

Synthesis and reactivity of binuclear copper(I) complexes of 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (L¹). Crystal structures of [Cu₂(μ-L¹)₂(MeCN)₂][ClO₄]₂, [Cu₂(μ-L¹)₂(μ-η¹-C≡CPh)][ClO₄]·CHCl₃·H₂O and [Cu₂(μ-L¹)₂(μ-Cl)][ClO₄]·H₂O

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Reaction of 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (L¹) with 1 equivalent of [Cu(MeCN)₄][ClO₄] resulted in the formation of [Cu₂(μ-L¹)₂(MeCN)₂][ClO₄]₂ **1**. Complex **1** reacted with Li(C≡CPh) to give [Cu₂(μ-L¹)₂(μ-η¹-C≡CPh)][ClO₄] **2**, which underwent an alkynyl ligand-transfer reaction with [Pd(PBuⁿ)₃]₂Cl₂ to give [Cu₂(μ-L¹)₂(μ-Cl)][ClO₄] **3** and [Pd(PBuⁿ)₃](C≡CPh)Cl. Reaction of **1** with dimethyl acetylenedicarboxylate yielded [Cu₂(μ-L¹)₂(μ-MeO₂CC≡CCO₂Me)][ClO₄]₂ **4**, the alkynyl ligand of which can easily be displaced by bis(diphenylphosphino)methane (dppm) to give [Cu₂(μ-L¹)₂(μ-dppm)][ClO₄]₂ **5**. The crystal structures of **1**, **2**·CHCl₃·H₂O and **3**·H₂O 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 [Cu₂(PEt₂Ph)₄(μ-η¹-C≡CPh)₂],⁵ [Cu₂(tmch)₂(μ-η¹-C≡CPh)₂] (tmch = 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne),⁶ [(C₆H₁₁)₃P]Cu(μ-η¹-C≡CBu^t)₂Cu(PPh₃)₂,⁷ and [Cu₂(PPh₂Me)₄(μ-η¹-C≡CPh)]₂⁸ have been structurally characterized.

We have recently prepared a new tridentate phosphine, 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (L¹) in two steps. Reaction of Li(PPh₂) (generated 'in situ' from Ph₂PH and LiBuⁿ) 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 L¹. Reaction of L¹ with 1 equivalent of [Ag(MeCN)₄][ClO₄] resulted in the formation of [Ag₂(μ-L¹)₂(MeCN)₂][ClO₄]₂, which exhibits weak metal-metal interaction.⁹ We report here the synthesis and reactivity of the binuclear copper complex [Cu₂(μ-L¹)₂(MeCN)₂][ClO₄]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 ¹³C-{¹H} NMR spectra on a Bruker-300 spectrometer using SiMe₄ as the external standard and CDCl₃ as solvent and ³¹P-{¹H} NMR spectra on a Bruker-500 spectrometer at 202.45 MHz using

(PhO)₃P as the external standard and CDCl₃ as solvent. The complexes [Cu(MeCN)₄][ClO₄]¹⁰ and [Pd(PBuⁿ)₃]₂Cl₂¹¹ 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

[Cu₂(μ-L¹)₂(MeCN)₂][ClO₄]₂ **1.** To a solution containing 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (0.33 g, 1 mmol) in MeCN (20 cm³) was added solid [Cu(MeCN)₄][ClO₄] (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 (CH₂Cl₂): ν(C≡N) 2306.7 cm⁻¹. ¹H NMR (CDCl₃): 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). ³¹P-{¹H} NMR: δ 23.03 (Found: C, 48.74; H, 3.64; N, 9.99. Calc. for C₂₂H₁₉ClCuN₄O₄P: C, 49.54; H, 3.59; N, 10.51%).

[Cu₂(μ-L¹)₂(μ-η¹-C≡CPh)][ClO₄] **2.** To a solution of Li(C≡CPh) (0.3 mmol) in thf (40 cm³) (prepared 'in situ' by treating the corresponding alkyne with 1.60 M LiBuⁿ 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 CHCl₃ (30 cm³). Subsequent diffusion of diethyl ether into the concentrated solution gave **2**·H₂O as air-stable orange crystals (yield 0.26 g, 78%). IR (CH₂Cl₂): 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). ³¹P-{¹H} NMR: δ 12.01 (Found: C, 57.67; H, 3.68; N, 8.34. Calc. for C₄₈H₃₇ClCu₂N₆O₄P₂·H₂O: C, 57.40; H, 3.91; N, 8.37%).

Reaction of complex 2 with [Pd(PBuⁿ)₃]₂Cl₂. To a solution of complex **2**·H₂O (0.15 g, 0.15 mmol) in CH₂Cl₂ (20 cm³) was added [Pd(PBuⁿ)₃]₂Cl₂ (0.09 g, 0.15 mmol) in CH₂Cl₂ (5 cm³). 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 cm³). The deposited yellow solid

Table 1 Crystal data for complexes **1**, **2**·CHCl₃·H₂O and **3**·H₂O

	1	2 ·CHCl ₃ ·H ₂ O	3 ·H ₂ O
Formula	C ₄₄ H ₃₈ Cl ₂ Cu ₂ N ₈ O ₈ P ₂	C ₄₈ H ₃₇ ClCu ₂ N ₆ O ₄ P ₂ ·CHCl ₃ ·H ₂ O	C ₄₀ H ₃₂ Cl ₂ Cu ₂ N ₆ O ₄ P ₂ ·H ₂ O
<i>M</i>	1066.74	1123.69	938.65
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> na2 ₁ (no. 33)
<i>a</i> /Å	19.021(4)	12.839(1)	23.253(5)
<i>b</i> /Å	10.610(2)	13.220(1)	12.506(3)
<i>c</i> /Å	22.969(2)	16.624(1)	14.950(3)
<i>a</i> /°		93.29(1)	
<i>β</i> /°	90.40(3)	102.88(1)	
<i>γ</i> /°		96.79(1)	
<i>V</i> /Å ³	4635(2)	2721.1(3)	4347(2)
<i>Z</i>	4	2	4
<i>F</i> (000)	2176	1144	1912
<i>D</i> _c /g cm ⁻³	1.529	1.349	1.433
<i>μ</i> /cm ⁻¹	1.16	1.08	1.22
Collection range, 2 θ /°	4–52	4–52	4–52
Goodness of fit	1.18	1.02	1.76
No. unique reflections (<i>R</i> _{int})	7638 (0.037)	7622 (0.00)	4042 (0.047)
No. observed reflections	6372	4493	3559
[<i>I</i> ≥ 4 σ (<i>I</i>)]			
No. variables, <i>p</i>	595	701	508
<i>R</i> _F ^a	0.073	0.081	0.053
<i>R</i> _F ' ^b	0.093	0.114	0.068

^a *R*_F = $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^b *R*_F' = $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

was filtered off and dissolved in MeCN (5 cm³). Subsequent diffusion of diethyl ether into the concentrated solution gave **3**·H₂O as air-stable yellow crystals (yield 0.12 g, 84%). ¹H 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). ³¹P-¹H NMR: δ 17.33 (Found: C, 51.54; H, 3.48; N, 9.00. Calc. for C₄₀H₃₂Cl₂Cu₂N₆O₄P₂·H₂O: C, 51.18; H, 3.65; N, 8.96%). The filtrate and Et₂O washings of the solid were concentrated to give a pale yellow residue which was purified by column chromatography using CH₂Cl₂ as the eluent to give colorless solid [Pd(PBuⁿ)₂(C≡CPh)Cl], 73 mg (75%). IR (CH₂Cl₂): ν (C≡C) 2045.7 cm⁻¹. ¹H NMR (CDCl₃): 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). ¹³C-¹H NMR (CDCl₃): δ 14.38 (s, CH₃), 23.44 (t, *J* = 27, CH₂CH₃), 24.98 (t, *J* = 13, CH₂CH₂CH₃), 27.00 (s, PCH₂), 96.79 (t, *J* = 4, PdC≡C), 106.39 (t, *J* = 18 Hz, PdC) and 126.00–131.18 (C₆H₅). ³¹P-¹H NMR: δ 22.24.

[Cu₂(μ -L)¹)₂(μ -MeO₂CC≡CCO₂Me)][ClO₄]₂ **4**. To a solution of complex **1** (0.32 g, 0.30 mmol) in MeCN (20 cm³) was added neat dimethyl acetylenedicarboxylate (37 μ l, 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 cm³, and diethyl ether (20 cm³) was added to give **4**·MeCN as a red powder, 0.26 g (77%). IR (CH₂Cl₂): ν (C≡N) 2306.5, ν (C=O) 1725.7 and ν (C≡C), acting as four-electron donor 1606.6 cm⁻¹. ¹H 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). ¹³C-¹H NMR (CDCl₃): δ 52.80 (s, OCH₃), 127.58–133.96 (C₆H₅, C₃H₃N, C₃H₃N₂) and 160.50 (s, C=O); signals for two alkyne carbon atoms were not observed. ³¹P-¹H NMR: δ 34.31 (Found: C, 49.37; H, 3.60; N, 8.24. Calc. for C₄₆H₃₈Cl₂Cu₂N₆O₁₂P₂·CH₃CN: 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 cm³) 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%).

¹H NMR (CDCl₃): 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). ³¹P-¹H NMR: δ 21.10 and 8.27 (Found: C, 56.82; H, 3.96; N, 6.12. Calc. for C₆₅H₅₄Cl₂Cu₂N₆O₈P₂: C, 57.02; H, 3.98; N, 6.14%).

X-Ray crystallography

Crystals of complexes **1** and **3**·H₂O were obtained by vapor diffusion of diethyl ether into their MeCN solutions, those of **2**·CHCl₃·H₂O by slow diffusion of diethyl ether into a chloroform solution of **2**·H₂O.

The intensity data were collected at 294 K on a Rigaku RAXIS IIC imaging-plate diffractometer using Mo-K α radiation (λ = 0.710 73 Å) from a rotating-anode generator operating at 50 kV and 90 mA (2 θ_{\min} = 4, 2 θ_{\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 ABSOR¹⁴ 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**·CHCl₃·H₂O there are two independent CHCl₃ molecules that have half site occupancy and are also orientationally disordered; in the model adopted for refinement the disordered CHCl₃ and ordered ClO₄⁻ 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 CHCl₃ 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.

CCDC reference number 186/882.

Table 2 Selected bond lengths (Å) and angles (°) in complexes **1**, **2**·CHCl₃·H₂O and **3**·H₂O

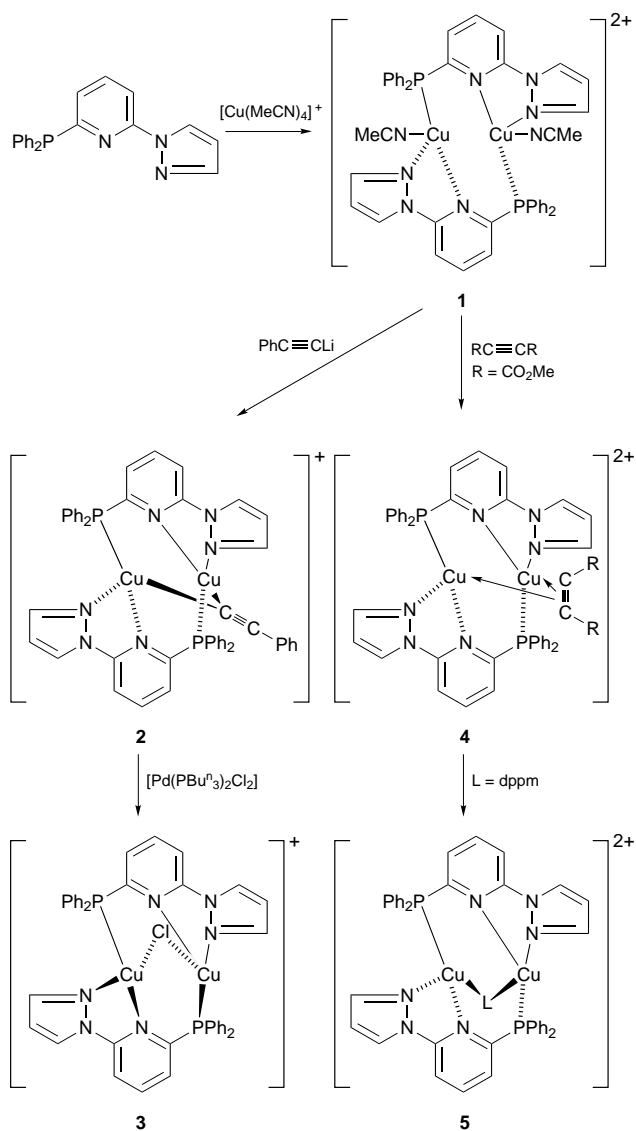
Complex 1			
Cu(1)···Cu(1a)	3.599(1)	Cu(2)···Cu(2b)	3.617(1)
Cu(1)–P(1)	2.208(1)	Cu(2)–P(2)	2.197(1)
Cu(1)–N(1a)	2.123(3)	Cu(2)–N(5b)	2.112(4)
Cu(1)–N(3a)	2.086(3)	Cu(2)–N(7b)	2.084(3)
Cu(1)–N(4)	1.989(4)	Cu(2)–N(8)	1.997(4)
P(1)–Cu(1)–N(1a)	107.1(1)	P(2)–Cu(2)–N(5b)	107.2(1)
P(1)–Cu(1)–N(3a)	127.4(1)	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 ₂ O			
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 ₂ O			
Cu(1)···Cu(2)	2.758(1)	Cu(2)–P(2)	2.182(2)
Cu(1)–P(1)	2.190(2)	Cu(2)–N(1)	2.089(6)
Cu(1)–N(4)	2.042(6)	Cu(2)–N(3)	2.119(5)
Cu(1)–N(6)	2.094(5)	Cu(2)–Cl(1)	2.386(2)
Cu(1)–Cl(1)	2.409(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 (L¹) with 1 equivalent of [Cu(MeCN)₄][ClO₄] resulted in the formation of [Cu₂(μ-L¹)₂(MeCN)₂][ClO₄]₂ **1** (Scheme 1), in which the two L¹ 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 [Cu₂(μ-L²)₃(MeCN)]⁺ [L² = 2-(diphenylphosphino)pyridine] and is in accord with 3.584(1) Å in [Cu₂(μ-L²)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 [Cu₃L³(MeCN)₂][PF₆]⁺ [L³ = 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 LiBuⁿ) reacts in thf to give the alkynylcopper(I) complex **2**. This reaction is different from that of Li(C≡CPh) with [Cu₂(μ-dppm)₂(MeCN)₂]²⁺ which usually yields trinuclear^{20–22} or tetranuclear¹⁷ copper(I) clusters. One possible reason is the different steric hindrance and rigidity of the L¹ 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**·CHCl₃·H₂O with atomic numbering. The structure consists of a binuclear Cu₂C core in which a phenylacetylide ligand bridges the two metal centers. Each copper atom in the molecule is in a distorted tetrahedral 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 μ-η¹ 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

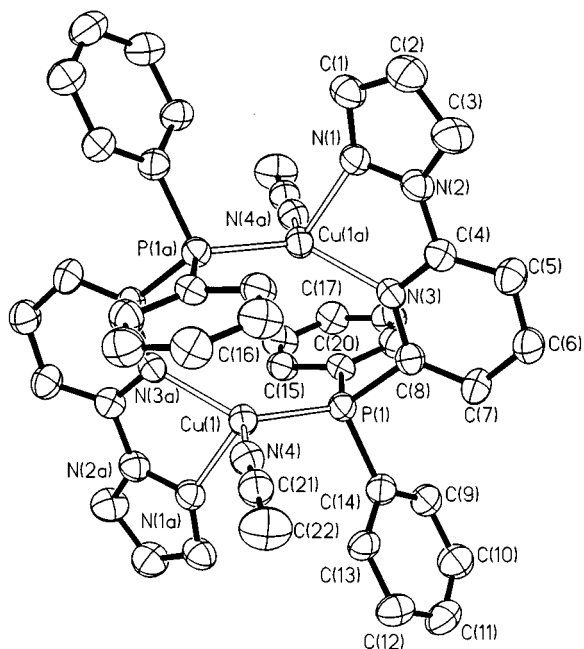


Fig. 1 Perspective view (35% thermal ellipsoids) of one of the two independent, centrosymmetric $[\text{Cu}_2(\mu\text{-L})_2(\text{MeCN})_2]^{2+}$ cations in complex **1**

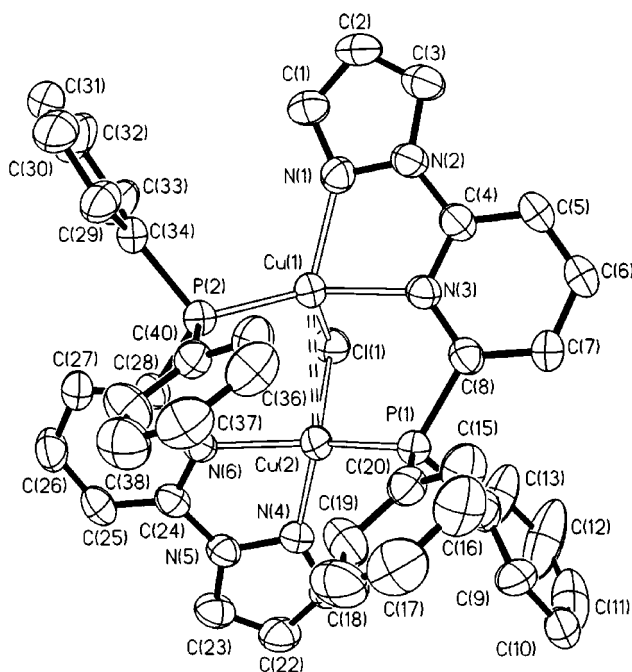


Fig. 3 Perspective view (35% thermal ellipsoids) of $[\text{Cu}_2(\mu\text{-L})_2(\mu\text{-Cl})]^+$ cation in complex **3**· H_2O

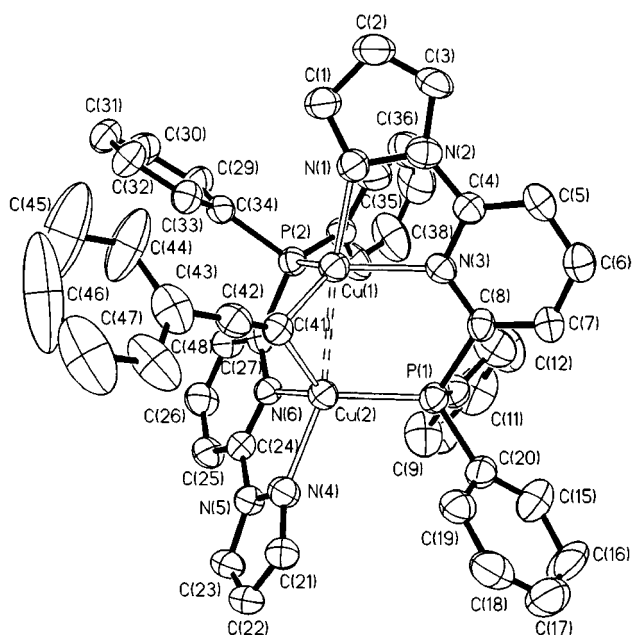


Fig. 2 Perspective view (35% thermal ellipsoids) of the $[\text{Cu}_2(\mu\text{-L})_2(\mu\text{-}\eta^1\text{-C}\equiv\text{CPh})]^+$ cation in complex **2**· CHCl_3 · H_2O

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 $\text{Cu}\cdots\text{Cu}$ 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 $\text{Cu}\cdots\text{Cu}-\text{C}$ bridging angles, $\text{Cu}(1)\cdots\text{Cu}(2)-\text{C}(41)$ 53.0(2)° and $\text{Cu}(2)\cdots\text{Cu}(1)-\text{C}(41)$ 51.8(2)°. Short $\text{Cu}\cdots\text{Cu}$ contacts have also been observed in the complexes $[(\text{C}_6\text{H}_{11})_3\text{P}]\text{Cu}(\mu\text{-C}\equiv\text{CBu}^t)_2\text{Cu}(\text{PPh}_3)_2$ 2.389(1) Å⁷ and $[\text{Cu}_2(\text{PPh}_2\text{Me})_4(\mu\text{-}\eta^1\text{-C}\equiv\text{CPh})]$ 2.454(1) Å.⁸

Reaction of complex **2** with an equimolar quantity of $[\text{Pd}(\text{P}(\text{Bu}^n)_3)_2\text{Cl}_2]$ in dichloromethane solution at room temperature gives the corresponding alkynylpalladium complex $[\text{Pd}(\text{P}(\text{Bu}^n)_3)_2(\text{C}\equiv\text{CPh})\text{Cl}]$ accompanied by formation of $[\text{Cu}_2(\mu\text{-L})_2(\mu\text{-Cl})][\text{ClO}_4]$. The reaction is believed to proceed through

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 $[\{\text{Cu}(\text{PPh}_3)(\text{C}\equiv\text{CSiMe}_3)_n\}_4]$ with $[\text{Pd}(\text{PET}_3)_2\text{Cl}_2]$ ²⁵ and $[\{\text{Cu}(\text{C}\equiv\text{CR})\}_n]$ 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 $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum of $[\text{Pd}(\text{PBu}^n)_2(\text{C}\equiv\text{CPh})\text{Cl}]$ shows the signals of alkynyl carbons at δ 106.39 and 96.79 as triplets due to $^{31}\text{P}\text{-}^{13}\text{C}$ 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 $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR spectra also indicate the formation of the monoalkynylpalladium complex. The complex $[\text{Cu}_2(\mu\text{-L})_2(\mu\text{-Cl})][\text{ClO}_4]$ **3**, separated from the reaction mixture as an Et_2O -insoluble solid, has been characterized by elemental analysis, ^1H and $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR spectroscopy and X-ray crystallography.

Fig. 3 shows a perspective drawing of the cation in crystalline complex **3**· H_2O with atomic numbering. The molecular structure is very similar to that of **2**· CHCl_3 · H_2O except that the phenylacetylide bridge is here replaced by a chloro bridge. The bond length of 2.758(1) Å for $\text{Cu}(1)\cdots\text{Cu}(2)$ is much shorter than that of complex **1**, but longer than that of **2**. The difference in $\text{Cu}\cdots\text{Cu}$ distances in **3** and **2** can be explained by the greater intermolecular steric hindrance of the neighboring ligands $\text{Cl}^-/\text{phosphine}$ in contrast to $\text{PhC}\equiv\text{C}/\text{phosphine}$ in the binuclear complexes. This value is significantly longer than that [2.386(4) Å] in the mixed-valence $\text{Cu}^{\text{I}}\text{-Cu}^{\text{II}}$ complex $[\text{Cu}_2\text{Cl}_3\text{L}^4]$ ($\text{L}^4 = 4\text{-methyl-1,8-naphthyridine}$).²⁶ The $\text{Cu}-\text{Cl}$ distances of 2.386(2) and 2.409(2) Å are consistent with those of 2.379(1) Å in $[\{(\text{P}(\text{H}_3)\text{P})\text{Cu}_2(\mu\text{-Cl})_2(\mu\text{-pyz})\}_n]$ ^{27a} ($\text{pyz} = \text{pyrazine}$) and 2.360(1), 2.369(1) Å in $[\text{Cu}_2(\mu\text{-Cl})_2\text{L}^5]$ [$\text{L}^5 = \text{phenylenebis}(\text{diisopropylphosphine})$].^{27b}

Reaction of complex **1** with dimethyl acetylenedicarboxylate resulted in ready formation of $[\text{Cu}_2(\mu\text{-L})_2(\mu\text{-MeO}_2\text{CC}\equiv\text{CCO}_2\text{-Me})][\text{ClO}_4]_2$ **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 ¹³C-¹H} NMR (CDCl₃) spectrum, the resonances of OCH₃ (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 decomposes slowly on exposure to air to give **1** and MeO₂CC≡CCO₂Me. Reaction of **4** with dppm at room temperature readily gives the substituted product [Cu₂(μ-L¹)₂(μ-dppm)](ClO₄)₂ **5**, indicating that the Cu–P σ interaction is much stronger than copper–alkyne π interaction. The ¹H NMR spectrum of **5** displays a methylene resonance as a triplet centered at δ 3.15, which is indicative of ³¹P–¹H coupling (4.2 Hz). The ³¹P-¹H} NMR spectrum shows two singlets at δ 21.10 and 8.27, which are assigned to the phosphorus resonances of the co-existing L¹ and dppm ligands.

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