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Products of the reaction between copper(I) phenoxide and triphenylphosphine

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Abstract

Two phenolatocopper(I) derivatives, viz. $[Cu_4(PPh_3)_4(OPh)_4]$ (1) and $[Cu_2(PPh_3)_3(OPh)_2]$ (2), where $Ph = C_6H_5$, have been prepared by the addition of triphenylphosphine to copper(I) phenoxide, obtained from mesitylcopper(I) and phenol. Characterisation by means of crystal structure determination showed **1** to be a tetramer with a cubane-type Cu_4O_4 core in which Cu–O distances range from 2.05(2)–2.26(2) Å. Complex **2** is a μ_2-phenoxide dimer in which one copper(I) centre is four-coordinated by two phenoxide and two triphenylphosphine ligands, while the other is coordinated by a single triphenylphosphine ligand and thus three-coordinated. Complex **1** crystallises as the solvate $[Cu_4(PPh_3)_4(OPh)_4] \cdot (C_6H_5CH_3)_2$ in the monoclinic space group $P2_1/c$ with $a = 14.822(7)$, $b = 23.160(4)$, $c = 28.193(6)$ Å, $\beta = 98.64(2)°$, $V = 9569(5)$ Å^3 at -90 °C and $Z = 4$; full-matrix least-squares refinement yielded $R = 0.082$ for 529 parameters and 3931 observed reflections. $[Cu_2(PPh_3)_3(OPh)_2]$ (2) crystallises in the triclinic space group $P\bar{1}$ with $a = 13.948(4)$, $b = 16.846(2)$, $c = 12.480(3)$ Å, $\alpha = 94.92(2)$, $\beta = 110.45(2)$, $\gamma = 95.96(2)°$, $V = 2709(2)$ Å^3 at -120 °C and $Z = 2$; full-matrix least-squares refinement yielded $R = 0.063$ for 328 parameters and 2507 observed reflections. The effect of increasing the PPh_3:CuOPh ratio on the stability of the phenoxide is discussed in terms of the coordination geometry and consequent accessibility of the metal to small molecules.

Keywords: Crystal structures; Copper(I) complexes; Phenoxide complexes; Phosphine complexes

1. Introduction

Owing to their lability, relatively few copper(I) phenoxides have been isolated and characterised by means of crystal structure determination, uncharged aryloxides having hitherto been isolated only in the presence of stabilising ancillary ligands such as phosphines [1–5], isocyanides [4,6,7], or with heteroatomic substituents on the aryl group as stabilising components [8]. Recently, we have prepared tetrameric *o*-allylphenolatocopper(I), which is stabilised by π coordination of the ligand to copper(I) [9]. The reactions of triphenylphosphine derivatives of phenolatocopper(I) have been discussed extensively (see, e.g., Refs. [1,5,10–12]). Despite this, only the structure of $[Cu_2(PPh_3)_4(OPh)_2]$ is yet known: this compound is a μ_2-bridged phenolatocopper(I) dimer containing four-coordinated copper(I) [5]. Our interest in isolating and determining the structures of the analogues with lower Cu:PPh_3 ratios, viz 1:1 and 1:1.5, was to see if the greater lability of these compounds, as compared with that of $[Cu_2(PPh_3)_4(OPh)_2]$, could be rationalised in terms of a lower coordination number for copper(I) and thus greater accessibility of the metal towards small gaseous molecules in the 1:1 and 1:1.5 complexes. For instance, the 1:1 dimer $[Cu_2(PPh_3)_2(O^tBu)_2]$, in which copper(I) is three-coordinated, reacts readily with dihydrogen [13].

2. Experimental

All operations, apart from melting-point determination, were carried out under nitrogen or argon using standard Schlenk or special low-temperature techniques [14]. Triphenylphosphine was recrystallised from a hot ethanol solution. Both phenol and triphenylphosphine were dried in vacuo, dissolved in toluene and the solutions stored under argon. Mesitylcopper(I) was prepared as described previously [15–17].

2.1. Syntheses

2.1.1. Preparation of $[Cu_4(PPh_3)_4(OPh)_4] \cdot (C_6H_5CH_3)_2$ (1)

Excess phenol (1.1 mmol) in toluene (0.5 ml) was added to a toluene solution (3 ml) of mesitylcopper(I) (0.55 mmol). The pale yellow solution was stirred vigorously

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whereupon a yellow precipitate, presumably copper(I) phenoxide, $[Cu(OPh)_n]$, formed almost immediately. (On attempted isolation this precipitate rapidly became green.) After stirring of the slurry for 10 min, PPh_3 (0.55 mmol) dissolved in toluene (0.5 ml) was added dropwise so that the precipitate dissolved completely, forming a deep yellow solution. This solution was stirred overnight and then centrifuged. Crystals were grown by evaporation of the solution until precipitation started. The precipitate was then dissolved by heating, and the solution was allowed to stand, first at ambient temperature and then at 4 °C. Complex **1** crystallises as colourless plates which acquire a yellowish hue on isolation, and which decompose rapidly on heating, precluding melting-point determination, and on prolonged exposure to air.

2.1.2. *Preparation of $[Cu_2(PPh_3)_3(OPh)_2]$ (2)*

Complex **2** was prepared in an analogous way to **1** from phenol (1.1 mmol in 0.5 ml toluene) and mesitylcopper(I) (0.55 mmol in 3 ml toluene), with addition of PPh_3 (0.83 mmol in 0.8 ml toluene) to the resulting suspension of $[Cu(OPh)_n]$ in toluene. $[Cu(OPh)_n]$ dissolved forming a pale yellow solution, which was stirred overnight and then centrifuged. Colourless cubic-shaped crystals of **2**, which decomposed on heating and on prolonged exposure to air, were obtained by addition of hexane to the pale yellow solution until precipitation started. The precipitate was then dissolved by heating, and the resulting solution was allowed to stand, first at ambient temperature and then in a refrigerator. Crystal decomposition prevented determination of the melting-point of **2**. Crystals of **1** and of $[Cu_2(PPh_3)_4(OPh)_2]$ [5], the latter characterised by melting-point determination [1], were also obtained, it was possible to suppress the formation of **1** by addition of an excess of triphenylphosphine over the PPh_3:Cu ratio of 1.5:1. However, a PPh_3:Cu molar ratio of 2:1 yielded solely $[Cu_2(PPh_3)_4(OPh)_2]$.

2.2. *Crystallography*

2.2.1. *$[Cu_4(PPh_3)_4(OPh)_4]\cdot(C_6H_5CH_3)_2$ (1)*

A colourless plate-like crystal was mounted in a glass capillary under argon at −150 °C [14] and transferred at the same temperature to a Rigaku AFC6R diffractometer. Diffracted intensities were measured (cf. Table 1) using graphite-monochromated radiation from an RU200 rotating anode source operated at 9 kW (50 kV, 180 mA). The ω-2θ scan mode was employed with a 2θ scan rate of 8.0° min^{-1} and a ω scan width of $(0.59+0.30\tan\theta)°$. Weak reflections $(I<10\sigma(I))$ were rescanned up to three times and counts were accumulated to improve counting statistics. Stationary background counts were recorded on each side of the reflections, the ratio of peak counting versus background counting time being 2:1. Three reflections monitored at regular intervals (after every 150 reflections) showed no evidence of crystal decay. Intensities were corrected for Lorentz and polarisation effects and an empirical correction, based on azimuthal scans for several reflections, was made for the effects of absorption (max., min. transmission factors: 1.00, 0.89). Cell constants were determined from the setting angles of 16 reflections in the range $14.0<2\theta<16.1°$. Of the 17330 unique reflections measured, 3931 had $I>3.0\sigma(I)$ and were considered observed. The structure was solved by direct methods (MITHRIL [18]), and subsequent electron-density calculations. Full-matrix least-squares refinement, with anisotropic thermal parameters for the copper and phosphorus atoms, and isotropic thermal parameters for the oxygen and carbon atoms, and with hydrogen atoms as a fixed contribution in calculated positions (C–H = 0.95 Å; $B=1.2B$ of the carrying carbon atom) gave $R=0.082$ $(R_w=0.107)$ for 529 parameters and 3931 observed reflections. The maximum and minimum values in the final difference map were 1.6 and -0.6 e $Å^{-3}$, respectively. Reflections were weighted according to $w=[\sigma^2(F_o)]^{-1}$. Further details concerning the crystal structure determination are given in Table 1.

Table 1
Crystallographic data for $[Cu_4(PPh_3)_4(OPh)_4]\cdot(C_6H_5CH_3)_2$ (**1**) and $[Cu_2(PPh_3)_3(OPh)_2]$ (**2**)

	1	**2**
Formula	$C_{110}H_{96}Cu_4O_4P_4$	$C_{66}H_{55}Cu_2O_2P_3$
M_r	1860.0	1100.2
Space group	$P2_1/c$ (No. 14) [19a]	$P\bar{1}$ (No. 2) [19a]
Unit-cell dimensions		
a (Å)	14.822(7)	13.948(4)
b (Å)	23.160(4)	16.846(2)
c (Å)	28.193(6)	12.480(3)
α (°)		94.92(2)
β (°)	98.64(2)	110.45(2)
γ (°)		95.96(2)
V (Å)	9569(5)	2709(2)
Z	4	2
D_c (g cm^{-3})	1.29	1.35
$F(000)$	3856	1140
μ(Mo $K\alpha$) (cm^{-1})	9.95	9.17
Crystal size (mm)	0.20×0.20×0.10	0.10×0.10×0.10
T (°C) (data collection)	−90	−120
2θ limits (°)	$5<2\theta<50$	$5<2\theta<50$
ω Scan rate (° min^{-1})	8	8
Data collected	18061	8035
No. unique data	17330	7613
No. with $I>3.0\sigma(I)$	3931	2507
No. parameters refined	529	328
R	0.082	0.063
R_w	0.107	0.072

2.2.2. *$[Cu_2(PPh_3)_3(OPh)_2]$ (2)*

Diffracted intensities from a cubic-shaped crystal, mounted as above, were measured (cf. Table 1) using a Rigaku AFC6R diffractometer. Additional intensity data collection parameters were as for **1**, except that the ω scan width was $(0.94+0.30\tan\theta)°$, weak reflections were rescanned up to seven times, and the cell constants were determined from the setting angles for 16 reflections in the range $14.4<2\theta<21.9°$. No correction was made for the effects of absorption. Of the 7613 unique reflections measured, 2507

Table 2
Selected coordinates and equivalent isotropic thermal parameters (Å^2) for $[Cu_4(PPh_3)_4(OPh)_4]\cdot(C_6H_5CH_3)_2$ (1) [a]

Atom	*x*	*y*	*z*	B_{eq} [b]/*B*
Cu(1)	0.2947(2)	0.1789(1)	0.2993(1)	2.7(2)
Cu(2)	0.2046(2)	0.1458(1)	0.3916(1)	2.7(2)
Cu(3)	0.2731(2)	0.0486(1)	0.3264(1)	2.6(2)
Cu(4)	0.0971(2)	0.1282(1)	0.2854(1)	2.6(2)
P(1)	0.3599(5)	0.2438(3)	0.2630(3)	2.9(4)
P(2)	0.2085(5)	0.1576(3)	0.4676(2)	2.8(4)
P(3)	0.3524(5)	−0.0261(3)	0.3139(3)	3.0(4)
P(4)	−0.0456(5)	0.1418(3)	0.2602(2)	2.6(4)
O(1)	0.220(1)	0.1060(7)	0.2650(6)	2.5(4)
O(2)	0.327(1)	0.1267(7)	0.3592(5)	2.5(4)
O(3)	0.154(1)	0.0741(7)	0.3497(5)	2.4(4)
O(4)	0.173(1)	0.1945(7)	0.3305(5)	2.3(4)
C(1)	0.230(2)	0.092(1)	0.221(1)	2.9(6)
C(2)	0.165(2)	0.082(1)	0.183(1)	5.1(8)
C(3)	0.185(3)	0.068(2)	0.138(1)	6(1)
C(4)	0.273(3)	0.067(2)	0.131(1)	8(1)
C(5)	0.343(3)	0.071(2)	0.166(1)	7(1)
C(6)	0.323(2)	0.084(1)	0.212(1)	4.5(8)
C(7)	0.408(2)	0.129(1)	0.3878(8)	2.0(5)
C(8)	0.472(2)	0.173(1)	0.3813(9)	3.2(6)
C(9)	0.559(2)	0.176(1)	0.410(1)	4.1(7)
C(10)	0.579(2)	0.133(1)	0.445(1)	4.2(7)
C(11)	0.517(2)	0.089(1)	0.453(1)	3.8(7)
C(12)	0.435(2)	0.088(1)	0.424(1)	3.4(7)
C(13)	0.092(2)	0.039(1)	0.363(1)	3.2(6)
C(14)	0.028(2)	0.057(1)	0.389(1)	3.3(6)
C(15)	−0.037(2)	0.021(1)	0.405(1)	4.3(7)
C(16)	−0.038(2)	−0.036(1)	0.393(1)	4.0(7)
C(17)	0.025(2)	−0.057(1)	0.366(1)	4.1(7)
C(18)	0.087(2)	−0.019(1)	0.3502(9)	2.7(6)
C(19)	0.139(2)	0.247(1)	0.3300(8)	1.5(5)
C(20)	0.102(2)	0.272(1)	0.286(1)	3.3(6)
C(21)	0.063(2)	0.329(1)	0.285(1)	4.9(8)
C(22)	0.063(2)	0.357(1)	0.329(1)	4.8(7)
C(23)	0.104(2)	0.334(1)	0.373(1)	4.2(7)
C(24)	0.140(2)	0.279(1)	0.3726(9)	2.7(6)

[a] E.s.d.s are given in parentheses.

[b] B_{eq} is defined as $(8\pi^2/3)\ \Sigma_i\Sigma_j U_{ij}a_i*a_j*\mathbf{a}_i\cdot\mathbf{a}_j$.

had $I > 3.0\sigma(I)$ and were considered observed. The structure was solved by direct methods (MITHRIL [18]) and subsequent electron density calculations. Full-matrix least-squares refinement as for **1** gave $R=0.063$ ($R_w=0.072$) for 328 parameters and 2507 observed reflections. The maximum and minimum values in the final difference map were 0.48 and −0.49 e Å^{-3}, respectively. Reflections were weighted according to $w=[\sigma^2(F_o)]^{-1}$. Additional information is to be found in Table 1.

Selected fractional coordinates and equivalent isotropic thermal parameters for **1** and **2** are given in Tables 2 and 3, and selected bond distances and angles in Tables 4 and 5, respectively. The crystallographic numbering of the cores of **1** and **2** is as in Figs. 1 and 2. Atomic scattering factors and anomalous dispersion corrections were taken from Ref. [19b]; all calculations were performed using the TEXSAN [20] software package. Structural illustrations have been drawn with ORTEP [21].

Table 3
Selected coordinates and equivalent isotropic thermal parameters (Å^2) for $[Cu_2(PPh_3)_3(OPh)_2]$ (2) [a]

Atom	*x*	*y*	*z*	B_{eq} [b]/*B*
Cu(1)	0.2028(2)	0.2998(1)	0.8558(2)	1.72(8)
Cu(2)	0.3129(2)	0.2167(1)	0.7131(2)	2.01(8)
P(1)	0.0412(3)	0.3231(3)	0.7690(4)	1.7(2)
P(2)	0.3074(3)	0.3272(3)	1.0411(4)	1.8(2)
P(3)	0.3863(3)	0.1449(3)	0.6263(4)	1.9(2)
O(1)	0.2274(8)	0.1834(6)	0.805(1)	2.1(4)
O(2)	0.2915(8)	0.3262(6)	0.7544(9)	2.0(4)
C(1)	0.194(1)	0.110(1)	0.820(1)	1.6(3)
C(2)	0.246(1)	0.045(1)	0.813(1)	2.3(3)
C(3)	0.207(1)	−0.032(1)	0.831(2)	2.8(4)
C(4)	0.117(2)	−0.042(1)	0.851(2)	4.6(5)
C(5)	0.064(2)	0.020(1)	0.856(2)	4.8(5)
C(6)	0.101(1)	0.095(1)	0.842(2)	3.3(4)
C(7)	0.287(1)	0.3858(9)	0.694(1)	1.4(3)
C(8)	0.316(1)	0.466(1)	0.747(1)	2.5(3)
C(9)	0.313(1)	0.530(1)	0.685(1)	2.3(3)
C(10)	0.275(1)	0.516(1)	0.562(1)	2.5(4)
C(11)	0.242(1)	0.438(1)	0.509(2)	3.6(4)
C(12)	0.248(1)	0.374(1)	0.575(1)	2.2(3)

[a] E.s.d.s are given in parentheses.

[b] B_{eq} is defined as $(8\pi^2/3)\ \Sigma_i\Sigma_j U_{ij}a_i*a_j*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table 4
Selected interatomic distances (Å) and angles (°) in $[Cu_4(PPh_3)_4(OPh)_4]\cdot(C_6H_5CH_3)_2$ (1)

Cu(1)–O(1)	2.17(2)	Cu(4)–O(3)	2.26(2)
Cu(1)–O(2)	2.07(2)	Cu(4)–O(4)	2.19(2)
Cu(1)–O(4)	2.16(2)	Cu(4)–P(4)	2.152(8)
Cu(1)–P(1)	2.130(8)	O(1)–C(1)	1.30(3)
Cu(2)–O(2)	2.19(2)	O(2)–C(7)	1.35(2)
Cu(2)–O(3)	2.11(2)	O(3)–C(13)	1.33(3)
Cu(2)–O(4)	2.05(2)	O(4)–C(19)	1.31(2)
Cu(2)–P(2)	2.152(7)	Cu(1)···Cu(2)	3.193(5)
Cu(3)–O(1)	2.23(2)	Cu(1)···Cu(3)	3.140(5)
Cu(3)–O(2)	2.13(2)	Cu(1)···Cu(4)	3.125(5)
Cu(3)–O(3)	2.06(2)	Cu(2)···Cu(3)	3.167(5)
Cu(3)–P(3)	2.152(8)	Cu(2)···Cu(4)	3.199(5)
Cu(4)–O(1)	2.05(2)	Cu(3)···Cu(4)	3.260(5)
O(1)–Cu(1)–O(2)	87.1(6)	O(1)–Cu(3)–O(2)	84.1(6)
O(1)–Cu(1)–O(4)	84.6(6)	O(1)–Cu(3)–O(3)	81.7(6)
O(2)–Cu(1)–O(4)	82.4(6)	O(2)–Cu(3)–O(3)	84.2(6)
O(1)–Cu(1)–P(1)	125.0(5)	O(1)–Cu(3)–P(3)	119.4(5)
O(2)–Cu(1)–P(1)	137.7(5)	O(2)–Cu(3)–P(3)	125.3(5)
O(4)–Cu(1)–P(1)	123.1(5)	O(3)–Cu(3)–P(3)	143.0(5)
O(2)–Cu(2)–O(3)	81.5(6)	O(1)–Cu(4)–O(3)	81.2(6)
O(2)–Cu(2)–O(4)	82.0(6)	O(1)–Cu(4)–O(4)	86.7(6)
O(3)–Cu(2)–O(4)	86.9(6)	O(3)–Cu(4)–O(4)	80.0(6)
O(2)–Cu(2)–P(2)	122.7(5)	O(1)–Cu(4)–P(4)	144.3(5)
O(3)–Cu(2)–P(2)	127.8(5)	O(3)–Cu(4)–P(4)	125.2(5)
O(4)–Cu(2)–P(2)	137.2(5)	O(4)–Cu(4)–P(4)	118.7(5)
Cu(1)–O(1)–Cu(4)	95.5(7)	Cu(2)–O(3)–Cu(3)	99.0(7)
Cu(1)–O(1)–Cu(3)	91.0(6)	Cu(2)–O(3)–Cu(4)	94.1(6)
Cu(3)–O(1)–Cu(4)	99.1(7)	Cu(3)–O(3)–Cu(4)	97.9(6)
Cu(1)–O(2)–Cu(2)	97.0(7)	Cu(1)–O(4)–Cu(2)	98.6(7)
Cu(1)–O(2)–Cu(3)	96.7(6)	Cu(1)–O(4)–Cu(4)	91.9(6)
Cu(2)–O(2)–Cu(3)	94.3(6)	Cu(2)–O(4)–Cu(4)	97.7(6)

Table 5
Selected interatomic distances (Å) and angles (°) in $[Cu_2(PPh_3)_3(OPh)_2]$ (2)

Cu(1)–O(1)	2.11(1)	Cu(2)–O(2)	1.95(1)
Cu(1)–O(2)	2.10(1)	Cu(2)–P(3)	2.119(5)
Cu(1)–P(1)	2.227(5)	O(1)–C(1)	1.32(2)
Cu(1)–P(2)	2.238(5)	O(2)–C(7)	1.30(2)
Cu(2)–O(1)	2.00(1)	Cu(1)···Cu(2)	3.069(3)
P(1)–Cu(1)–O(1)	113.4(3)	O(1)–Cu(2)–O(2)	85.5(4)
P(1)–Cu(1)–O(2)	110.4(3)	Cu(1)–O(1)–Cu(2)	96.7(4)
P(2)–Cu(1)–O(1)	103.8(3)	Cu(1)–O(2)–Cu(2)	98.4(4)
P(2)–Cu(1)–O(2)	107.8(3)	Cu(1)–O(1)–C(1)	133.9(9)
P(1)–Cu(1)–P(2)	130.3(2)	Cu(2)–O(1)–C(1)	129.2(9)
O(1)–Cu(1)–O(2)	79.3(4)	Cu(1)–O(2)–C(7)	126.7(9)
P(3)–Cu(2)–O(2)	145.3(3)	Cu(2)–O(2)–C(7)	127.0(9)
P(3)–Cu(2)–O(1)	129.1(3)		

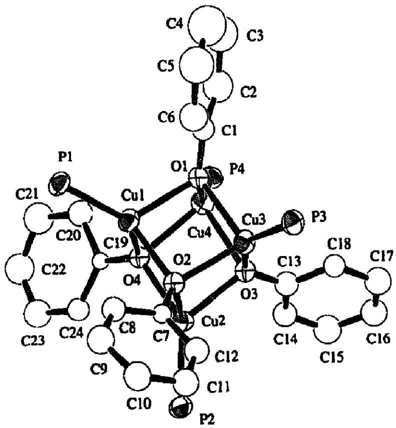

Fig. 1. The tetrameric core of $[Cu_4(PPh_3)_4(OPh)_4]$ in $[Cu_4(PPh_3)_4(OPh)_4]\cdot(C_6H_5CH_3)_2$ (1) showing the crystallographic numbering. The aryl groups of the triphenylphosphine ligands have been excluded for clarity. The thermal envelopes enclose 50% probability.

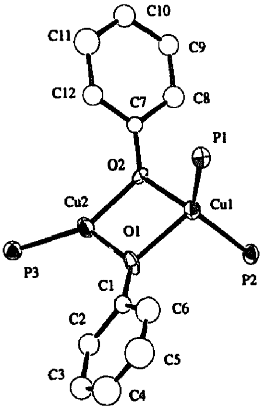

Fig. 2. $[Cu_2(PPh_3)_3(OPh)_2]$ (2) showing the crystallographic numbering. The aryl groups of the triphenylphosphine ligands have been excluded for clarity. The thermal envelopes enclose 50% probability.

3. Results and discussion

The reaction between methylcopper(I) and phenols or alcohols has been demonstrated to be an effective preparatory method for copper(I) alkoxides and phenoxides [22]. Mesitylcopper(I) has been used in an analogous manner for the preparation of copper(I) t-butoxide from t-butyl alcohol [15], of copper(I) amides from the relevant amines [16], and of copper(I) silyloxides from the corresponding silanols [23]. By reacting mesitylcopper(I) and phenol in toluene, a yellow precipitate of copper(I) phenoxide has been obtained, which decomposes rapidly on exposure to the atmosphere. Three stable copper(I) phenoxides have been prepared, viz. $[Cu_4(PPh_3)_4(OPh)_4]\cdot(C_6H_5CH_3)_2$ (1), $[Cu_2(PPh_3)_3(OPh)_2]$ (2) and $[Cu_2(PPh_3)_4(OPh)_2]$ (3), by addition of the appropriate amounts of triphenylphosphine. It is not, however, possible to obtain 2 as a sole product: whereas a stoichiometric PPh_3:CuOPh addition of 1:1 results in solvated $[Cu_4(PPh_3)_4(OPh)_4]$, and of 1:2 in $[Cu_2(PPh_3)_4(OPh)_2]$, a PPh_3:CuOPh addition ratio of 1:1.5 yields a mixture of all three compounds. By increasing the PPh_3:CuOPh addition ratio from 1:1.5 towards 1:2, it is possible to suppress the formation of 1. This is in accordance with the proposed [1] equilibrium between the three species in solution in which 1 and $[Cu_2(PPh_3)_4(OPh)_2]$ are formed from 2 by loss or addition of PPh_3, respectively. The tendency towards decomposition on heating and exposure to air and moisture appears to be dependent on the PPh_3:Cu ratio, complex 3 being the most robust of the three, while complex 1 is somewhat more labile than 2.

The 1:1 CuOPh:PPh_3 complex, $[Cu_4(PPh_3)_4(OPh)_4]$, is a tetramer with a cubane-type core (cf. Fig. 1), a structure suggested previously as being a likely candidate for this species [5]. For $Cu_4L_4X_4$ entities, in which X = halide, a regular, rather than a distorted, cubane-type core has been shown both experimentally [24] and theoretically [25] to be the favored conformation when L is a pure σ donor. When L has π^* acceptor properties (e.g. L = olefin), the coordination geometry of copper(I) distorts from tetrahedral to trigonal–pyramidal, resulting in two isomers which differ as to the positioning of the four long Cu–X bonds within the cubane-type core [25]. Thus, as expected for L = σ donor, the Cu_4O_4 core of 1 is fairly regular. The Cu–O distances range from 2.05(2) to 2.26(2) Å and the core angles range from 80.0(6) to 99.1(7)°, with the Cu–O–Cu angles less acute than O–Cu–O (see Table 4). This contrasts with the Cu_4O_4 core in o-allylphenolatocopper(I), $[Cu_4(OC_6H_4CH_2C(H){=}CH_2)_4]$, which exhibits tub-like distortion, in which four long Cu···O contacts are arranged as two mutually orthogonal parallel pairs [9]. In the present case there is a tendency towards an opposite distortion involving one short and two longer Cu–O bonds associated with each copper(I) (see Table 4). The shorter Cu–O distances are situated within the cube such that they form parallel pairs which are orthogonal, consistent with C_2 symmetry of the cube (cf. Fig. 1). However, although the four copper(I) centres in 1 are all somewhat distorted from tetrahedral, with some O–Cu–P angles of approximately 140°, (cf. Table 4), these distortions lie primarily in the angles, i.e. there is no tendency towards trigonal–pyramidal copper(I) coordination geometry. Hence severe distortion of the Cu_4O_4 core, resulting from trigonal–pyramidal copper(I) coordination geometry as discussed for $(olefin)_4Cu_4X_4$ (X = halide) [25] is not observed. The large values of some of the O–Cu–P angles can undoubtedly be attributed to bending of the triphenylphosphine groups away from the core in order to reduce steric crowding.

Another structural possibility for $[Cu_4(PPh_3)_4(OPh)_4]$ is the 'step-like' structure, as first observed for $[Cu_4X_4(PPh_3)_4]$ (X = halide) complexes by Churchill and Kalra [26,27]. Since then, numerous derivatives of copper(I) halides containing cubane or step Cu_4X_4 cores have been documented [24,28]. Recently, $[Cu_2(PPh_3)_4(OPh)_2]$ has been used as a precursor for the formation of alkynylcopper(I) complexes with cubane cores [12]. Step-like tetranuclear alkynylcopper(I) complexes are also known [29].

Whereas $[Cu_2(PPh_3)_4(OPh)_2]$ has been shown to be a symmetrical dimer, in which both copper(I) centres are four-coordinated (related by a crystallographic diad through the bridging phenolato ligands [5]), **2** is a dimer in which one copper(I) centre is three-coordinated and the other four-coordinated (cf. Fig. 2). This is similar to the situation in $[Cu_2(PPh_3)_3Cl_2]$ [30]. The four-coordinated copper(I) centre has distorted tetrahedral geometry, with an acute O(1)–Cu(1)–O(2) angle of 79.3(4)°, similar to the values for the counterparts, 80.6(5) and 80.4(6)°, determined for $[Cu_2(PPh_3)_4(OPh)_2]$ [5].

The Cu_2O_2 core in **2** is approximately planar, with a mean deviation of 0.008 Å from the least-squares plane through Cu(1), Cu(2), O(1) and O(2). As in $[Cu_2(PPh_3)_4(OPh)_2]$ [5], the –OPh groups in **2** (cf. Fig. 2) are twisted with respect to the Cu_2O_2 plane, the dihedral angles between this plane and the best planes through the aryl groups being 26.3 and 53.5°, respectively. The phenoxy groups are, moreover, slightly bent out of the Cu_2O_2 plane, the O(2)···O(1)–C(1) and O(1)···O(2)–C(7) angles being 174.3(9) and 156(1)°, respectively.

The three-coordinated copper(I) centre in **2** exhibits distorted trigonal-planar geometry with large deviations of the bond angles from 120° (cf. Table 5). Cu(2) is displaced 0.022 Å from the plane through O(1), O(2) and P(3). Cu(2)–P(3) and the Cu(2)–O distances are all, as expected, slightly shorter than the counterparts involving the four-coordinated centre, Cu(1). The non-bonded Cu···Cu separation, 3.069(3) Å, is slightly shorter than the Cu···Cu separations in the two crystallographically independent dimers of $[Cu_2(PPh_3)_4(OPh)_2]$, viz 3.242(4) and 3.243(4) Å, respectively [5].

It is interesting that reaction of equimolar amounts of $[Cu_4(O^tBu)_4]$ and triphenylphosphine result in the dimer $[Cu_2(PPh_3)_2(O^tBu)_2]$, in which copper(I) is three-coordinated, a molecule whose conformation is such that the metals are unusually accessible to incoming molecules such as H_2 [13]. In the present investigation an analogous reaction, whereby alkyl is replaced by aryl, i.e. in which a 1:1 Cu:OPh compound, $[Cu(OPh)_n]$, is allowed to react with an equimolar amount of triphenylphosphine, gives tetrameric $[Cu_4(PPh_3)_4(OPh)_4]$, in which copper(I) is four-coordinated, and therefore unlikely to be accessible to external molecules, the dimer/tetramer formation presumably being attributable to the difference in size between O^tBu and OPh. On the other hand, given that the compound with $CuOPh:PPh_3$ stoichiometry of 1:1.5 is a dimer, **2**, containing one three-coordinated and one four-coordinated copper(I) centre, and that of stoichiometry 1:2 is a dimer comprised of two four-coordinated copper(I) centres [5], it is somewhat surprising that **1** crystallises as a tetramer, containing distorted tetrahedrally coordinated copper(I), rather than with a structure analogous to that of $[Cu_2(PPh_3)_2(O^tBu)_2]$ [13]. Indeed, such a structure for the 1:1 compound would have been far more in keeping with the observed increase in lability along the series $Cu:PPh_3$ = 1:2, 1:1.5 and 1:1.

4. Supplementary material

Complete lists of fractional coordinates and equivalent isotropic thermal parameters, bond distances and angles are available from the authors upon request.

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