DALTON
FULL PAPER

Synthesis and reactivity of binuclear copper(I) complexes of 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (L^1). Crystal structures of $[Cu_2(\mu\text{-}L^1)_2(MeCN)_2][ClO_4]_2$, $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}\eta^1\text{-}C{\equiv}CPh)][ClO_4]\cdot CHCl_3\cdot H_2O$ and $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}Cl)][ClO_4]\cdot H_2O$

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Reaction of 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (L^1) with 1 equivalent of $[Cu(MeCN)_4][ClO_4]$ resulted in the formation of $[Cu_2(\mu\text{-}L^1)_2(MeCN)_2][ClO_4]_2$ **1**. Complex **1** reacted with Li(C≡CPh) to give $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}\eta^1\text{-}C{\equiv}CPh)][ClO_4]$ **2**, which underwent an alkynyl ligand-transfer reaction with $[Pd(PBu^n_3)_2Cl_2]$ to give $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}Cl)][ClO_4]$ **3** and $[Pd(PBu^n_3)_2(C{\equiv}CPh)Cl]$. Reaction of **1** with dimethyl acetylenedicarboxylate yielded $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}MeO_2CC{\equiv}CCO_2Me)][ClO_4]_2$ **4**, the alkynyl ligand of which can easily be displaced by bis(diphenylphosphino)methane (dppm) to give $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}dppm)][ClO_4]_2$ **5**. The crystal structures of **1**, **2**·$CHCl_3\cdot H_2O$ and **3**·H_2O have been determined.

Transition-metal alkynyl complexes have been widely studied in the last decade.[1] The interest mainly stems from two aspects: (a) the versatile reactivity of the co-ordinated acetylide group in its complexes,[2] which are useful precursors for the synthesis of other organometallic species; (b) the ability of the acetylide group to bond to transition metals, forming a large number of mono- and poly-nuclear complexes that display an unusually rich variety of bonding modes.[3]

In the context of the chemistry of alkynylcopper(I), development has been hampered by the lack of general methods for the synthesis of its derivatives and their insolubility in common solvents, which preclude their structural characterization in many cases. Previous studies have focused mainly on the polynuclear alkynylcopper derivatives,[4] and binuclear alkynyl complexes have received relatively little attention. To date, only a few binuclear complexes, namely $[Cu_2(PEt_2Ph)_4(\mu\text{-}\eta^1\text{-}C{\equiv}CPh)_2]$,[5] $[Cu_2(tmch)_2(\mu\text{-}\eta^1\text{-}C{\equiv}CPh)_2]$ (tmch = 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne),[6] $[\{(C_6H_{11})_3P\}Cu(\mu\text{-}\eta^1\text{-}C{\equiv}CBu^t)_2Cu(PPh_3)_2]$[7] and $[Cu_2(PPh_2Me)_4(\mu\text{-}\eta^1\text{-}C{\equiv}CPh)_2]$[8] have been structurally characterized.

We have recently prepared a new tridentate phosphine, 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (L^1) in two steps. Reaction of $Li(PPh_2)$ (generated '*in situ*' from Ph_2PH and $LiBu^n$) with 2,6-dichloropyridine at low temperature yielded the monosubstituted product 2-chloro-6-(diphenylphosphino)pyridine, which in turn reacted with potassium pyrazolate to give L^1. Reaction of L^1 with 1 equivalent of $[Ag(MeCN)_4][ClO_4]$ resulted in the formation of $[Ag_2(\mu\text{-}L^1)_2(MeCN)_2][ClO_4]_2$, which exhibits weak metal–metal interaction.[9] We report here the synthesis and reactivity of the binuclear copper complex $[Cu_2(\mu\text{-}L^1)_2(MeCN)_2][ClO_4]_2$.

Experimental

General procedure, measurements and materials

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. The solvents were purified by standard methods. Infrared spectra were measured on a Perkin-Elmer 1600 spectrometer, ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra on a Bruker-300 spectrometer using $SiMe_4$ as the external standard and $CDCl_3$ as solvent and $^{31}P\text{-}\{^1H\}$ NMR spectra on a Bruker-500 spectrometer at 202.45 MHz using $(PhO)_3P$ as the external standard and $CDCl_3$ as solvent. The complexes $[Cu(MeCN)_4][ClO_4]$[10] and $[Pd(PBu^n_3)_2Cl_2]$[11] were prepared from literature procedures.

CAUTION: While none of these perchlorate complexes has proved to be shock sensitive, nevertheless proper care should always be taken.[12]

Preparations

$[Cu_2(\mu\text{-}L^1)_2(MeCN)_2][ClO_4]_2$ 1. To a solution containing 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (0.33 g, 1 mmol) in MeCN (20 cm^3) was added solid $[Cu(MeCN)_4][ClO_4]$ (0.33 g, 1 mmol). The resulting solution was stirred at room temperature for 30 min. Subsequent diffusion of diethyl ether into the concentrated solution gave **1** as air-stable colorless crystals (yield 0.49 g, 92%). IR (CH_2Cl_2): ν(C≡N) 2306.7 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.56 (d, $J = 0.7$, 2 H), 8.12 (m, 2 H), 8.00 (m, 4 H), 7.28 (m, 20 H), 6.99 (m, 2 H), 6.54 (t, $J = 1.0$ Hz, 2 H) and 2.02 (s, 6 H). $^{31}P\text{-}\{^1H\}$ NMR: δ 23.03 (Found: C, 48.74; H, 3.64; N, 9.99. Calc. for $C_{22}H_{19}ClCuN_4O_4P$: C, 49.54; H, 3.59; N, 10.51%).

$[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}\eta^1\text{-}C{\equiv}CPh)][ClO_4]$ 2. To a solution of Li(C≡CPh) (0.3 mmol) in thf (40 cm^3) (prepared '*in situ*' by treating the corresponding alkyne with 1.60 M $LiBu^n$ at 0 °C) was added complex **1** (0.32 g, 0.30 mmol) at room temperature. The resulting mixture was stirred for 12 h and evaporated to dryness, giving a solid residue which was then extracted with $CHCl_3$ (30 cm^3). Subsequent diffusion of diethyl ether into the concentrated solution gave **2**·H_2O as air-stable orange crystals (yield 0.26 g, 78%). IR (CH_2Cl_2): ν(C≡C) 2065.7 cm^{-1}. ^1H NMR: δ 8.49 (d, $J = 0.7$, 2 H), 8.14 (m, 2 H), 7.90 (m, 4 H), 7.43 (m, 5 H), 7.30 (m, 20 H), 6.86 (m, 2 H) and 6.54 (t, $J = 0.6$ Hz, 2 H). $^{31}P\text{-}\{^1H\}$ NMR: δ 12.01 (Found: C, 57.67; H, 3.68; N, 8.34. Calc. for $C_{48}H_{37}ClCu_2N_6O_4P_2\cdot H_2O$: C, 57.40; H, 3.91; N, 8.37%).

Reaction of complex 2 with $[Pd(PBu^n_3)_2Cl_2]$. To a solution of complex **2**·H_2O (0.15 g, 0.15 mmol) in CH_2Cl_2 (20 cm^3) was added $[Pd(PBu^n_3)_2Cl_2]$ (0.09 g, 0.15 mmol) in CH_2Cl_2 (5 cm^3). The resulting solution was stirred at room temperature for 6 h and evaporated to dryness, giving a solid residue which was extracted with diethyl ether (20 cm^3). The deposited yellow solid

Table 1 Crystal data for complexes **1**, **2**·$CHCl_3$·H_2O and **3**·H_2O

	1	**2**·$CHCl_3$·H_2O	**3**·H_2O
Formula	$C_{44}H_{38}Cl_2Cu_2N_8O_8P_2$	$C_{48}H_{37}ClCu_2N_6O_4P_2\cdot CHCl_3\cdot H_2O$	$C_{40}H_{32}Cl_2Cu_2N_6O_4P_2\cdot H_2O$
M	1066.74	1123.69	938.65
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$Pna2_1$ (no. 33)
a/Å	19.021(4)	12.839(1)	23.253(5)
b/Å	10.610(2)	13.220(1)	12.506(3)
c/Å	22.969(2)	16.624(1)	14.950(3)
α/°		93.29(1)	
β/°	90.40(3)	102.88(1)	
γ/°		96.79(1)	
V/Å^3	4635(2)	2721.1(3)	4347(2)
Z	4	2	4
F(000)	2176	1144	1912
D_c/g cm^{-3}	1.529	1.349	1.433
μ/cm^{-1}	1.16	1.08	1.22
Collection range, 2θ/°	4–52	4–52	4–52
Goodness of fit	1.18	1.02	1.76
No. unique reflections (R_{int})	7638 (0.037)	7622 (0.00)	4042 (0.047)
No. observed reflections [$\lvert F\rvert \geqslant 4\sigma(F)$]	6372	4493	3559
No. variables, *p*	595	701	508
R_F[a]	0.073	0.081	0.053
R_F'[b]	0.093	0.114	0.068

[a] $R_F = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$. [b] $R_F' \equiv [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$.

was filtered off and dissolved in MeCN (5 cm^3). Subsequent diffusion of diethyl ether into the concentrated solution gave **3**·H_2O as air-stable yellow crystals (yield 0.12 g, 84%). ^{1}H NMR: δ 8.48 (d, *J* = 0.7, 2 H), 8.20 (m, 2 H), 8.06 (m, 4 H), 7.28 (m, 20 H), 7.00 (m, 2 H) and 6.56 (t, *J* = 0.90 Hz, 2 H). ^{31}P-{^{1}H} NMR: δ 17.33 (Found: C, 51.54; H, 3.48; N, 9.00. Calc. for $C_{40}H_{32}Cl_2Cu_2N_6O_4P_2\cdot H_2O$: C, 51.18; H, 3.65; N, 8.96%). The filtrate and Et_2O washings of the solid were concentrated to give a pale yellow residue which was purified by column chromatography using CH_2Cl_2 as the eluent to give colorless solid [Pd(PBu^n_3)$_2$(C≡CPh)Cl], 73 mg (75%). IR (CH_2Cl_2): ν(C≡C) 2045.7 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.28–7.23 (m, 5 H), 1.99–1.92 (m, 12 H), 1.60–1.55 (m, 12 H), 1.45–1.42 (m, 12 H) and 0.95 (t, *J* = 3.5 Hz, 18 H). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 14.38 (s, CH_3), 23.44 (t, *J* = 27, CH_2CH_3), 24.98 (t, *J* = 13, $CH_2CH_2CH_3$), 27.00 (s, PCH_2), 96.79 (t, *J* = 4, PdC≡C), 106.39 (t, *J* = 18 Hz, PdC) and 126.00–131.18 (C_6H_5). ^{31}P-{^{1}H} NMR: δ 22.24.

[Cu_2(μ-L^1)$_2$(μ-$MeO_2CC{\equiv}CCO_2Me$)][ClO_4]$_2$ 4. To a solution of complex **1** (0.32 g, 0.30 mmol) in MeCN (20 cm^3) was added neat dimethyl acetylenedicarboxylate (37 μl, 1.0 equivalent) at −20 °C. Product formation was almost instantaneous, judging by the appearance of a deep burgandy color. The cooling bath was removed at this point, after which the solvent was concentrated to about 5 cm^3, and diethyl ether (20 cm^3) was added to give **4**·MeCN as a red powder, 0.26 g (77%). IR (CH_2Cl_2): ν(C≡N) 2306.5, ν(C=O) 1725.7 and ν(C≡C), acting as four-electron donor) 1606.6 cm^{-1}. ^{1}H NMR: δ 8.31 (d, *J* = 0.7, 2 H), 8.07 (m, 2 H), 7.84 (m, 2 H), 7.26 (m, 20 H), 7.00 (m, 2 H), 6.45 (t, *J* = 1.0 Hz, 2 H) and 3.40 (s, 6 H). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 52.80 (s, OCH_3), 127.58–133.96 (C_6H_5, C_5H_3N, $C_3H_3N_2$) and 160.50 (s, C=O); signals for two alkyne carbon atoms were not observed. ^{31}P-{^{1}H} NMR: δ 34.31 (Found: C, 49.37; H, 3.60; N, 8.24. Calc. for $C_{46}H_{38}Cl_2Cu_2N_6O_{12}P_2\cdot CH_3CN$: C, 49.36; H, 3.54; N, 8.40%).

Reaction of complex 4 with bis(diphenylphosphino)methane (dppm). To a solution of complex **4** (0.34 g, 0.30 mmol) in MeCN (20 cm^3) was added solid dppm (0.12 g, 0.30 mmol) at room temperature; the resulting mixture was stirred for 30 min. Subsequent diffusion of diethyl ether into the concentrated solution gave **5** as air-stable pale yellow crystals (0.36 g, 88%). ^{1}H NMR ($CDCl_3$): δ 8.66 (d, *J* = 0.8, 2 H), 8.26 (d, *J* = 1.5, 4 H), 7.60 (m, 2 H), 7.43–6.91 (m, 40 H), 6.53–6.43 (m, 6 H) and 3.15 (t, *J* = 4.2 Hz, 2 H). ^{31}P-{^{1}H} NMR: δ 21.10 and 8.27 (Found: C, 56.82; H, 3.96; N, 6.12. Calc. for $C_{65}H_{54}Cl_2Cu_2N_6O_8P_2$: C, 57.02; H, 3.98; N, 6.14%).

X-Ray crystallography

Crystals of complexes **1** and **3**·H_2O were obtained by vapor diffusion of diethyl ether into their MeCN solutions, those of **2**·$CHCl_3$·H_2O by slow diffusion of diethyl ether into a chloroform solution of **2**·H_2O.

The intensity data were collected at 294 K on a Rigaku RAXIS IIC imaging-plate diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{min} = 4$, $2\theta_{max} = 52°$, 36.5° oscillation frames in the range 0–180°, exposure 8 min per frame).[13] A self-consistent semiempirical absorption correction based on Fourier-coefficient fitting of symmetry-equivalent reflections was applied using the ABSOR[14] program.

The crystal structures were determined by direct methods. In complex **1** both independent dinuclear cations have crystallographically imposed $\bar{1}$ molecular symmetry. In **2**·$CHCl_3$·H_2O there are two independent $CHCl_3$ molecules that have half site occupancy and are also orientationally disordered; in the model adopted for refinement the disordered $CHCl_3$ and ordered ClO_4^- groups were subjected to interatomic distance restraints (C–Cl 1.760 ± 0.005, Cl···Cl 2.93 ± 0.01, Cl–O 1.420 ± 0.005 and O···O 2.30 ± 0.01 Å). For all three compounds the positions of all non-hydrogen atoms except those associated with the disordered $CHCl_3$ groups in **2** were refined anisotropically. Hydrogen atoms were placed in their idealized positions (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure-factor calculation in the final stage of full-matrix least-squares refinement.

All computations were performed on an IBM-compatible 486 personal computer with the SHELXTL PC program package.[15] Information concerning X-ray data collection and structure refinement of all compounds is summarized in Table 1. Selected bond distances and angles are given in Table 2.

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Table 2 Selected bond lengths (Å) and angles (°) in complexes **1**, **2**·$CHCl_3$·H_2O and **3**·H_2O

Complex **1**

Cu(1)···Cu(1a)	3.599(1)	Cu(2)···Cu(2b)	3.617(1)
Cu(1)–P(1)	2.208(1)	Cu(2)–P(2)	2.197(1)
Cu(1)–N(1a)	2.123(3)	Cu(2)–N(5b)	2.112(4)
Cu(1)–N(3a)	2.086(3)	Cu(2)–N(7b)	2.084(3)
Cu(1)–N(4)	1.989(4)	Cu(2)–N(8)	1.997(4)
P(1)–Cu(1)–N(1a)	107.1(1)	P(2)–Cu(2)–N(5b)	107.2(1)
P(1)–Cu(1)–N(3a)	127.4(1)	P(2)–Cu(2)–N(7b)	126.9(1)
P(1)–Cu(1)–N(4)	114.0(1)	P(2)–Cu(2)–N(8)	121.5(1)
N(1a)–Cu(1)–N(3a)	79.0(1)	N(5b)–Cu(2)–N(7b)	79.0(1)
N(1a)–Cu(1)–N(4)	105.4(1)	N(5b)–Cu(2)–N(8)	100.0(2)
N(3a)–Cu(1)–N(4)	114.3(1)	N(7b)–Cu(2)–N(8)	108.4(1)

Complex **2**·$CHCl_3$·H_2O

Cu(1)···Cu(2)	2.516(1)	C(41)–C(42)	1.18(1)
Cu(1)–P(1)	2.238(2)	Cu(2)–P(2)	2.235(2)
Cu(1)–C(41)	2.045(9)	Cu(2)–C(41)	2.078(9)
Cu(1)–N(4)	2.073(7)	Cu(2)–N(1)	2.097(7)
Cu(1)–N(6)	2.156(6)	Cu(2)–N(3)	2.109(7)
P(1)–Cu(1)–N(4)	109.6(2)	P(2)–Cu(2)–N(1)	108.2(2)
P(1)–Cu(1)–N(6)	111.7(2)	P(2)–Cu(2)–N(3)	122.0(2)
P(1)–Cu(1)–C(41)	123.7(2)	P(2)–Cu(2)–C(41)	114.2(2)
N(4)–Cu(1)–C(41)	116.4(3)	N(6)–Cu(1)–C(41)	108.7(3)
N(4)–Cu(1)–N(6)	77.4(3)	N(1)–Cu(2)–N(3)	77.7(3)
N(1)–Cu(2)–C(41)	115.4(3)	N(3)–Cu(2)–C(41)	113.8(3)
Cu(1)–C(41)–C(42)	148.1(7)	Cu(2)–C(41)–C(42)	135.3(8)
Cu(1)–Cl(1)–Cu(2)	70.2(1)		

Complex **3**·H_2O

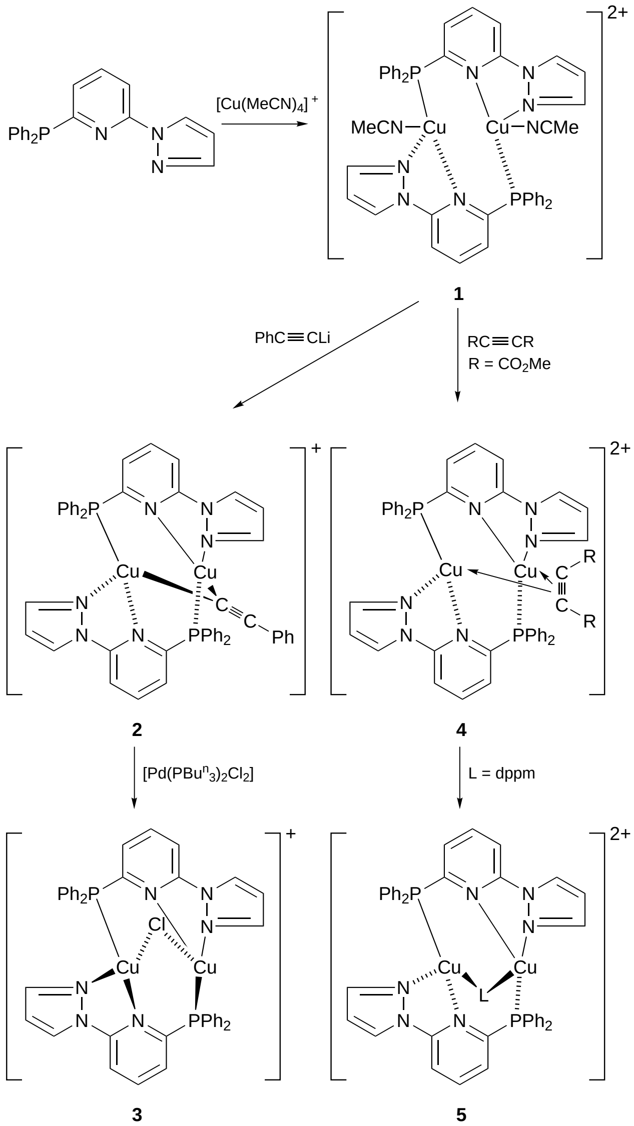
Cu(1)···Cu(2)	2.758(1)		
Cu(1)–P(1)	2.190(2)	Cu(2)–P(2)	2.182(2)
Cu(1)–N(4)	2.042(6)	Cu(2)–N(1)	2.089(6)
Cu(1)–N(6)	2.094(5)	Cu(2)–N(3)	2.119(5)
Cu(1)–Cl(1)	2.409(2)	Cu(2)–Cl(1)	2.386(2)
P(1)–Cu(1)–N(4)	115.5(2)	P(2)–Cu(2)–N(1)	115.0(2)
P(1)–Cu(1)–N(6)	140.0(1)	P(2)–Cu(2)–N(3)	131.8(1)
P(1)–Cu(1)–Cl(1)	110.4(1)	P(2)–Cu(2)–Cl(1)	115.2(1)
N(4)–Cu(1)–Cl(1)	108.4(2)	N(1)–Cu(2)–Cl(1)	112.2(2)
N(6)–Cu(1)–Cl(1)	98.3(1)	N(3)–Cu(2)–Cl(1)	99.0(1)
N(4)–Cu(1)–N(6)	78.8(2)	N(1)–Cu(2)–N(3)	78.1(2)

Symmetry codes: a $1 - x, 1 - y, -z$; b $2 - x, 1 - y, -z$.

Results and Discussion

Reaction of 2-(diphenylphosphino)-6-(pyrazolyl)pyridine (L^1) with 1 equivalent of $[Cu(MeCN)_4][ClO_4]$ resulted in the formation of $[Cu_2(\mu\text{-}L^1)_2(MeCN)_2][ClO_4]_2$ **1** (Scheme 1), in which the two L^1 ligands exhibit a head-to-tail configuration as revealed by X-ray crystallography.

A perspective view of the centrosymmetric dinuclear cation of complex **1** (only one of the two independent molecules is shown) is displayed in Fig. 1. Each copper center exhibits distorted tetrahedral geometry with ligation by one P and two N atoms from the phosphine ligand, and one N atom from the acetonitrile ligand. The Cu···Cu distance [3.599(1) Å for Cu(1)···Cu(1a) and 3.617(1) Å for Cu(2)···Cu(2b)] is much longer than that of 2.721(3) Å in $[Cu_2(\mu\text{-}L^2)_3(MeCN)]^+$ [16] [L^2 = (2-diphenylphosphino)pyridine] and is in accord with 3.584(1) Å in $[Cu_2(\mu\text{-}L^2)_2(MeCN)]^+$.[17] The Cu–N bond lengths of 2.123(3), 2.086(3) Å for Cu(1) and 2.112(4), 2.084(3) Å for Cu(2) are typical for a copper(I) center bound by nitrogen heterocycles.[18] The N–Cu–N 'bite angles' of 79.0(1)° for Cu(1) and 79.0(1)° for Cu(2) for the bidentate pyridylpyrazole fragments are as expected for relatively rigid 1,4-diamine ligands, and the values are very similar to that [78.9(3)°] found in $[Cu_3L^3_2(MeCN)_2][PF_6]$ [L^3 = 2,6-bis(5-methylpyrazol-3-yl)-pyridine].[19]



Scheme 1

Equimolar quantities of complex **1** and Li(C≡CPh) (prepared '*in situ*' from the alkyne and $LiBu^n$) reacts in thf to give the alkynylcopper(I) complex **2**. This reaction is different from that of Li(C≡CPh) with $[Cu_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ which usually yields trinuclear[20–22] or tetranuclear[17] copper(I) clusters. One possible reason is the different steric hindrance and rigidity of the L^1 and dppm ligands. Complex **2** is the first example of a single acetylide bridge between two copper atoms.

Fig. 2 shows a perspective drawing of the cation in crystalline complex **2**·$CHCl_3$·H_2O with atomic numbering. The structure consists of a binuclear Cu_2C core in which a phenylacetylide ligand bridges the two metal centers. Each copper atom in the molecule is in a distorted terahedral co-ordination environment (ignoring the Cu···Cu interaction). The C≡C distance of 1.18(1) Å in **2** is typical of that found for a terminal carbon–carbon triple bond. The C(41)–C(42)–C(43) bond angle of 175.8(9)° is close to linear, and the average Cu···C distance of 3.07 Å between C(42) and the copper atoms is suggestive of little or no metal–alkynyl π interaction. Thus the acetylide ligand is best formulated as a $\mu\text{-}\eta^1$ bridge. However, the acetylide bridge is unsymmetric, showing a significantly bent orientation, as reflected by the Cu–C distances [2.045(9) Å for Cu(1)–C(41), 2.078(9) Å for Cu(2)–C(41)] and the Cu–C–C angles [148.1(7)° for Cu(1)–C(41)–C(42), 135.3(8)° for Cu(2)–C(41)–C(42)]. The Cu(1)···Cu(2) distance of 2.516(1) Å, which is shorter than the interatomic separation found in

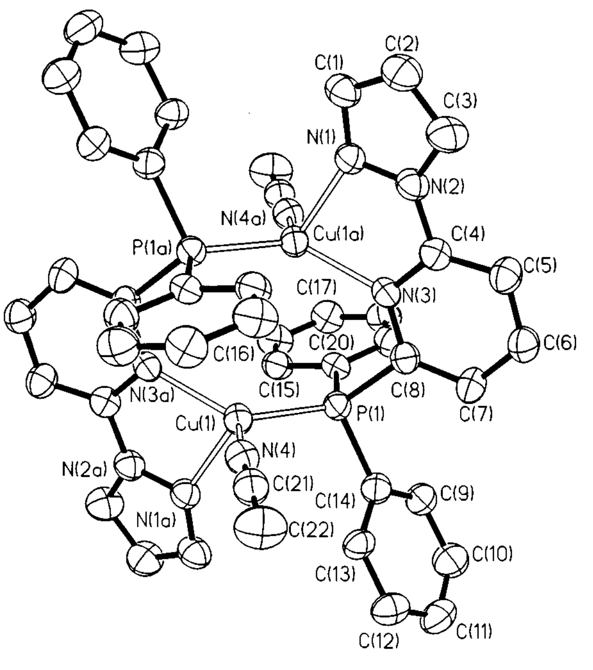


Fig. 1 Perspective view (35% thermal ellipsoids) of one of the two independent, centrosymmetric $[Cu_2(\mu\text{-}L^1)_2(MeCN)_2]^{2+}$ cations in complex **1**

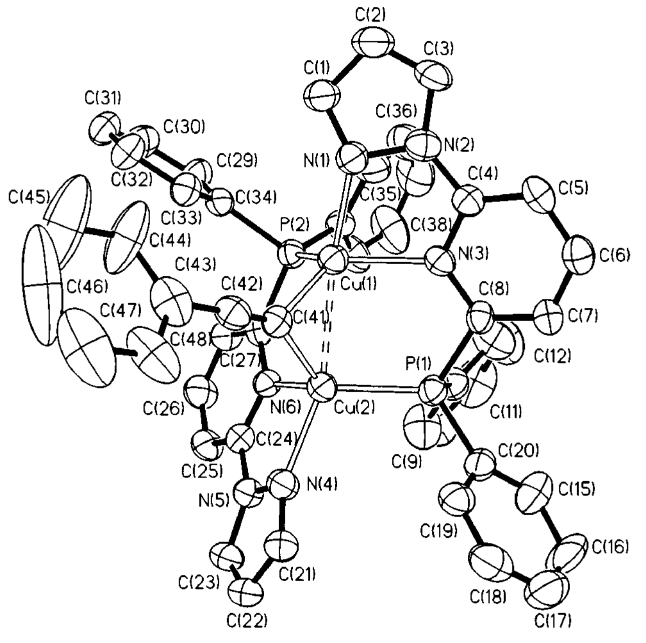


Fig. 2 Perspective view (35% thermal ellipsoids) of the $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}\eta^1\text{-}C{\equiv}CPh)]^+$ cation in complex **2**$\cdot CHCl_3\cdot H_2O$

metallic copper (2.56 Å), is not uncommon in organocopper systems,[23] and may be suggestive of some weak interaction between two copper(I) centers. The short Cu···Cu contact in **2** may simply be due to the desire for both Cu atoms to maximize σ bonding with sp orbitals of the acetylide ligand, as is indicated by the very acute Cu···Cu–C bridging angles, Cu(1)···Cu(2)–C(41) 53.0(2)° and Cu(2)···Cu(1)–C(41) 51.8(2)°. Short Cu···Cu contacts have also been observed in the complexes $[\{(C_6H_{11})_3P\}Cu(\mu\text{-}C{\equiv}CBu^t)_2Cu(PPh_3)_2]$ 2.389(1) Å[7] and $[Cu_2(PPh_2Me)_4(\mu\text{-}\eta^1\text{-}C{\equiv}CPh)_2]$ 2.454(1) Å.[8]

Reaction of complex **2** with an equimolar quantity of $[Pd(PBu^n_3)_2Cl_2]$ in dichloromethane solution at room temperature gives the corresponding alkynylpalladium complex $[Pd(PBu^n_3)_2(C{\equiv}CPh)Cl]$ accompanied by formation of $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}Cl)][ClO_4]$. The reaction is believed to proceed through

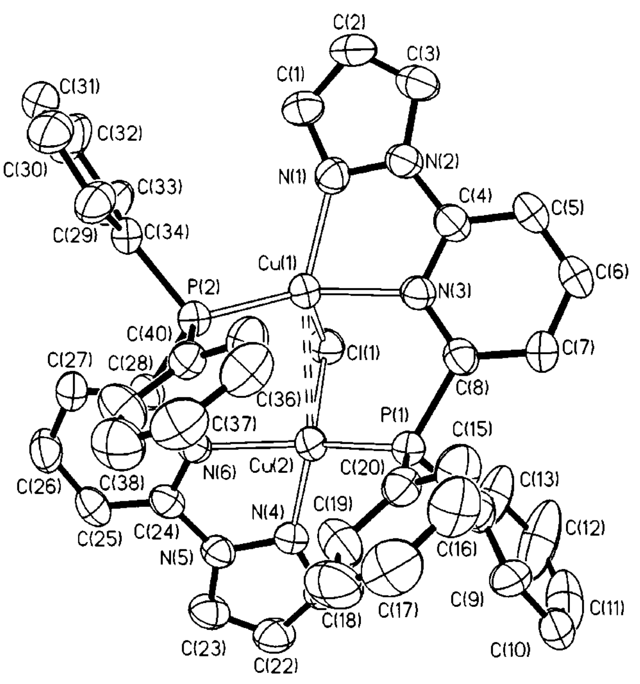


Fig. 3 Perspective view (35% thermal ellipsoids) of $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}Cl)]^+$ cation in complex **3**$\cdot H_2O$

alkynyl ligand transfer from Cu^I to Pd^{II} accompanied by transfer of the chloride ligand to the Cu^I. This process is important in the coupling reaction of terminal alkynes with organic halides using palladium(II) phosphine complexes and CuI as catalysts.[24b] Similar transfer reactions are also found in the reaction of $[\{Cu(PPh_3)(C{\equiv}CSiMe_3)\}_4]$ with $[Pd(PEt_3)_2Cl_2]$[25] and $[\{Cu(C{\equiv}CR)\}_n]$ with chloro complexes of Ni^{II}, Pd^{II} and Pt^{II}.[24] The above irreversible alkynyl transfer reactions from copper to Group 10 transition metals suggest a lower thermodynamic stability of the copper(I)–alkynyl bond as compared to the bond between the alkynyl group and Group 10 transition metals. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of $[Pd(PBu^n_3)_2(C{\equiv}CPh)Cl]$ shows the signals of alkynyl carbons at δ 106.39 and 96.79 as triplets due to ^{31}P–^{13}C coupling. The former signals, which have a larger coupling constant (18 Hz) than the latter (4 Hz), are assigned to the carbon atoms bonded to the palladium center. Proton and $^{31}P\text{-}\{^1H\}$ NMR spectra also indicate the formation of the monoalkynylpalladium complex. The complex $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}Cl)][ClO_4]$ **3**, separated from the reaction mixture as an Et_2O-insoluble solid, has been characterized by elemental analysis, ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy and X-ray crystallography.

Fig. 3 shows a perspective drawing of the cation in crystalline complex **3**$\cdot H_2O$ with atomic numbering. The molecular structure is very similar to that of **2**$\cdot CHCl_3\cdot H_2O$ except that the phenylacetylide bridge is here replaced by a chloro bridge. The bond length of 2.758(1) Å for Cu(1)···Cu(2) is much shorter than that of complex **1**, but longer than that of **2**. The difference in Cu···Cu distances in **3** and **2** can be explained by the greater intermolecular steric hindrance of the neighboring ligands Cl^-/phosphine in contrast to PhC≡C/phosphine in the binuclear complexes. This value is significantly longer than that [2.386(4) Å] in the mixed-valence Cu^I–Cu^{II} complex $[Cu_2Cl_3L^4]$ (L^4 = 4-methyl-1,8-naphthyridine).[26] The Cu–Cl distances of 2.386(2) and 2.409(2) Å are consistent with those of 2.379(1) Å in $[\{(Ph_3P)Cu_2(\mu\text{-}Cl)_2(\mu\text{-}pyz)\}_\infty]$[27a] (pyz = pyrazine) and 2.360(1), 2.369(1) Å in $[Cu_2(\mu\text{-}Cl)_2L^5]$ [L^5 = phenylenebis(diisopropylphosphine)].[27b]

Reaction of complex **1** with dimethyl acetylenedicarboxylate resulted in ready formation of $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-}MeO_2CC{\equiv}CCO_2Me)][ClO_4]_2$ **4**, in which the bridging alkynyl unit serves as a four-electron donor, contributing a pair of π electrons to each

16-electron copper center. The IR spectrum of **4**·MeCN shows characteristic absorption of the C≡N group at 2306.5 cm^{-1}, the C=O group at 1725.7 cm^{-1} and the donor C≡C group at 1606.6 cm^{-1}. Drastic lowering of the observed C≡C stretching frequency from the normal alkyne region (2100–2260 cm^{-1}), caused by the strong π-donor behavior of the bridging alkynyl ligand, has been reported in binuclear copper(I) complexes containing the same π-donor bridge and a macrocyclic amine ligand.[28] In the ^{13}C-{^{1}H} NMR ($CDCl_3$) spectrum, the resonances of OCH_3 (δ 52.80) and C=O (δ 160.50) of dimethyl acetylenedicarboxylate were observed, but the resonance for the C≡C carbon atoms was not detectable.

However, the phenyl-substituted alkyne PhCC≡CCPh does not react with complex **1** under the same conditions even over a very long time. One plausible reason for enhancement of the reactivity of dimethyl acetylenedicarboxylate toward dicopper complex **2** is significant stabilization of the Cu–C bond of the product caused by the electron-withdrawing group on the alkyne.

Complex **4** is air-stable in the solid state as a 1 : 1 MeCN solvate, but its MeCN solution discomposes slowly on exposure to air to give **1** and $MeO_2CC{\equiv}CCO_2Me$. Reaction of **4** with dppm at room temperature readily gives the substituted product $[Cu_2(\mu\text{-}L^1)_2(\mu\text{-dppm})][ClO_4]_2$ **5**, indicating that the Cu–P σ interaction is much stronger than copper–alkyne π interaction. The ^{1}H NMR spectrum of **5** displays a methylene resonance as a triplet centered at δ 3.15, which is indicative of ^{31}P–^{1}H coupling (4.2 Hz). The ^{31}P-{^{1}H} NMR spectrum shows two singlets at δ 21.10 and 8.27, which are assigned to the phosphorus resonances of the co-existing L^1 and dppm ligands.

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References

1 For general reviews see, R. Nast, *Coord. Chem. Rev.*, 1983, **47**, 89; A. J. Carty, *Pure Appl. Chem.*, 1982, **54**, 113; M. I. Bruce, *Pure Appl. Chem.*, 1986, **58**, 553; 1990, **6**, 1021; N. M. Kostic and R. F. Fenske, *Organometallics*, 1982, **1**, 974.

2 M. F. Lappert, R. Pearce and P. I. W. Yarrow, *Chem. Rev.*, 1983, **83**, 135; A. A. Cherkas, L. H. Randall, S. A. MacLaughlin, G. N. Mott, N. J. Taylor and A. J. Carty, *Organometallics*, 1988, **7**, 1115 and refs. therein.

3 P. R. Raithby and M. J. Rosales, *Adv. Inorg. Chem. Radiochem.*, 1985, **29**, 169; E. Sappa, A. Tiripicchio and P. Braunstein, *Coord. Chem. Rev.*, 1985, **65**, 219.

4 See, for example, R. W. M. ten Hoedt, J. G. Noltes, G. van Koten and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1978, 1800; G. van Koten, R. W. M. ten Hoedt and J. G. Noltes, *J. Org. Chem.*, 1977, **42**, 2705; *J. Organomet. Chem.*, 1977, **113**, 13; D. M. Knotter, A. L. Spek and G. van Koten, *J. Chem. Soc., Chem. Commun.*, 1989, 1738; M. D. Knotter, A. L. Spek, D. M. Grove and G. van Koten, *Organometallics*, 1992, **11**, 4083; M. G. B. Drew, F. S. Esho and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1982, 1347; L. Naldini, F. Demartin, M. Manassero, M. Sansoni, G. Rassu and A. Zoroddu, *J. Organomet. Chem.*, 1985, **279**, C42; V. W. W. Yam, W.-K. Lee and K.-K. Cheung, *J. Chem. Soc., Dalton Trans.*, 1996, 2335; V. W. W. Yam, S. W.-K. Choi, C.-L. Chan and K.-K. Cheung, *Chem. Commun.*, 1996, 2067; V. W. W. Yam, W. K.-M. Fung and K.-K. Cheung, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1100; M. P. Gamasa, J. Gimeno, E. Lastra, A. Aguirre and S. García-Granda, *J. Organomet. Chem.*, 1989, **378**, C11; V. W. W. Yam, W.-K. Lee and T.-F. Lai, *Organometallics*, 1993, **12**, 2383; F. Olbrich, J. Kopf and E. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1077.

5 P. W. R. Corfield and G. J. Gainsford, *Am. Cryst. Assoc., Abstr. Papers (Summer)*, 1970, 83.

6 F. Olbrich, U. Behrens and E. Weiss, *J. Organomet. Chem.*, 1994, **472**, 365.

7 A. J. Edwards, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russel and D. S. Wright, *Organometallics*, 1994, **13**, 4967.

8 V. W. W. Yam, W.-K. Lee, K.-K. Cheung, H.-K. Lee and W.-P. Leung, *J. Chem. Soc., Dalton Trans.*, 1996, 2889.

9 S.-M. Kuang, Z.-Z. Zhang, Q.-G. Wang and T. C. W. Mak, *Inorg. Chim. Acta*, submitted for publication.

10 G. J. Kubas, *Inorg. Synth.*, 1979, **19**, 90.

11 F. G. Mann and D. Purie, *J. Chem. Soc.*, 1935, 154.

12 W. C. Wolsey, *J. Chem. Educ.*, 1973, **50**, A335; K. N. Raymond, *Chem. Eng. News*, 1983, **61**, 4.

13 J. Tanner and K. Krause, *The Rigaku Journal*, 1994, **11**, 4; 1990, **7**, 28; K. L. Krause and G. N. Phillips Jr., *J. Appl. Crystallogr.*, 1992, **25**, 146; M. Sato, M. Yamamoto, K. Imada, Y. Katsube, N. Tanaka and T. Higashi, *J. Appl. Crystallogr.*, 1992, **25**, 348.

14 T. Higashi, ABSOR, An Empirical Absorption Correction Based on Fourier Coefficient Fitting, Rigaku Corporation, Tokyo, 1995.

15 *SHELXLPC V5.0 Reference Manual*, Siemens Analytical X-Ray Instruments, Madison, WI, 1995.

16 E. Lastra, M. P. Gamasa, J. Gimeno, M. Lanfranchi and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1989, 1499.

17 M. P. Gamasa, J. Gimeno, E. Lastra and X. Solans, *J. Organomet. Chem.*, 1988, **346**, 227.

18 M. Melnik, L. Macaskova and C. E. Holloway, *Coord. Chem. Rev.*, 1993, **126**, 71.

19 A. T. Baker, D. C. Craig and G. Dong, *Inorg. Chem.*, 1996, **35**, 1091.

20 J. Diéz, M. P. Gamasa, J. Gimeno, A. Aguirre and S. García-Granda, *Organometallics*, 1991, **10**, 380.

21 J. Diéz, M. P. Gamasa, J. Gimeno, E. Lastra, A. Aguirre and S. García-Granda, *Organometallics*, 1993, **12**, 2213.

22 V. W. W. Yam, W.-K. Lee, K.-K. Cheung, B. Crystall and D. Phillips, *J. Chem. Soc., Dalton Trans.*, 1996, 3283.

23 G. van Koten, S. L. James and J. B. H. Jastrzebski, in *Comprehensive Organometallic Chemistry II*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 3, p. 75.

24 (*a*) Y. Fujikura, K. Sonogashira and N. Hagihara, *Chem. Lett.*, 1975, 1067; (*b*) K. Sonogashira, T. Yatake, Y. Tohda, S. Takahashi and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 1977, 291; (*c*) H. Ogawa, T. Joh, S. Takahashi and K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, 1988, 561.

25 K. Osakada, T. Takizawa and T. Yamamoto, *Organometallics*, 1995, **14**, 3531.

26 D. Gatteschi, C. Meali and L. Sacconi, *Inorg. Chem.*, 1976, **15**, 2774.

27 (*a*) M. Henary, J. L. Wootton, S. I. Khan and J. I. Zink, *Inorg. Chem.*, 1997, **36**, 796; (*b*) R. T. Baker, J. C. Calabrese and S. A. Westcott, *J. Organomet. Chem.*, 1995, **498**, 109.

28 G. M. Villacorta, D. Gibson, I. D. Williams and S. J. Lippard, *J. Am. Chem. Soc.*, 1985, **107**, 6732; G. M. Villacorta, D. Gibson, I. D. Williams, E. Whang and S. J. Lippard, *Organometallics*, 1987, **6**, 2426.

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