 (s, >NH), 7.66–7.08 (m, aromatic), 2.30 (s, C–CH_3), 2.17 (s, P–CH_2CH_2–P).

2.2.8. $[CuBr(dppe)(etObztztH)]_2$

Pale-yellow crystals. Yield: 70%, m.p. 177°C. *Anal.* Calc. for $C_{70}H_{66}Br_2Cu_2N_2O_2P_4S_4$: C, 55.8; H, 4.4; N, 1.8. Found: C, 55.3; H, 4.6; N, 2.0%. UV–Vis (λ, log ε): 331 (4.37); 247 (4.30). IR (cm^{-1}): 3033 m, 2925 w, 1601 vs, 1483 vs, 1427 vs, 1398 s, 1332 s, 1260 s, 1224 vs, 1099 s, 1044 vs, 1026 vs, 943 m, 877 m, 740 vs, 692 vs, 668 s, 584 s, 512 vs, 489 s, 421 m. ^{1}H NMR: δ 13.84 (s, >NH), 7.86–7.05 (m, aromatic), 4.07 (q, O–CH_2–C), 2.16 (s, P–CH_2CH_2–P), 1.45 (t, CH_3–C).

2.3. Collection and reduction of X-ray data

The unit cell and intensity data were collected on a Delft Instruments FAST diffractometer using the routines ENDEX, REFINE and MADONL in the MADNES software [7] and processed using ABSMAD [8]; detailed procedures are described by Darr et al. [9]. Absence of crystal decay in the X-ray beam was confirmed by checking equivalent reflections at the beginning and end of data collection, which lasted about 8 h. The structure was solved with SIR-92 [10] and refined with SHELX93 [11]. Details of crystal data and structure refinement and bond lengths (Å) and angles (°) are given in Tables 1 and 2, respectively. The copper, bromine, sulfur, phosphorus, nitrogen and carbon atoms were refined with anisotropic temperature factors. The hydrogen atoms were allowed to ride on their attached atoms with common isotropic temperature factors for methyl and non-methyl hydrogens. An absorption correction was made with DIFABS [12].

Table 1
Crystal data and structure refinement

Empirical formula	$C_{31}H_{29}BrCuNP_2S$
Formula weight	653.00
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	11.783(5)
b (Å)	15.539(5)
c (Å)	16.157(5)
β (°)	93.375(5)
Volume (Å^3)	2953(2)
Z	4
D_{calc} (Mg m^{-3})	1.469
Absorption coefficient (mm^{-1})	2.293
F(000)	1328
Crystal size (mm)	$0.21\times0.14\times0.05$
θ range for data collection (°)	1.82–25.05
Index ranges (°)	$-13\leq h\leq10$ $-16\leq k\leq17$ $-16\leq l\leq18$
Reflections collected	12213
Independent reflections	4526 [$R_{int}=0.0761$]
Observed reflections [$I>2\sigma(I)$]	3171
Refinement method	full-matrix least squares on F^2
Number of parameters	335
Goodness-of-fit on F^2 (S)	0.884
Final R indices [$I>2\sigma(I)$]	$R_1=0.0335$, $wR_2=0.0709$
R indices (all data)	$R_1=0.0521$, $wR_2=0.0815$
Final weighting scheme	Calc. $w=1/[\sigma^2(F_o^2)+(0.0146P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Residual diffraction max. (e Å^{-3})	0.371
Residual diffraction min. (e Å^{-3})	-0.342

Table 2
Bond lengths (Å) and angles (°)

Br–Cu	2.5693(12)	C(9)–C(10)	1.373(7)
Cu–P(2) # 1 [a]	2.2564(13)	C(10)–C(11)	1.380(6)
Cu–P(1)	2.2778(12)	C(12)–C(13)	1.359(6)
Cu–S	2.3456(13)	C(12)–C(17)	1.403(6)
S–C(1)	1.709(4)	C(13)–C(14)	1.400(7)
P(1)–C(6)	1.827(4)	C(14)–C(15)	1.350(8)
P(1)–C(12)	1.830(4)	C(15)–C(16)	1.377(7)
P(1)–C(18)	1.843(4)	C(16)–C(17)	1.373(7)
P(2)–C(20)	1.824(4)	C(18)–C(19)	1.525(5)
P(2)–C(26)	1.838(4)	C(20)–C(25)	1.389(5)
P(2)–C(19)	1.837(4)	C(20)–C(21)	1.398(6)
P(2)–Cu(1) # 1	2.2564(13)	C(21)–C(22)	1.370(6)
N(1)–C(1)	1.331(5)	C(22)–C(23)	1.372(6)
N(1)–C(2)	1.356(5)	C(23)–C(24)	1.380(6)
C(1)–C(5)	1.409(6)	C(24)–C(25)	1.387(6)
C(2)–C(3)	1.352(6)	C(26)–C(27)	1.372(5)
C(3)–C(4)	1.391(6)	C(26)–C(31)	1.393(5)
C(4)–C(5)	1.375(6)	C(27)–C(28)	1.390(5)
C(6)–C(11)	1.362(6)	C(28)–C(29)	1.354(6)
C(6)–C(7)	1.399(6)	C(29)–C(30)	1.374(7)
C(7)–C(8)	1.394(6)	C(30)–C(31)	1.391(5)
C(8)–C(9)	1.350(7)		
P(2) # 1–Cu–P(1)	123.14(4)	C(4)–C(5)–C(1)	119.5(5)
P(2) # 1–Cu–S	105.64(5)	C(11)–C(6)–C(7)	117.6(4)
P(1)–Cu–S	109.06(5)	C(11)–C(6)–P(1)	119.3(3)
P(2) # 1–Cu–Br	107.38(4)	C(7)–C(6)–P(1)	123.0(3)
P(1)–Cu–Br	101.25(3)	C(8)–C(7)–C(6)	120.3(5)
S–Cu–Br	109.98(3)	C(9)–C(8)–C(7)	120.2(5)
C(1)–S–Cu	108.7(2)	C(8)–C(9)–C(10)	120.2(5)
C(6)–P(1)–C(12)	102.7(2)	C(9)–C(10)–C(11)	119.5(5)
C(6)–P(1)–C(18)	99.5(2)	C(6)–C(11)–C(10)	122.1(4)
C(12)–P(1)–C(18)	107.3(2)	C(13)–C(12)–C(17)	117.8(4)
C(6)–P(1)–Cu	118.54(13)	C(13)–C(12)–P(1)	125.6(4)
C(12)–P(1)–Cu	111.62(12)	C(17)–C(12)–P(1)	116.6(4)
C(18)–P(1)–Cu	115.63(13)	C(12)–C(13)–C(14)	121.3(5)
C(20)–P(2)–C(26)	104.5(2)	C(15)–C(14)–C(13)	119.7(6)
C(20)–P(2)–C(19)	103.0(2)	C(14)–C(15)–C(16)	120.6(5)
C(26)–P(2)–C(19)	101.8(2)	C(17)–C(16)–C(15)	119.5(5)
C(20)–P(2)–Cu # 1	109.71(14)	C(16)–C(17)–C(12)	121.1(5)
C(26)–P(2)–Cu # 1	117.06(13)	C(19)–C(18)–P(1)	115.2(2)
C(19)–P(2)–Cu # 1	119.00(14)	C(18)–C(19)–P(2)	112.3(2)
C(1)–N(1)–C(2)	125.4(4)	C(25)–C(20)–C(21)	117.6(4)
N(1)–C(1)–C(5)	116.1(4)	C(25)–C(20)–P(2)	123.9(3)
N(1)–C(1)–S	121.6(3)	C(21)–C(20)–P(2)	117.9(3)
C(5)–C(1)–S	122.3(4)	C(22)–C(21)–C(20)	121.2(4)
C(3)–C(2)–N(1)	119.6(4)	C(21)–C(22)–C(23)	120.9(4)
C(2)–C(3)–C(4)	117.9(4)	C(22)–C(23)–C(24)	118.9(4)
C(5)–C(4)–C(3)	121.5(5)	C(23)–C(24)–C(25)	120.7(4)
C(24)–C(25)–C(20)	120.6(4)	C(29)–C(28)–C(27)	120.4(4)
C(27)–C(26)–C(31)	119.8(4)	C(28)–C(29)–C(30)	120.8(4)
C(27)–C(26)–P(2)	122.3(3)	C(29)–C(30)–C(31)	119.6(4)
C(31)–C(26)–P(2)	117.7(3)	C(30)–C(31)–C(26)	119.6(4)
C(26)–C(27)–C(28)	119.8(4)		

[a] Atomic coordinates transposed by $-x+3/2$, $-y+1/2$, $-z+1$.

3. Results and discussion

The complexes were prepared by reacting equimolar quantities of copper(I) bromide and 1,2-bis-(diphenylphosphino)ethane (dppe), followed by the addition of one equivalent of the appropriate thione (L) in dry acetone solution. This procedure, frequently used for the preparation of copper(I) halide complexes containing both heterocyclic thiones and triphenyl- or tritolylphosphine ligands, gave monomeric complexes of the formula $[CuX(PPh_3)_2L]$ [3] or dimers $[CuX(PPh_3)L]_2$ with the two copper centres being bridged either by the halogen [13] or by the thione-S atom [14]. In this work we expected that replacement of the monodentate phosphine by the bidentate dppe would lead to the formation of chelated products; however, this was not the case.

All the complexes are coloured solids soluble in chloroform, methanol, ethanol, acetone and acetonitrile. They are stable in air and moisture and can be, after the isolation, manipulated in air without appreciable decomposition. Their solutions are non-conducting in acetone and chloroform. Room temperature magnetic measurements confirm the diamagnetic nature of the compounds.

3.1. Spectroscopy

The electronic absorption spectra of the complexes in chloroform solutions are dominated by broad bands in the regions 240–250 and 280–330 nm attributable to intraligand transitions of the dppe, since the uncoordinated dppe also absorbs strongly in this region.

The infrared spectra of the compounds, recorded in the range 4000–250 cm^{-1}, show, apart from the existence of strong phosphine bands, all of the bands required by the presence of the heterocyclic thione ligands. In detail they exhibit the usual four 'thioamide bands' in the regions ~1510, 1320, 1000 and 750 cm^{-1}, although in some cases partly masked by strong phosphine absorptions, as well as the characteristic NH stretching vibrations observed in the 3050–3160 cm^{-1} region. The shifts observed for these bands due to coordination (upward shifts of 15–35 cm^{-1} for thioamide I, downward shifts of 10–30 cm^{-1} for thioamide II and III) in combination with the lack of ν(SH) bands at ca. 2500–2600 cm^{-1} [15] signify the exclusive S-coordination mode of the thione ligands.

The prevailance of the thione tautomer in the complexes is further confirmed by the ^{1}H NMR spectra of the compounds, which display, apart from the signals expected for the phosphine and thione ligands, a single resonance at $\delta \sim 12–14$ ppm attributed to the NH proton.

3.2. Description of the structure

The ability of 1,2-bis(diphenylphosphino)ethane (dppe) to chelate Cu(I) is well known and a few double-chelated cationic $Cu(dppe)_2^+$ species have been observed [16,17]. Most of the structurally characterized binuclear copper(I) complexes involving dppe ligands are, however, of the type $[Cu_2(dppe)_3L_2]$ [18–23], in which the diphosphine units act at the same time both as chelating ligands for each of the copper atoms and as a bridge between them. The double bridging coordination mode realized in the case of the complex under investigation is quite common for univalent Group 1B metal complexes of bis(diphenylphosphino)methane (dppm) [24–27].

Bond lengths and angles are given in Table 2. The atomic arrangement in the complex is shown in Fig. 1. The basic structural unit of $[Cu(dppe)(py2SH)Br]_2$ is a dimer in which the two monomers are related by inversion. The two copper atoms are doubly bridged by two dppe ligands to form a ten-membered $Cu_2P_4C_4$ ring. The slightly distorted tetrahedral coordination around copper is completed by one sulphur atom from the thione ligand and one bromine atom.

The Cu–S and Cu–Br bond lengths lie in the range normally observed for tetrahedrally coordinated copper(I) complexes with terminal bromine and thione-sulphur donors [28]. The two individual Cu–P distances of 2.2564(13) and 2.2778(12) Å are somewhat shorter than those found for bridging dppe in other dimeric copper(I) complexes, e.g. $[Cu_2Cl_2(dppe)_3]$ (2.284(6) Å) [20] and $[Cu_2(3\text{-}Me_3Sipyt)_2(dppe)_3]$ (2.294(3) Å) [23].

The irregularities in the tetrahedral coordination geometry about the copper(I) centre are best reflected in the values of the bond angles, since only three of them are close to the ideal tetrahedral value. As expected, the largest angle [P–Cu–P = 123.14(4)°] arises between the two most bulky ligands, whereas the presence of intramolecular hydrogen bonds between the bromine and the N(1)H, C(4)H(4) and C(19)H(19A) hydrogen [N(1)···Br = 3.226(3) Å, N(1)–H = 0.880(4) Å, H···Br = 2.367(3) Å, N(1)–H–Br = 165.1(3)°; C(4)···Br = 3.585(5) Å, C(4)–H(4) = 0.951(7) Å, H(4)···Br = 2.902(5) Å, C(4)–H(4)–Br = 129.6(5)°; C(19)···Br = 3.582(4) Å, C(19)–H(19) = 0.990(5) Å, H(19)···Br = 2.703(4) Å, C(19)–H(19)–Br = 148.1(4)°] could be responsible for the moderate narrowing of the P(1)–Cu–Br angle [101.25(3)°]. It is interesting to note that all these angles are in qualitative agreement with the corresponding values already observed for a series of monomeric copper(I) halide complexes that contain one heterocyclic thione and two monodentate triphenylphosphine ligands, exhibiting the same $CuSP_2X$ core [28]. Given that steric constrains between the ligands are of significance in achieving minimum energy arrangements around the metal centre, this fact indicates that the steric requirements of the bridging dppe units within the dimer $[Cu(dppe)(py2SH)Br]_2$ are approximately of the same magnitude as those of the triphenylphosphine ligands in the monomeric complexes $[Cu(PPh_3)_2(S)X]$ [29]. It seems plausible, therefore, to invoke steric reasons in order to explain the feature of the complex under investigation, the most energetically favourable

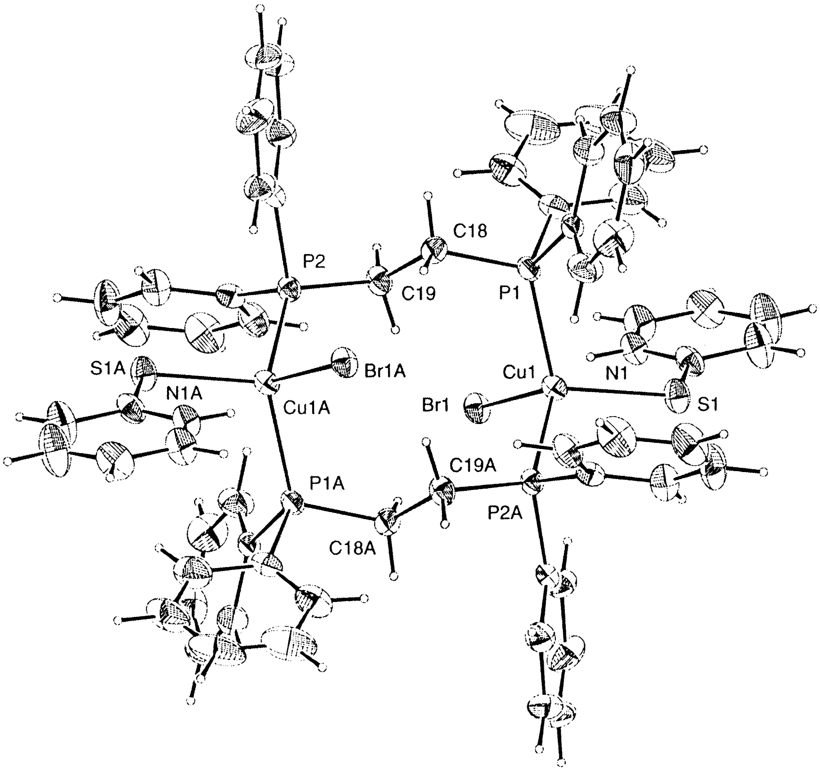

Fig. 1. A view of the complex with atom labels. Displacement ellipsoids are shown at the 50% probability level.

situation being manifested by the appearance of doubly bridged dppe ligands but not by the formation of five-membered chelate rings.

4. Supplementary material

Supplementary data are available free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk) quoting the deposition number CCDC-114060.

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