An unusual coordination mode of acetylide ligands: synthesis of tetranuclear copper(I) complexes containing μ_3-η^1 acetylide bridging ligands. Crystal structure of [Cu(μ_3-η^1-C≡CPh)- (Ph$_2$Ppy-P)]$_4$ (Ph$_2$Ppy = 2-(diphenylphosphine)pyridine)

M. Pilar Gamasa, José Gimeno★, Elena Lastra,

Departamento de Química Organometálica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo (Spain)

and Xavier Solans

Departamento de Cristalografía y Mineralogía, Facultad de Geología, Martí y Franqués s/n Universidad de Barcelona, 08028 Barcelona (Spain)
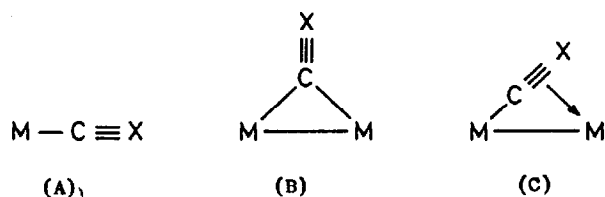
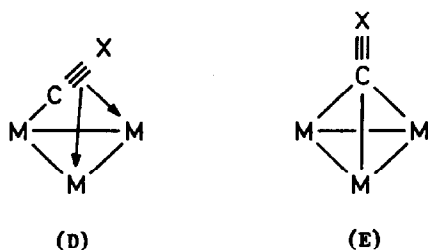(Received October 7th, 1987)

Abstract

The preparation and properties of novel tetranuclear copper(I) complexes of the type [Cu(C≡CR)(L–L)]$_4$ (L–L = 2-(diphenylphosphine)pyridine (Ph$_2$Ppy), R = ^{t}Bu, Ph; L–L = bis(diphenylphosphino)methane (dppm), R = Ph) are described. The crystal structure of [Cu(μ_3-η^1-C≡CPh)(Ph$_2$Ppy-P)]$_4$ has been determined by X-ray diffraction. Crystals are monoclinic, space group $C2/c$ with $Z = 4$ in a unit cell of dimensions a 14.859(3), b 24.405(4), c 23.279(4) Å and β 95.35(2)°; refinement gave $R = 0.056$ for 3586 reflections with $I \geq 2.5\sigma(I)$. The molecule consists of a tetrahedral "cluster" of copper atoms bearing four μ_3-η^1 phenylacetylide and four monodentate P-bonded 2-(diphenylphosphine)pyridine ligands (Ph$_2$Ppy-P). IR, ^{1}H and ^{31}P{^{1}H} NMR data are discussed.

Introduction

Substituted acetylides display a wide range of coordination features in transition metal complexes and much information is available about them [1,2]. Structural analogies between metal carbonyl and acetylide complexes, which were noted in early work by Nast [3], are now well established. Thus, RC≡C⁻ exhibits bonding modes, analogous to those known for carbon monoxide, namely terminal "end on" (η^1) (A), "symmetrical" doubly-bridging [4] (μ_2-η^1) (B), and "side on" σ–π doubly-bridging [4c, 5] (μ_2-η^2) (C) or triply-bridging [5d, 6] (μ_3-η^2) (D).
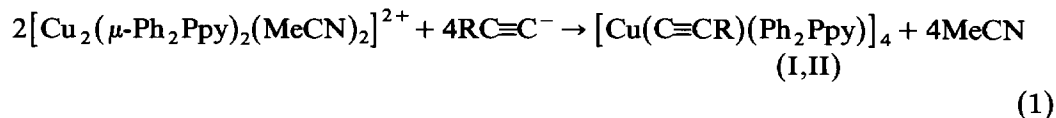
$$M — C \equiv X$$

(A),

(B)

(C)

X = O, CR

(D)

(E)

We describe here the synthesis and properties of novel tetranuclear copper(I) substituted acetylide complexes $[Cu(\mu_3\text{-}\eta^1\text{-}C\equiv CR)(L-L)]_4$ (L–L = 2-(diphenylphosphine)pyridine (Ph$_2$Ppy), R = ^{t}Bu, Ph; L–L = bis(diphenylphosphino)methane (dppm), R = Ph). An X-ray structural determination of $[Cu(\mu_3\text{-}\eta^1\text{-}C\equiv CPh)(Ph_2Ppy\text{-}P)]_4$ has shown it to involve a distorted tetrahedral arrangement of copper atoms bonded to four acetylide ligands displaying a triply bridging σ-bonding mode (E), which is well known in the coordination chemistry of carbon monoxide. Recently, a further example, that also represents a novel bonding analogy with metal carbonyls, namely $[Cu(\mu_3\text{-}\eta^1\text{-}C\equiv CPh)(PPh_3)]_4$ has been reported [7].

Results and discussion

Treatment of a solution of $[Cu_2(\mu\text{-}Ph_2Ppy)_2(MeCN)_2][BF_4]_2$ [8] in CH$_2$Cl$_2$/MeOH (3/1) with HC$\equiv$CR (R = Ph, ^{t}Bu) under argon in the presence of an excess of potassium hydroxide gives a yellow solution from which complexes I and II can be isolated (eq. 1):

$$2[Cu_2(\mu\text{-}Ph_2Ppy)_2(MeCN)_2]^{2+} + 4RC\equiv C^- \rightarrow [Cu(C\equiv CR)(Ph_2Ppy)]_4 + 4MeCN$$
$$(I,II)$$

$$(1)$$

(I: R = Ph; II: R = ^{t}Bu)

$[Cu_2(\mu\text{-}dppm)_2(MeCN)_2][BF_4]_2$ [9] reacts similarly with the phenylacetylide salt under the same conditions to give the complex $[Cu(C\equiv CPh)(dppm)]_4$ (III).

The compounds were isolated as crystalline yellow (I), orange (II) and pale cream (III) air stable solids, but their solutions in either chlorinated solvents or toluene decompose in the presence of air. The IR spectra (Nujol mulls) of I and III exhibit weak $\nu(C\equiv C)$ absorptions at 2024 and 2030 cm^{-1}, respectively, and no $\nu(B-F)$

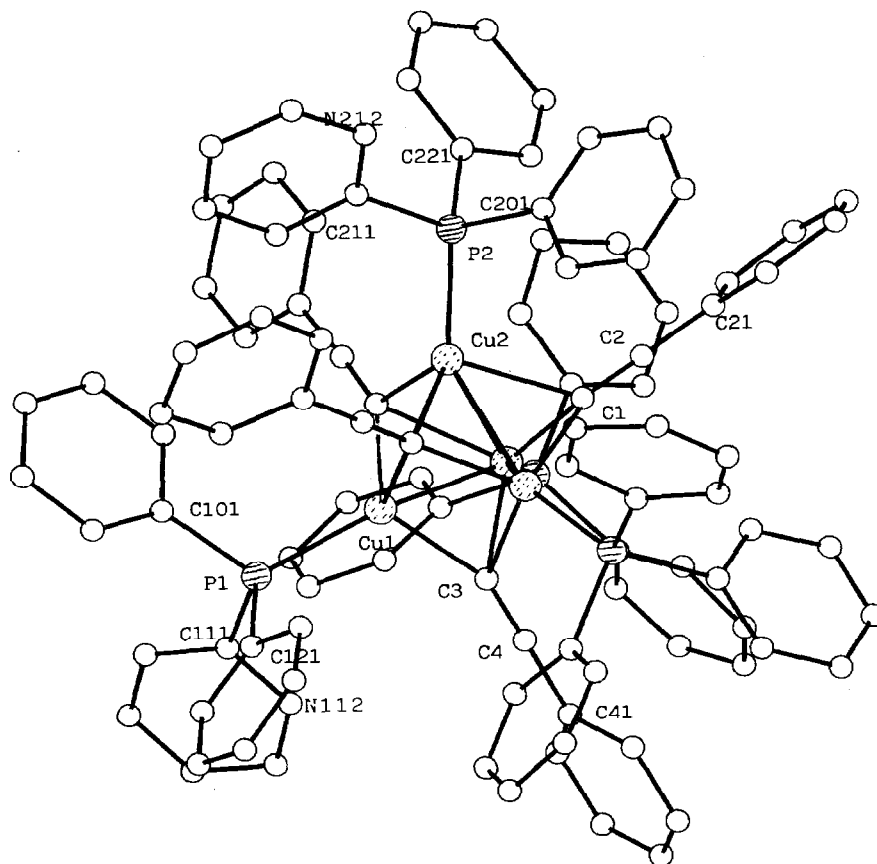Fig. 1. Molecular structure of $[Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(Ph_2Ppy\text{-}P)]_4$ (I), showing the atom numbering.

absorptions are observed. Conductivity data (in nitromethane) show the complexes to be non-electrolyte, but molecular weight measurements (osmometric methods) in toluene could not be carried out owing to extensive decompositions. The ^1H and $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ exhibit the expected resonances for the ligands, although no structural information can be obtained (see Experimental).

In order to know the molecularity of these compounds and to establish unambiguously the bonding features of the acetylide ligands, the crystal structure of I was determined by X-ray diffraction. The results are summarized in Tables 1–3 and the structure is shown in Fig. 1 and 2 along with the atomic numbering scheme.

The molecule consists of a "cluster" of four copper atoms in the vertex of an essentially tetrahedron bearing four monodentate P-bonded 2-(diphenylphosphine) pyridine ($Ph_2Ppy\text{-}P$) molecules and four $\mu_3\text{-}\eta^1$ phenylacetylide ligands and shows a molecular and crystallographic two-fold axis. Every copper atom displays a distorted tricapped trigonal pyramidal coordination bonded to three carbon atoms of three 2-phenylacetylide ligands, one phosphorus atom, and, formally, to three copper atoms. The copper-acetylide triple bridges are clearly asymmetric, with Cu–C bonds lengths in the range 2.053(8)–2.345(8) Å, significantly longer than those found in copper carbonyl complexes [10,11] i.e. $[Cu_2(tmen)_2(\mu\text{-}CO)(\mu\text{-}Ph\text{-}CO_2)]^+$ (tmen = tetramethylethylenediamine), $[Cu(CO)(O^tBu)]_4$ d(Cu–CO) 1.75 and 1.80 Å, respectively. The linearity of the phenylacetylide ligands (average bond
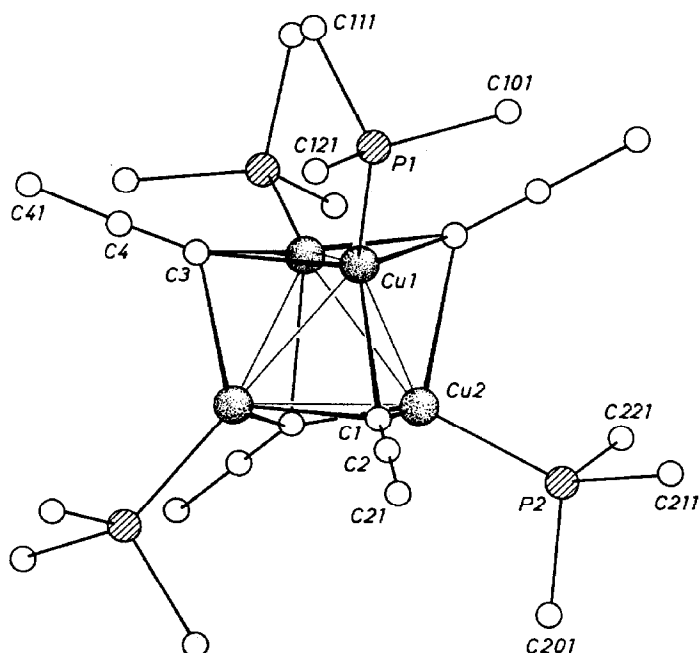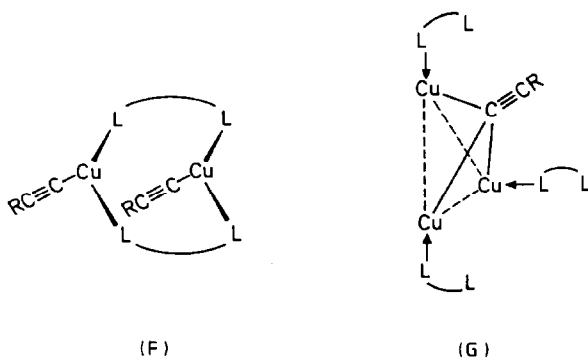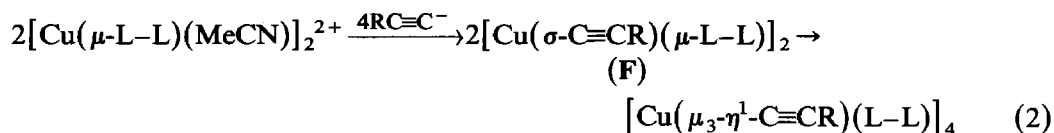
Fig. 2. A view of the molecular structure of I in which pyridine rings and phenyl groups have been omitted.

angles, 178°) and the short average C≡C distances, 1.21(1) Å, typical of a triple bond (1.205 Å in the free acetylene), are consistent with negligible electronic back-donation from the metal to the ligand and with the absence of ligand-to-metal π-bonding. Thus, the metal-acetylide bonding can be considered to be of a pure σ type, as observed for the copper-acetylide doubly bridging complexes (μ_2-η^1) in $Cu_6(C_6H_4NMe_2$-2)$_4(\mu_2$-η^1-C≡CC$_6H_4$Me-4)$_2$ (d(C≡C) 1.175 Å; d(Cu–C) 1.98–2.13 Å) [4b] and in $Cu_4(\mu_2$-η^1-C≡CPh)$_2(\mu_3$-η^2-C≡CPh)$_2$(PMe$_3$)$_4$ (d(C≡C) 1.22–1.24 Å; d(Cu–C) 1.96–2.22 Å) [4a], in which two of the four phenylethynyl groups are only σ-bonded in a linear fashion and the other two are additionally π-bonded, showing some distortion from the linearity of the phenylethynyl system (C–C–C bond angles: 154°). The average Cu–P bond length of 2.23(1) Å is less than the estimated value of 2.45 Å for a single covalent bond [12]. Copper–copper distances are in the range 2.525(1)–2.686(1) Å, similar to that found in [Cu(μ_3-η^1-C≡CPh)(PPh$_3$)]$_4$ [7] but shorter than those in [CuIPEt$_3$]$_4$ (d 2.927 Å) [11a], [CuIAsEt$_3$]$_4$ (d 2.78 Å) [11a] or [Cu(O^{t}Bu)(CO)]$_4$ (d 3.04 Å) [11b] complexes, where the copper atoms also form a tetrahedral skeleton in a cubane type structure with the iodide or t-butoxide anion acting as triple bridging ligands. Although those distances are shorter than in the case of metallic copper (d 2.86 Å), extended Hückel calculations for several analogous polynuclear copper(I) complexes involving a comparable range of copper–copper distances have indicated [13] that there is only a weak, or negligible, metal–metal bonding interaction. The bonding in the electron deficient "Cu$_3$C≡CPh" moiety can be described as typical of a four-centre two-electron system.

The mechanism of the formation of the tetranuclear compounds I–III is not well understood. Although, no intermediate complexes have been isolated, probably

(F)   (G)

coordinatively and/or electron unsaturated copper(I) binuclear derivatives such as $[Cu_2(\sigma\text{-}C\equiv CR)_2(\mu\text{-}L\text{-}L)_2]$ (F) could be formed (eq. 2).

$$2[Cu(\mu\text{-}L\text{-}L)(MeCN)]_2^{2+} \xrightarrow{4RC\equiv C^-} 2[Cu(\sigma\text{-}C\equiv CR)(\mu\text{-}L\text{-}L)]_2 \rightarrow$$

$$\mathbf{(F)}$$

$$[Cu(\mu_3\text{-}\eta^1\text{-}C\equiv CR)(L\text{-}L)]_4 \qquad (2)$$

In any case, it seems that the tendency for formation of 4c-2e "$Cu_3C\equiv CR$" system (G) is greater than that for formation of Cu–N or Cu–P bonds, since the bidentate phosphines are only monodentate P-bonded, as shown in the crystal structure for I.

Experimental

Infrared spectra in the ν(CO) stretching region were recorded on a Perkin–Elmer 577 spectrophotometer using dichloromethane solutions or Nujol mulls between NaCl plates. Conductivities were measured at room temperature in acetone or nitromethane (5×10^{-4} M solutions) with a Jenway PCM3 Conductivity Meter. Carbon, hydrogen and nitrogen analyses were carried out with a Perkin–Elmer 240 microanalyzer. Molecular weights were determined with a Knauer vapour-pressure osmometer (2×10^{-3} M solutions). NMR spectra were recorded on a Varian FT-80A spectrometer at 79.54 (^{1}H) or 32.20 MHz (^{31}P) using SiMe$_4$ and 85% H$_3$PO$_4$ as internal or external standard reference respectively.

All reactions were carried out under argon and the solvents were dried before use. The ligands were prepared as described previously [14,15].

Preparation of the complexes $[Cu(\mu_3\text{-}\eta^1\text{-}C\equiv CR)(L\text{-}L)]_4$ (I: L–L = Ph$_2$Ppy, R = Ph; II: L–L = Ph$_2$Ppy, R = ^{t}Bu; III: L–L = dppm, R = Ph)

General procedure. To a mixture of 2 mmol of the acetylene and 4 mmol of KOH in 30 ml of a ca. 3/1 CH$_2$Cl$_2$/MeOH was added a solution in CH$_2$Cl$_2$ of $[Cu(\mu\text{-}L\text{-}L)(MeCN)]_2$ [BF$_4$]$_2$ [8,9] (0.5 mmol). The solution turned yellow instantaneously. After 12 h of stirring at room temperature the solvents were removed in vacuo and the residues were extracted in toluene. Partial evaporation of the filtered solution and addition of diethyl ether (15 ml) gave the desired complexes, which were washed with diethyl ether and recrystallized from toluene/hexane (yields 65–70%) as yellow (I), orange (II) and pale cream (III) microcrystalline solids.

I. Found: C, 69.1; H, 4.4; N, 3.2. $C_{100}H_{76}Cu_4N_4P_4$ calcd.: C, 70.2; H, 4.5; N, 3.3%. NMR: ^1H (C_6D_6), δ 7.02 (76 H, m, Ph) ppm; ^{31}P {^1H} (C_6D_6), δ 0.02 (s, br) ppm. IR (Nujol mulls): ν(C≡C) 2024 w cm^{-1}; (Ph$_2$Ppy): 1572m, 1561sh, 1437m, 1422m, 1267m, 1197m, 1097s, 1027m, 802m, 748s, 717w, 687s cm^{-1}.

II. Found: C, 66.5; H, 5.5; N, 3.6. $C_{92}H_{92}Cu_4N_4P_4$ calcd.: C, 67.7; H, 5.6; N, 3.4%. NMR: ^1H (C_6D_6), δ 7.01 (56 H, m, Ph) and δ 0.99 (36 H, s, ^tBu) ppm; ^{31}P {^1H} (C_6D_6), δ −1.76 ppm. IR (Nujol mulls): (Ph$_2$Ppy) 1577m, 1562sh, 1442s, 1427m, 1267m, 1097s, 1027m, 802m, 747s, 727w, 697s cm^{-1}.

III. Found: C, 70.6; H, 4.98. $C_{132}H_{108}Cu_4P_8$ calcd.: C, 72.2; H, 4.9%. NMR: ^1H (CDCl$_3$), δ 7.15 (100H, m, Ph) and δ 3.15 (8H, m, CH$_2$) ppm; ^{31}P\{^1H\} (CH$_2$Cl$_2$) δ −5.76 (s, br) ppm. IR (Nujol mulls): ν(C≡C) 2030 cm^{-1}. (dppm): 1590m, 1480s, 1432s, 1195w, 1095m, 1025m, 995m, 755s, 735s, 715m, 695s cm^{-1}.

Structure determination of [Cu(μ_3-η^1-C≡CPh)(Ph$_2$Ppy)]$_4$ (I)

Crystal data. $C_{100}H_{76}Cu_4N_4P_4$, $M = 1711.8$ monoclinic, space group $C2/c$, a 14.859(3), b 24.405(4), c 23.279(4) Å, β 95.35(2)°, U 8405(5) Å^3, D_c 1.352 g cm^{-3}, $Z = 4$, $F(000) = 3520$, (Mo-K_α radiation) 0.71069 Å, μ 11.65 cm^{-1}. 288 K.

Table 1

Main bond lengths (Å) for compound I ^{a}

Cu(2)–Cu(1)	2.686(1)	C(104)–C(102)	1.359(16)
P(1)–Cu(1)	2.220(2)	C(105)–C(104)	1.439(17)
C(1)–Cu(1)	2.237(8)	C(106)–C(105)	1.387(15)
C(3)–Cu(1)	2.182(7)	N(112)–C(111)	1.338(15)
Cu(1)–Cu(1)I	2.638(2)	C(116)–C(111)	1.430(13)
Cu(2)–Cu(1)I	2.525(2)	C(113)–N(112)	1.389(16)
C(1)I–Cu(1)	2.107(8)	C(114)–C(113)	1.393(21)
C(3)–Cu(2)	2.345(8)	C(115)–C(114)	1.365(24)
Cu(2)–Cu(2)	2.594(2)	C(116)–C(115)	1.419(18)
Cu(2)–P(2)	2.241(2)	C(122)–C(121)	1.358(12)
Cu(2)–C(1)I	2.101(8)	C(126)–C(121)	1.353(12)
		C(123)–C(122)	1.377(14)
Cu(2)–C(3)I	2.053(8)	C(124)–C(123)	1.396(15)
C(2)–C(1)	1.201(10)	C(125)–C(124)	1.339(14)
C(21)–C(2)	1.431(10)	C(126)–C(125)	1.404(14)
C(22)–C(21)	1.376(12)	C(202)–C(201)	1.394(10)
C(26)–C(21)	1.367(13)	C(203)–C(202)	1.384(13)
C(23)–C(22)	1.377(15)	C(204)–C(203)	1.389(16)
C(24)–C(23)	1.343(19)	C(206)–C(205)	1.378(14)
C(25)–C(24)	1.358(20)	N(212)–C(211)	1.319(10)
C(26)–C(25)	1.397(15)	C(216)–C(211)	1.370(13)
C(4)–C(3)	1.211(11)	C(213)–N(212)	1.361(11)
C(41)–C(4)	1.460(11)	C(214)–C(213)	1.350(14)
C(42)–C(41)	1.379(14)	C(215)–C(214)	1.366(15)
C(46)–C(41)	1.402(13)	C(216)–C(215)	1.394(14)
C(43)–C(42)	1.414(16)	C(222)–C(221)	1.390(12)
C(44)–C(43)	1.329(19)	C(226)–C(221)	1.368(10)
C(45)–C(44)	1.391(18)	C(223)–C(222)	1.372(16)
C(46)–C(45)	1.429(15)	C(224)–C(223)	1.348(16)
C(102)–C(101)	1.393(12)	C(225)–C(224)	1.355(17)
C(106)–C(101)	1.390(14)	C(226)–C(225)	1.407(12)
C(103)–C(102)	1.385(13)		

^{a} Symmetry code $I = 2 - x$, y, $\frac{3}{2} - z$.

Table 2. Main bond angles (°) for compound I [a]

Cu(1)I–Cu(1)–Cu(2)	56.6(1)	C(21)–C(2)–C(1)	177.0(8)
Cu(1)I–Cu(1)–Cu(2)I	62.6(1)	C(22)–C(21)–C(2)	121.5(7)
Cu(2)–Cu(1)–Cu(2)I	59.6(1)	C(26)–C(21)–C(2)	120.5(7)
Cu(1)I–Cu(1)–P(1)	143.3(1)	C(26)–C(21)–C(22)	117.9(8)
Cu(2)–Cu(1)–P(1)	157.7(1)	C(23)–C(22)–C(21)	120.4(9)
Cu(2)I–Cu(1)–P(1)	131.7(1)	C(24)–C(23)–C(22)	(11)
Cu(1)I–Cu(1)–C(1)	50.4(2)	C(25)–C(24)–C(23)	(12)
Cu(2)–Cu(1)–C(1)	94.5(2)	C(26)–C(25)–C(24)	117.7(12)
Cu(2)I–Cu(1)–C(1)	51.9(2)	C(25)–C(26)–C(21)	122.0(10)
P(1)–Cu(1)–C(1)	107.2(2)	Cu(2)–C(3)–Cu(1)	72.7(2)
Cu(1)I–Cu(1)–C(1)I	54.9(2)	C(4)–C(3)–Cu(1)	121.0(6)
Cu(2)–Cu(1)–C(1)I	50.3(2)	C(4)–C(3)–Cu(2)	128.7(6)
Cu(2)I–Cu(1)–C(1)I	102.7(2)	Cu(1)–C(3)–Cu(2)I	73.1(2)
P(1)–Cu(1)–C(1)I	125.5(2)	Cu(2)I–C(3)–C(4)	156.2(6)
C(1)–Cu(1)–C(1)	104.2(3)	C(41)–C(4)–C(3)	179.0(8)
Cu(1)I–Cu(1)–C(3)	101.5(2)	C(42)–C(41)–C(4)	124.4(8)
Cu(2)–Cu(1)–C(3)	56.5(2)	C(46)–C(41)–C(4)	118.5(8)
Cu(2)I–Cu(1)–C(3)	51.1(2)	C(46)–C(41)–C(42)	117.0(8)
P(1)–Cu(1)–C(3)	112.5(2)	C(43)–C(42)–C(41)	122.8(10)
C(1)–Cu(1)–C(3)	101.8(3)	C(44)–C(43)–C(42)	118.5(11)
C(1)I–Cu(1)–C(3)	102.9(3)	C(45)–C(44)–C(43)	123.1(11)
Cu(1)–Cu(2)–Cu(1)I	60.7(1)	C(46)–C(45)–C(44)	117.6(11)
Cu(1)–Cu(2)–Cu(2)I	57.1(1)	C(45)–C(46)–C(41)	120.8(9)
Cu(1)I–Cu(2)–Cu(2)I	63.3(1)	C(106)–C(101)–C(102)	120.6(8)
Cu(1)–Cu(2)–P(2)	139.5(1)	C(103)–C(102)–C(101)	117.9(8)
Cu(1)I–Cu(2)–P(2)	152.5(1)	C(104)–C(103)–C(102)	121.4(10)
Cu(2)I–Cu(2)–P(2)	139.2(1)	C(105)–C(104)–C(103)	122.2(9)
Cu(1)–Cu(2)–C(1)I	50.4(2)	C(106)–C(105)–C(104)	115.1(11)
Cu(1)I–Cu(2)–C(1)I	57.0(2)	C(105)–C(106)–C(101)	122.4(10)
Cu(2)I–Cu(2)–C(1)I	100.7(2)	C(116)–C(111)–N(112)	122.9(9)
P(2)–Cu(2)–C(1)I	116.6(2)	C(113)–N(112)–C(111)	118.2(10)
Cu(1)–Cu(2)–C(3)I	103.6(2)	C(114)–C(113)–N(112)	122.3(13)
Cu(1)I–Cu(2)–C(3)I	55.8(2)	C(115)–C(114)–C(113)	118.8(13)
Cu(2)I–Cu(2)–C(3)I	59.3(2)	C(116)–C(115)–C(114)	121.1(11)
P(2)–Cu(2)–C(3)I	115.9(2)	C(115)–C(116)–C(111)	116.5(10)
C(1)I–Cu(2)–C(3)I	111.4(3)	C(126)–C(121)–C(122)	117.7(8)
Cu(1)–P(1)–C(101)	118.2(5)	C(123)–C(122)–C(121)	120.3(8)
Cu(1)–P(1)–C(111)	114.9(5)	C(124)–C(123)–C(122)	121.5(9)
C(101)–P(1)–C(111)	102.7(7)	C(125)–C(124)–C(123)	118.5(9)
Cu(1)–P(1)–C(121)	111.8(5)	C(126)–C(125)–C(124)	118.7(9)
C(101)–P(1)–C(121)	103.1(7)	C(125)–C(126)–C(121)	123.3(9)
C(111)–P(1)–C(121)	104.6(7)	C(203)–C(202)–C(201)	124.2(8)
Cu(2)–P(2)–C(201)	116.2(5)	C(204)–C(203)–C(202)	116.0(8)
Cu(2)–P(2)–C(211)	115.9(5)	C(216)–C(211)–N(212)	123.7(7)
Cu(201)–P(2)–C(211)	99.7(7)	C(213)–N(212)–C(211)	119.2(8)
Cu(2)–P(2)–C(221)	114.6(5)	C(214)–C(213)–N(212)	120.5(8)
C(201)–P(2)–C(221)	104.8(7)	C(215)–C(214)–C(213)	120.0(9)
C(211)–P(2)–C(221)	103.7(7)	C(216)–C(215)–C(214)	120.2(11)
Cu(1)–C(1)–Cu(1)I	74.7(2)	C(215)–C(216)–C(211)	116.3(9)
Cu(1)–C(1)–Cu(2)I	71.1(2)	C(226)–C(221)–C(222)	118.2(7)
Cu(1)I–C(1)–Cu(2)I	79.3(2)	C(223)–C(222)–C(221)	119.8(9)
Cu(1)–C(1)–C(2)	128.7(6)	C(224)–C(223)–C(222)	121.0(10)
Cu(1)I–C(1)–C(2)	120.2(6)	C(225)–C(224)–C(223)	121.0(10)
Cu(2)I–C(1)–C(2)	153.4(6)	C(226)–C(225)–C(224)	118.5(9)
		C(225)–C(226)–C(221)	121.1(8)

[a] Symmetry code $I = 2 - x$, y, $\frac{3}{2} - z$.

Table 3. Final atomic coordinates ($\times 10^4$) and thermal parameters for compound I

Atom	x/a	y/b	z/c	B_{eq}
Cu(1)	108888(7)	22128(4)	75981(4)	4.74(4)
Cu(2)	98239(6)	14603(3)	80354(3)	3.91(4)
P(1)	121135(16)	27203(8)	75283(8)	5.07(11)
P(2)	51570(12)	41191(6)	12166(7)	3.21(8)
C(1)	10020(6)	2297(3)	6765(3)	5.41(42)
C(2)	9955(5)	2678(3)	6438(3)	4.28(36)
C(21)	9922(5)	3125(3)	6038(3)	4.54(39)
C(22)	9398(6)	3580(4)	6108(4)	7.29(56)
C(23)	9405(8)	4013(4)	5729(6)	9.71(76)
C(24)	9931(9)	3999(5)	5290(5)	9.41(77)
C(25)	10460(11)	3560(5)	5201(5)	10.74(86)
C(26)	10457(8)	3124(4)	5591(4)	8.19(62)
C(3)	11185(5)	1337(3)	7616(3)	4.07(36)
C(4)	11900(5)	1165(3)	7836(3)	4.33(39)
C(41)	12757(5)	947(4)	8098(3)	5.19(44)
C(42)	13582(8)	1036(6)	7887(4)	9.70(77)
C(43)	14401(7)	822(6)	8154(6)	10.34(85)
C(44)	14376(8)	536(6)	8638(6)	9.83(83)
C(45)	13578(8)	423(6)	8884(5)	9.82(77)
C(46)	12761(6)	653(5)	8615(4)	7.84(60)
C(101)	7974(6)	3458(3)	7369(3)	5.45(44)
C(102)	7349(7)	3749(4)	7004(4)	6.28(49)
C(103)	7481(8)	4308(4)	6946(5)	7.64(63)
C(104)	8158(9)	4573(4)	7266(5)	8.45(68)
C(105)	8803(9)	4288(4)	7657(5)	9.80(74)
C(106)	8651(9)	3731(4)	7709(5)	9.08(69)
C(111)	6906(8)	2535(3)	6965(3)	6.45(51)
N(112)	6068(7)	2632(4)	7106(4)	6.81(55)
C(113)	5346(9)	2485(5)	6715(6)	10.79(84)
C(114)	5468(11)	2251(6)	6182(7)	11.77(100)
C(115)	6326(12)	2143(5)	6048(5)	11.32(86)
C(116)	7088(7)	2294(4)	6428(4)	7.73(58)
C(121)	7474(6)	2664(3)	8187(3)	5.08(42)
C(122)	7129(6)	3095(3)	8462(4)	6.25(49)
C(123)	6857(7)	3032(4)	9008(5)	7.36(61)
C(124)	6913(6)	2526(5)	9289(4)	6.45(53)
C(125)	7256(7)	2099(4)	9020(4)	7.33(57)
C(126)	7531(7)	2177(4)	8465(4)	7.40(56)
C(201)	8782(5)	800(3)	9107(3)	3.62(34)
C(202)	8004(6)	704(3)	8737(3)	4.77(42)
C(203)	7162(6)	599(4)	8921(4)	6.17(53)
C(204)	7120(6)	580(4)	9514(5)	6.76(59)
C(205)	12124(7)	−690(4)	10104(4)	6.26(53)
C(206)	11295(6)	−794(3)	10302(3)	4.80(42)
C(211)	10082(5)	153(3)	8624(3)	3.62(34)
N(212)	9726(5)	−229(3)	8933(3)	4.13(36)
C(213)	9880(6)	−765(4)	8816(4)	6.25(52)
C(214)	10394(6)	−906(3)	8391(5)	6.22(52)
C(215)	10781(8)	−508(4)	8082(6)	9.99(78)
C(216)	10608(7)	44(3)	8185(4)	7.15(56)
C(221)	10679(5)	1047(3)	9390(3)	4.04(36)
C(222)	10921(9)	1594(4)	9472(4)	9.34(65)
C(223)	11534(10)	1739(5)	9924(5)	11.58(82)
C(224)	11965(8)	1355(5)	10263(4)	8.29(66)
C(225)	11777(7)	816(5)	10185(4)	7.66(61)
C(226)	11125(6)	663(3)	9736(4)	5.58(44)

A prismatic crystal (0.1 × 0.1 × 0.15 mm) was selected and mounted on a Philips PW1100 four circle diffractometer. Unit-cell parameters were determined from 25 reflections ($4 \leq \theta \leq 12°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo-K_α radiation, using the ω-scan technique, with scan width 0.8° and scan speed 0.03° s^{-1}. hkl, $\bar{h}kl$ and $h\bar{k}l$ and $\bar{h}\bar{k}l$ set were collected, $R_{int} = 0.032$. 3586 independent reflections were measured in the range $2 \leq \theta \leq 25°$; 3470 of which were taken as observed on the criterion $I \geq 2.5$ $\sigma(I)$. Three reflections were measured every 2 h, and no significant intensity decay was observed. Lorentz polarization, but not absorption, corrections were made.

The structure was solved by direct methods, using the MULTAN84 system of computer programs [16] and refined by full-matrix least-squares, using the SHELX76 program [17]. The function minimized was $\Sigma w[[F_0] - [F_c]]^2$, where $w = (\sigma^2(F_0) + 0.0027[F_0]^2)$. 22 hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor, and the remaining atoms were refined anisotropically. The final R value was 0.056 (R_w 0.060) for all observed reflections.

The main bond lengths, main bond angles and final atomic coordinates and thermal parameters for compound I are shown in Tables 1–3.

Acknowledgement

References

1 A.J. Carty, Pure Appl. Chem., 54 (1982) 113.; R. Nast, Coord. Chem. Rev., 47 (1982) 89.
2 P.R. Raithby and M.J. Rosales, Adv. Inorg. Chem. Radiochem., 29 (1985) 169.
3 R. Nast, Chem. Soc. (London) Spec. Publ., 13 (1959) 103.
4 (a) P.W.R. Corfield and H.M.M. Shearer, Acta Crystallogr., 21 (1966) 957; (b) R.W.M. ten Hoedt, J.G. Noltes, G. van Koten, and A.L. Spek, J. Chem. Soc., Dalton Trans., (1978) 1800; (c) A.J. Carty, N.J. Taylor, and W.F. Smith, J. Chem. Soc., Chem. Commun., (1979) 750; (d) N.A. Bell, J.W. Nowell, G.E. Coates and H.M.M. Shearer, J. Organomet. Chem., 273 (1984) 179; B. Morosin and J. Howatson, ibid., 29 (1971) 7.
5 (a) O.M. Abu-Salah and M.I. Bruce, M.R. Churchill, and S.A. Bezman, J. Chem. Soc., Chem. Commun., (1972) 858; M.R. Churchill and S.A. Bezman, Inorg. Chem., 13 (1974) 1418; (b) O.M. Abu-Salah, M.I. Bruce, M.R. Churchill, and B.G. DeBoer, J. Chem. Soc., Chem. Commun., (1974) 688; (c) W.F. Smith, J. Yule, N.J. Taylor, H.N. Paik, and A.J. Carty, Inorg. Chem., 16 (1977) 1593; (d) A.J. Carty, S.A. MacLanghlin, and N.J. Taylor, Organometallics, (1981) 1013; (e) O.M. Abu-Salah and C.B. Knobler, J. Organomet. Chem., 302 (1986) C10.
6 A.J. Carty, S.A. MacLanghlin, and N.J. Taylor, J. Organomet. Chem., 204 (1981) C27; M. Catti, G. Gervasio, and S.A. Mason, J. Chem. Soc., Dalton Trans., (1977) 2260.
7 L. Naldini, F. DeMartin, M. Manassero, M. Sansoni, G. Rassu, and M.A. Zoroddu, J. Organomet. Chem., 279 (1985) C42.
8 E. Lastra, M.P. Gamasa, J. Gimeno, M. Lanfranchi and A. Tiripicchio, unpublished results.
9 J. Diez, M.P. Gamasa, J. Gimeno, A. Tiripicchio, and M. Tiripicchio Camellini, J. Chem. Soc. Dalton Trans., (1987) 1275.
10 M. Pasquali, C. Floriani, A. Gaetani-Manfredotti, and C. Guastini, J. Am. Chem. Soc., 103 (1981) 185.
11 (a) M.R. Churchill and K.L. Kalra, Inorg. Chem., 13 (1974) 1899; (b) R.L. Geerts, J.C. Huffman, K. Folting, T.H. Lemmen, and K.G. Caulton, J. Am. Chem. Soc., 105 (1983) 3503.

12 L. Pauling, The Nature of the Chemical Bond, Cornell Univ., Press, 1960.

13 A. Avdeef and J.P. Fackler, Jr., Inorg. Chem., 17 (1978) 2182; P.K. Mehrotra and R. Hoffmann, Inorg. Chem., 17 (1978) 2187.

14 A.M. Aguiar and J. Beisler, J. Org. Chem., 29 (1964) 1660.

15 A. Maisonnet, J.P. Farr, M.M. Olmstead, C.T. Hunt and A.L. Balch, Inorg. Chem., 21 (1982) 3961.

16 P. Main, S.E. Fiske, S.L. Hull, L. Lesinger, G. Germain, J.P. Declercq, and M.M. Woolfson 1984 MULTAN. A system of computer programs for crystal structure determination from X-ray diffraction data, Univ. of York, England and Univ. of Louvain, Belgium.

17 G.M. Sheldrick (1976). SHELX. A computer program for crystal structure determination, Univ. of Cambridge, England.