Synthesis, Formation Constants and Structures of Ternary Copper(I) Complexes with 1,10-Phenanthroline and Alkynes[†]

Megumu Munakata,* Susumu Kitagawa, Ichiro Kawada, Masahiko Maekawa and Hisao Shimono Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka 577, Japan

Ternary copper(I) complexes with alkynes and 1,10-phenanthroline (phen) have been prepared and characterized by their formation constants, IR spectra, ¹H and ¹³C NMR spectra. The structures of three complexes, [Cu(phen)(HC=CR)]ClO₄ (R = H 1, Ph 2 or CO₂Et 3) have been determined using single-crystal X-ray methods. Each copper atom in all three complexes is co-ordinated to two nitrogen atoms of phen and an alkyne molecule in a trigonal-planar arrangement. The alkyne is sideways bonded onto the copper atom. The C=C bond distances of 1.190(7) (1), 1.218(13) (2) and 1.193(10) Å (3) are slightly longer than those of the free alkynes and indicate that π back donation from copper to the alkyne is weak. The reduction of the C=C stretching frequency for metal–alkyne complexes is correlated to the acetylenic bend-back angles and the lengthening of the C=C distance of the alkyne upon co-ordination. The copper–carbon and –nitrogen distances for 1 and 2 are essentially the same as those for the corresponding olefin complexes.

There has been considerable recent interest in the chemistry of small molecules linked to transition metals. Metal complexes with olefins play an important role in reactions that are catalysed by organotransition-metal compounds, such as hydrogenation, polymerization, cyclization, hydroformylation, isomerization and oxidation.¹ An understanding of this effect has been greatly assisted by structural studies. A large number of structural data are available on olefin complexes,² whereas there is a scarcity of similar data on complexes in which a discrete alkyne molecule is co-ordinated to a single transition metal. Other alkyne-transition-metal structures involve the alkyne molecule in a bridging position between two or more metal atoms.³

The interaction between a metal atom and an alkyne molecule results in a π -bonded complex in which the alkyne ligand adopts a *cis*-bent geometry.⁴ The magnitude of the deviation from linearity can be determined from the bend-back angle. Such phenomena for the alkyne ligand have been successfully explained by a modification of the Dewar–Chatt–Duncanson synergic bonding scheme.⁵ The ability of a d¹⁰ metal to π back bond decreases in the order Ni⁰ \approx Pt⁰ \gg Cu¹ > Ag^{1,6,7} Within the last few years the chemistry of π complexes of copper(1) having weak π -bond character has attracted attention in comparison with that of nickel(0) and platinum(0) which show strong π -bond character.

In this paper we report the synthesis, formation constants and structures of copper(I) complexes with alkynes such as acetylene, phenylacetylene and propiolic acid ethyl ester.

Experimental

General.—All operations were carried out under argon, ethylene or acetylene by using standard Schlenk or vacuum-line techniques. Tetrakis(acetonitrile)copper(I) perchlorate was prepared according to literature procedures.⁸ Acetone treated with potassium permanganate was dried over potassium carbonate from 4 Å molecular sieves. Acetonitrile was purified according to a literature procedure.⁹ The NMR spectra were obtained in $[{}^{2}H_{6}]$ acetone with a JEOL GX-270 spectrometer. All reported peak positions are relative to tetramethylsilane. Electronic spectra were recorded on a Hitachi spectrometer. Reagent grade 1,10-phenanthroline (phen) and its derivatives 5-nitro-, 5-chloro-, 5-methyl- and 5,6-dimethyl-1,10-phenanthroline were obtained from Wako Pure Chemical, Inc. All other chemicals were of reagent grade and were used without further purification.

Syntheses.—[Cu(phen)(HC=CH)]ClO₄ 1. Copper(11) perchlorate hexahydrate (0.25 mmol, 92.5 mg) and copper plates $(3 \times 3 \times 1 \text{ mm}, \text{five pieces})$ were stirred in acetone (5 cm^3) for 2 h under an acetylene atmosphere and an acetone solution (5 cm^3) of 1,10-phenanthroline (0.5 mmol, 90 mg) added. The mixture was stirred for 0.5 h and then filtered under acetylene pressure. The filtrate was sealed in a glass tube under acetylene, and upon standing for 3 d at 0 °C, white single crystals were obtained.

[Cu(phen)(HC=CPh)]ClO₄ 2. Tetrakis(acetonitrile) copper(1) perchlorate (0.25 mmol, 81.8 mg), phen (0.25 mmol, 45.1 mg) and phenylacetylene [0.25 mmol, 25.5 mg (27.4 μ l)] were stirred in acetone (5 cm³) for 1 h under an argon atmosphere and then filtered through sintered glass. The filtrate was sealed in a glass tube under argon, and upon standing for 3 d at 0 °C, pale yellow single crystals were obtained.

[Cu(phen)(HC=CCO₂Et)]ClO₄ 3. Copper(II) perchlorate hexahydrate (0.25 mmol, 92.5 mg) and copper plates ($3 \times 3 \times 1$ mm, five pieces) were stirred in acetone (5 cm^3) for 2 h under an ethylene atmosphere and an acetone solution (5 cm^3) of propiolic acid ethyl ester (0.5 mmol, 49 mg) and phen (0.5 mmol, 90 mg) was added. The mixture was stirred for 1 h under an argon atmosphere and then filtered. The filtrate was sealed under argon, and upon standing for 3 d at 0 °C, pale yellow single crystals were obtained.

Other $[Cu(L-L)(alkyne)]^+$ complexes. Other ternary alkyne complexes, $[Cu(L-L)(alkyne)]^+$ (L-L = phen, 5-nitro-, 5chloro-, 5-methyl- or 5,6-dimethyl-phenanthroline; alkyne =ethoxyacetylene, non-1-yne, dimethyl acetylenedicarboxylateor diphenylacetylene) were synthesised in the same manner as $for 3. The carbon monoxide complex <math>[Cu(phen)(CO)]^+$ was synthesised under carbon monoxide in the same manner as for 1.

[†] Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1992, Issue 1, pp. xx-xxv.

Table 1 Crystal data for $[Cu(phen)(HC=CR)]ClO_4$ (R = H 1, Ph 2 or CO₂Et 3)

Complex	1	2	3
Formula	C14H10ClCuN2O4	C ₂₀ H ₄ ClCuN ₂ O ₄	CH. ClCuN.O.
М	369.24	445.32	441.29
Colour	Colourless	Pale yellow	Pale vellow
Crystal size (mm)	$0.3 \times 0.4 \times 0.3$	$0.3 \times 0.3 \times 0.4$	$0.3 \times 0.3 \times 0.3$
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	Pbca	ΡĪ	$P2_1/a$
Cell constants:			-
a/Å	14.046(4)	10.052(4)	15.656(9)
b/Å	15.553(2)	11.218(4)	10.736(3)
$c/\text{\AA}$	12.747(2)	8.979(2)	12.318(6)
$\alpha/^{\circ}$	90	90.77(3)	90
β/°	90	108.48(3)	121.74
$\gamma/^{\circ}$	90	108.28(3)	90
$U/Å^3$	2784.7	904.6	1760.8
Ζ	8	2	4
$D_{\rm c}/{\rm g~cm^{-3}}$	1.761	1.635	1.664
Radiation (λ/\dot{A})	Mo-Ka (0.710 69)	Cu-Ka (1.541 78)	Cu-Ka (1.541 78)
2θ /°	2–55	2-120	2-120
No. of unique data used $(F > 3\sigma F_o)$	1669	2253	1995
R	0.043	0.072	0.064
R'	0.048	0.087	0.067
F(000)	1488.0	452.0	892.0
μ/cm^{-1}	17.83	33.301	34.981

 Table 2
 Atomic coordinates and non-hydrogen atoms for complex 1

 with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	у	z
Cu	0.453 48(4)	0.175 39(4)	0.140 48(5)
Cl	0.579 63(9)	0.108 67(9)	0.406 0(1)
C(1)	0.345 9(4)	0.008 6(4)	0.169 0(4)
C(2)	0.341 4(4)	-0.0802(4)	0.172 9(4)
C(3)	0.421 9(5)	-0.1274(3)	0.156 9(4)
C(4)	0.508 9(4)	-0.0853(3)	0.136 0(4)
C(5)	0.597 4(5)	-0.1277(3)	0.114 9(4)
C(6)	0.678 4(4)	-0.0841(4)	0.098 6(4)
C(7)	0.678 7(4)	0.007 0(3)	0.098 8(4)
C(8)	0.761 1(4)	0.057 0(4)	0.084 6(4)
C(9)	0.753 5(4)	0.144 3(4)	0.085 4(5)
C(10)	0.664 8(4)	0.183 6(3)	0.100 3(4)
C(11)	0.593 0(3)	0.051 7(3)	0.115 3(3)
C(12)	0.507 1(3)	0.004 6(3)	0.134 5(4)
C(21)	0.345 8(4)	0.252 2(4)	0.147 6(5)
C(22)	0.413 6(4)	0.296 0(3)	0.131 5(4)
N(1)	0.426 7(3)	0.050 7(3)	0.150 5(3)
N(2)	0.586 9(3)	0.139 0(3)	0.115 1(3)
O(1)	0.592 4(4)	0.024 8(3)	0.370 0(3)
O(2)	0.491 5(3)	0.142 7(3)	0.373 2(3)
O(3)	0.587 0(3)	0.111 0(3)	0.517 2(3)
O(4)	0.653 4(3)	0.159 8(3)	0.361 9(4)

X-ray Data Collection, Structure Solution and Refinement.— Crystals of complexes 1–3 were coated with paraffin to avoid decomposition in the air. Diffraction data were obtained on a Rigaku AFC-6B four-circle diffractometer at ambient temperature. Crystal data and details of measurements for the copper(1) alkyne complexes, [Cu(phen)(HC=CR)]ClO₄ (R = H, Ph or CO₂Et), are summarized in Table 1. Three standard reflections were monitored every 100 measurements and the decay of their intensities was within 5%. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied.

The structures were solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by blockdiagonal least-squares calculations. Reliability factors are defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.¹⁰ Hydrogen atoms were included as a fixed contribution in the last cycle;
 Table 3
 Atomic coordinates for non-hydrogen atoms for complex 2

 with e.s.d.s in parentheses

Atom	x	v	7
Cu	0.2704(1)	1.0120(1)	-
Cu	0.3794(1) 0.3216(2)	1.0130(1)	0.3022(2)
	0.2310(2)	1.4002(2)	0.1464(3)
O(1)	0.1100(8)	1.2810(7)	0.0983(10)
O(2)	0.3188(8)	1.4004(7)	0.3077(9)
0(3)	0.1752(10)	1.4982(8)	0.1377(13)
O(4)	0.3216(9)	1.4196(7)	0.0495(10)
N(1)	0.4837(7)	0.8905(6)	0.2881(9)
N(2)	0.5344(7)	1.1339(6)	0.2300(9)
C(1)	0.4625(9)	0.7743(8)	0.3226(12)
C(2)	0.5462(10)	0.7034(8)	0.2980(13)
C(3)	0.6503(10)	0.7531(9)	0.2276(13)
C(4)	0.6774(9)	0.8760(8)	0.1893(11)
C(5)	0.7856(9)	0.9378(9)	0.1163(12)
C(6)	0.8092(9)	1.0570(9)	0.0883(11)
C(7)	0.7254(8)	1.1310(8)	0.1225(11)
C(8)	0.7464(9)	1.2552(9)	0.1005(12)
C(9)	0.6610(10)	1.3171(8)	0.1354(13)
C(10)	0.5569(9)	1.2517(8)	0.2062(13)
C(11)	0.6183(8)	1.0730(7)	0.1914(10)
C(12)	0.5911(8)	0.9446(8)	0.2226(10)
C(21)	0.2325(10)	1.0776(8)	0.3321(12)
C(22)	0.1887(9)	0.9657(9)	0.3472(12)
C(23)	0.1036(8)	0.8445(8)	0.3762(11)
C(24)	0.0436(9)	0.8398(8)	0.4995(11)
C(25)	-0.0429(10)	0.7269(9)	0.5231(12)
C(26)	-0.0679(9)	0.6160(8)	0.4359(13)
$\tilde{C}(27)$	-0.0092(10)	0.6210(9)	0.3136(13)
C(28)	0.0789(9)	0.7337(9)	0.2863(11)
~(~~)	0.07.07(2)		

their positions were assumed to be in accord with the idealized geometry (C-H 1.00 Å), and their thermal parameters were assumed to be isotropic. The final R and R' values were 0.043 and 0.048 for 1, 0.072 and 0.087 for 2, and 0.064 and 0.067 for 3, respectively. All calculations were performed on a FACOM M-382 computer at the Data Processing Center of Kyoto University by using the program system KPPXRAY.¹¹ The final positional coordinates for non-hydrogen atoms of complexes 1, 2 and 3 are given in Tables 2, 3 and 4 respectively. Selected bond lengths and angles for 1–3 are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

 Table 4
 Atomic coordinates for non-hydrogen atoms for complex 3

 with e.s.d.s in parentheses

Atom	x	у	2
Cu	0.6445(1)	0.7928(1)	0.5084(1)
Cl	0.3680(2)	0.5175(2)	0.1417(2)
C(1)	0.4580(6)	0.8799(9)	0.2675(8)
C(2)	0.3923(7)	0.9756(10)	0.1924(8)
C(3)	0.4112(6)	1.0960(10)	0.2299(8)
C(4)	0.4982(6)	1.1246(8)	0.3495(8)
C(5)	0.5600(5)	1.0255(8)	0.4205(7)
C(6)	0.6489(5)	1.0475(7)	0.5428(7)
C(7)	0.6718(6)	1.1682(8)	0.5917(8)
C(8)	0.7595(7)	1.1823(9)	0.7138(9)
C(9)	0.8158(6)	1.0829(9)	0.7745(9)
C(10)	0.7884(6)	0.9656(9)	0.7201(8)
C(11)	0.5247(7)	1.2467(9)	0.4018(9)
C(12)	0.6069(7)	1.2679(8)	0.5179(9)
C(22)	0.6244(7)	0.6177(8)	0.4691(9)
C(24)	0.6987(6)	0.6286(7)	0.5720(8)
C(25)	0.7859(6)	0.5820(8)	0.6940(9)
C(26)	0.9081(11)	0.6232(14)	0.9061(13)
C(27)	0.9778(8)	0.7170(11)	0.9694(11)
N(1)	0.5407(4)	0.9051(6)	0.3789(6)
N(2)	0.7060(5)	0.9480(6)	0.6047(6)
O(1)	0.3880(7)	0.5348(11)	0.2666(8)
O(2)	0.3256(7)	0.4038(7)	0.1023(10)
O(3)	0.3058(8)	0.6069(8)	0.0638(11)
O(4)	0.4591(7)	0.5224(14)	0.1515(11)
O(21)	0.8264(5)	0.6674(6)	0.7791(6)
O(22)	0.8121(5)	0.4763(6)	0.7040(7)

Table 5 Selected bond distances (Å) and angles (°) for complexes 1–3 with e.s.d.s in parentheses

	1	2	3
Cu-N(1)	1.979(4)	1.997(8)	1.978(6)
Cu-N(2)	1.978(4)	2.000(7)	1.977(6)
CuC(21)	1.930(5)	1.922(12)	
Cu-C(22)	1.961(5)	1.995(10)	1.925(9)
Cu-C(24)			1.934(7)
C(21)-C(22)	1.190(7)	1.218(13)	
C(22)-C(24)			1.193(10)
		05.2(2)	04.5(0)
N(1)-Cu-N(2)	84.9(2)	85.3(3)	84.5(2)
N(1)-Cu-C(21)	117.0(2)	159.5(3)	
N(1)-Cu-C(22)	152.4(2)	123.3(4)	115.9(3)
N(2)-Cu-C(21)	157.6(2)	115.2(4)	
N(2)-Cu-C(22)	122.2(2)	150.8(4)	159.6(3)
C(21)-Cu-C(22)	35.6(2)	36.2(4)	
N(1)CuC(24)			151.8(3)
N(2)-Cu-C(24)			123.6(3)
C(22)-Cu-C(24)			36.0(3)
C(21)-C(22)-C(23)		162.8(12)	
C(22)-C(24)-C(25)		. ,	154.7(8)

Results

Structure of Complex 1.—The molecular structure in Fig. 1 consists of a three-co-ordinate copper cation and a well separated perchlorate anion. Two molecules of 1 face each other along the *c* axis and the mean interplane distance between the phen molecules is 3.42 Å. The copper atom is co-ordinated to two nitrogen atoms of the phen and to an acetylene molecule in a trigonal-planar arrangement. The dihedral angle between the planes defined by Cu, C(21), C(22) and Cu, N(1), N(2) is only 4.1°. The conformation of the side-bound acetylene is therefore in-plane with the acetylene carbons lying nearly coincident with the chelate plane of the Cu(phen) moiety. X-Ray structures of copper(1) complexes with ethylene have also shown that the most stable geometry is the trigonal in-plane conformation.¹² The Cu–N distances are comparable to the average value of 2.003(9) Å found for the ethylene complex [Cu(phen)(C₂H₄)]-



Fig. 1 Molecular structure of [Cu(phen)(CH=CH)]ClO₄



Fig. 2 Molecular structure of [Cu(phen)(CH=CPh)]ClO₄

 ClO_4 .¹³ The Cu–C distances are also comparable to the average value of 2.020(13) Å found for the ethylene complex. The C=C distance is essentially the same as those reported for the di-2-pyridylamine acetylene complex [Cu{NH(C₅H₄N)₂}(C₂H₂)]-BF₄¹⁴ and for free acetylene.¹⁵

Structure of Complex 2.—The overall structure (Fig. 2) consists of a three-co-ordinate copper(1) cation and a well separated perchlorate anion. There is no intermolecular overlap between the aromatic rings although the molecules of 2 face each other along the a axis. The copper atom is co-ordinated to two nitrogen atoms of phen and to the alkyne moiety of phenylacetylene. The overall structure is essentially the same as that for the acetylene analogue 1. The dihedral angle between the planes defined by Cu, C(21), C(22) and Cu, N(1), N(2) is 2.0° . The average Cu-N and Cu-C distances are almost the same as the corresponding distances of 1.985(6) (av.) and 1.999(5) Å (av.) in the styrene complex $[Cu(bipy)(C_2H_3Ph)]ClO_4$ (bipy = 2,2'-bipyridine).¹⁶ The co-ordinated phenylacetylene is no longer linear but displays a cis geometry with the phenyl rings bent at angles of about 17.2(12)° from the C(21)=C(22) bond axis. There appears to be no significant lengthening of the C=C bond upon co-ordination since the C=C distance [1.218(13) Å] can be compared with the average C≡C distance (1.20 Å)

 Table 6
 Formation constants of copper(1) complexes with alkynes, olefins and carbon monoxide in 0.3 mol dm⁻³ MeCN-acetone solution, ¹³C NMR chemical shifts and stretching frequencies of the co-ordinated alkynes

Complex	$\log(K/dm^3 mol^{-1})$	δ(¹³ CH≡)	$v(C \equiv C)^{a}/cm^{-1}$
$[Cu(phen)(HC=CH)]^+$	1.2 + 0.2		1800 (1974) ^b
[Cu(phen)(HC=COEt)] ⁺	1.7 ± 0.1		1852 (2146)
$[Cu(phen)(HC \equiv CC_7 H_{15})]^+$	1.8 ± 0.1		1941 (2126)
[Cu(phen)(PhC=CPh)] ⁺	0.64 ± 0.1		
$[Cu(phen)(HC=CCO_2Et)]^+$	1.6 ± 0.1		1887 (2120)
$[Cu(phen)(MeO_2CC \equiv CCO_2Me)]^+$	2.1 ± 0.1		. ,
[Cu(phen)(CO)] ⁺	1.4 ± 0.2		
[Cu(phen)(HC≡CPh)] ⁺	1.5 ± 0.1	79.7°	1921 (2116)
$[Cu(5NO_2-phen)(HC=CPh)]^+$	0.94 ± 0.1		
[Cu(5Cl-phen)(HC≡CPh)] ⁺	1.2 ± 0.1	79.6	
[Cu(5Me-phen)(HC=CPh)] ⁺	1.5 ± 0.1	79.8	
$[Cu(5,6Me_2-phen)(HC=CPh)]^+$	1.6 ± 0.1	79.9	
$[Cu(phen)(H_2C=CH_2)]^+$	2.2 ± 0.2^{d}		
$[Cu(phen){H_2C=CH(OEt)}]^+$	$-0.67 \pm 0.1^{c.d}$		

^a Error limits: $\pm 2 \text{ cm}^{-1}$. ^b Values for metal-free alkynes are given in parentheses. ^c δ 78.8 for metal-free HC=CPh. ^d Ref. 6.



Fig. 3 Molecular structure of [Cu(phen)(CH=CCO₂Et)]ClO₄

between free acetylene $(1.204 \text{ Å})^{14}$ and free diphenylacetylene [1.19(2) Å].¹⁷ The phenyl ring of the phenylacetylene is not perpendicular to the chelate plane defined by Cu, C(21) and C(22) but twisted by *ca*. 38° from it.

Structure of Complex 3.—Fig. 3 presents the molecular structure of 3 and indicates the numbering scheme. The copper atom is three-co-ordinate. The molecules of 3 stack alternately in a reverse direction along the *a* axis and the interplane distance between the phen molecules is 3.37 Å. The dihedral angle between the planes defined by Cu, C(22), C(24) and Cu, N(1), N(2) is 8.2°. The bond angles about the copper atom, C(22)-Cu-C(24), C(22)-Cu-N(1), N(1)-Cu-N(2) and N(2)-Cu-C(24), sum to 360° within experimental error. The angle C(22)-C(24)-C(25) is not linear but displays a geometry with the CO₂Et group bent back by an angle of 25.3° from the C=C bond axis. The C=C distance is a little shorter than those of 1 and 2.

IR and NMR Spectra.—The infrared spectra of the ternary copper(1) complexes with phen and alkynes have been measured, and they exhibit a band in the region 1800–1941 cm⁻¹ which is assigned to v(C=C) of the co-ordinated alkyne (Table 6). The band was not observed for the ternary complexes with diphenylacetylene or dimethyl acetylenedicarboxylate for reasons which were not entirely clear. Nickel, platinum, niobium, iridium and tungsten complexes with alkynes exhibit a larger co-ordination shift Δv (C=C) of 412–542 cm⁻¹ than do

the copper(1) complexes $[\Delta v = v(C \equiv C)(complex) - v(C \equiv C)-(free)]$.

The ¹H NMR spectrum of **2** showed a resonance at δ 5.14 due to the alkyne proton of the co-ordinated phenylacetylene, whereas the resonance of free phenylacetylene was observed at δ 3.98. To our knowledge there is only one previous report ¹⁴ of a ¹H NMR spectrum for a copper(1) alkyne complex, that for [Cu{NH(C₅H₄N)₂}(HC=CH)]BF₄, where the chemical shift of the acetylene protons is at δ 5.21. The ¹³C NMR spectra of complexes [Cu(L-L)(HC=CPh)]⁺ (L-L = phen or substituted phen derivatives) were measured and exhibited resonances assigned to the tertiary alkyne carbon HC= of the co-ordinated phenylacetylene (Table 6). The co-ordination shifts of ¹³C NMR resonances of the alkyne carbons, $\Delta\delta = 0.8$ –1.1 are very small compared with those (33–42 ppm) of platinum(0) complexes with alkynes ¹⁸ [$\Delta\delta = \delta$ (complex) – δ (free)].

Formation Constants of $[Cu(L-L)(alkyne)]^+$.—Formation constants of the alkyne complexes $[Cu(L-L)(alkyne)]^+$ given by equation (2) for the equilibrium process (1) were measured

 $[Cu(L-L)(solv)]^{+} + alkyne \Longrightarrow [Cu(L-L)(alkyne)]^{+} (1)$

 $K = [Cu(L-L)(alkyne)^+]/[Cu(L-L)(solv)^+][alkyne]$ (2)

spectrophotometrically in 0.3 mol dm⁻³ MeCN-acetone solution (solv = solvent or acetonitrile). Equation (2) can be written in terms of equation (3), where c_x , c_M and

$$K = c_{\mathbf{X}}/(c_{\mathbf{M}} - c_{\mathbf{X}})(c_{\mathbf{A}} - c_{\mathbf{X}})$$
(3)

 c_A are the concentration of $[Cu(L-L)(alkyne)]^+$, and the initial concentrations of $[Cu(L-L)(solv)]^+$ and alkyne, respectively. A reddish brown solution of $[Cu(L-L)(solv)]^+$ turns colourless with increasing alkyne concentration, indicating the formation of $[Cu(L-L)(alkyne)]^+$. The formation constant K for this system is given by equation (4)¹⁹ where $R = (A - A_C)/(A_0 - C)$

$$\log R = \log K + \log L \tag{4}$$

A) and $L = c_A - c_M(A - A_0)/(A_C - A_0)$. Here A is the absorbance at the alkyne concentration c_A , and A_0 and A_C are the absorbance of $[Cu(L-L)(solv)]^+$ and $[Cu(L-L)(alkyne)]^+$, at concentration c_M , respectively. The formation constant was obtained from the intercept at L = 1 for a linear plot of log R vs. log L. The formation constants of eleven alkyne complexes, and the carbon monoxide complex $[Cu(phen)(CO)]^+$, were measured and are summarized in Table 6. The values obtained do not differ greatly from those of the olefin complexes¹⁹ included in the Table.

Table 7 Structural data for metal complexes with alkynes

		Distance/Å				
No.	Compound	C≡C	Δd	Bend-back angle/°	$\Delta v(C=C)/cm^{-1}$	Ref.
1	[{Cu(PhCO₂)(PhC≡CPh)}₂]	1.224(18)	0.034(18)	21.5(7)	195	21
2	$[Cu{NH(C_{H_A}N)_{2}}(HC=CH)]^{+}$	1.188(11)	-0.016(11)	16(3)	179	14
3	$[Cu(phen)(HC=CH)]^+$	1.190(7)	-0.014(7)	15(3)	174	This work
4	[Cu(phen)(HC=CPh)] ⁺	1.218(13)		$17.2(12), 15(3)^{a}$	195	This work
5	[Cu(phen)(HC=CCO_Et)] ⁺	1.193(10)		25.3(8), 15(3) ^a	223	This work
6	[Pt(PPh ₂)(PhC=CPh)]	1.32(9)	0.13(9)	40	468 <i>^b</i>	36
7	[Ni(CNBu ¹)(PhC≡CPh)]	1.28(2)	0.09(2)	31(1)	412°	22
8	$[Pt(PPh_{2})_{2}(F_{2}CC=CCF_{2})]$	1.255(9)	. ,	39.9(5)	525 <i>°</i>	5
9	$[Nb(C_{\epsilon}H_{\epsilon})(CO)(PhC=CPh)_{2}]$	1.35(2)	0.16(2)	42(1)	493	26
10	[Nb(C _e H _e)(CO)(C _e Ph _e)(PhC≡CPh)]	1.26(4)	0.07(4)	39(3)	442	38
11	[W(CO)(PhC=CPh)]	1.30	0.11	40	542	27
12	trans-[PtMe(PPhMe_)](MeC=CMe)] ⁺	1.22(3)		8.16(3)	156	31
13	trans-[Pt(Cl)Me(AsMe_))(F_CC=CCF_)]	1.32(4)		30.45(4)	462	39
14	$[Ir(CO)(PPh_{2})_{2} \{C(CN)CHCCN\}(NCC=CCN)]$	1.29(2)		40(1)	521 ^d	34
15	$[PtMe{HB(N_2C_2H_3)_3}(F_3CC=CCF_3)]$	1.292(12)		34.4(4)	457	5
16	$[WO(C_5H_5)Ph(PhC=CPh)]$	1.29(3)	0.10(3)	35.38(4)	472	28
^a H−C≡	C Angle estimated by comparison with [Cu(phen)(HC	C≡CH)] ⁺ . ^b Rei	f. 35. ° Ref. 37. ^d	Ref. 40.		



Fig. 4 A plot of the lengthening of the C=C distance against the reduction of the C=C stretching frequency for metal complexes with alkynes (for numbers, see Table 7)

Discussion

It was found from the crystallographic study on the ternary copper(1) alkyne complexes that the metal–carbon and –nitrogen distances for acetylene and phenylacetylene are essentially the same as those for the corresponding olefins, ethylene and styrene, respectively.

Structural data on previously determined structures of metalalkyne complexes in which the alkyne is sideways bonded onto one metal atom are summarized in Table 7. $^{20-34}$ The C=C distances observed in this study, 1.190(7)-1.218(13) Å, are at the short end of the values found so far for metal-alkyne complexes.²⁰⁻³⁴ The high standard deviations on the structural data however make significant comparisons difficult. A useful criterion for evaluating the perturbation of the alkyne upon coordination is $\Delta v(C=C)$, the reduction in wavenumber of the symmetric stretching mode of the C=C bond resulting from coordination. A trend is found between Δd [C=C distance $(complex) - C \equiv C$ distance (free alkyne)] and $\Delta v(C \equiv C)$ (Table 7). The bonding in metal-olefin and -alkyne complexes consists of σ donation from the occupied π orbitals of the unsaturated ligand to the metal and π back donation from occupied d_x orbitals of the metal to unoccupied antibonding π^* orbitals of the ligand.⁵ This π back donation results in a lengthening of the acetylenic triple bond upon complexation. The low values of Δd found for the copper(I) complexes with alkynes indicate that π back donation in copper(I)-alkyne bonding is less predominant than σ donation.

The acetylenic bend-back angles, the departure of the alkyne ligand from linearity, provides a more useful criterion for evaluating this perturbation. Davies and Payne⁵ have reported that there is a reasonable straight-line relationship between the mean acetylenic bend-back angles and $\Delta v(C=C)$ for alkyne complexes of Pt⁰, Pt^{II}, Ni^{II}, Ir^I and W^{IV}. Fig. 4 indicates that this relationship also holds for copper(I) alkyne complexes; the stronger the metal-alkyne interaction, the greater is the departure of the co-ordinated alkyne from linearity. Increasing pK_a values of L-L tends to increase the formation constant (K) of ternary copper(I) complexes with phenylacetylene and L-L (Table 6).[†] The formation constants of ternary copper(1) complexes with ethylene $[Cu(L-L)(CH_2=CH_2)]^+$ increase complexes with ethylene [Cu(L-L)(CH₂=CH₂)] linearly with increasing pK_a of L-L because π back donation in copper-ethylene bonding is enhanced with increasing pK_a of L-L.19 The relationship between the formation constants of the phenylacetylene complexes and pK_a indicates that π back donation in copper-alkyne bonding is not negligible although it is weak. It is concluded that copper(I) complexes with alkynes resemble corresponding olefin complexes in molecular structure, metal-ligand distance and bonding.

The ¹³C NMR resonance of the tertiary acetylenic carbon of ternary copper(1) complexes $[Cu(L-L)(HC\equiv CPh)]^+$ is shifted downfield upon co-ordination this shift increasing with increasing pK_a of L-L (Table 6). The complexes $[Cu(L-L)(HC\equiv CPh)]^+$ dissociate partially in solution since the formation constants are not large. The observed resonances are averaged between those of the complex and free phenylacetylene owing to a rapid exchange reaction between both [equation (5)]. The small co-ordination shifts, $\Delta\delta$, are perhaps therefore

$$[Cu(L-L)(HC\equiv CPh)]^{+} + *HC\equiv CPh \rightleftharpoons$$
$$[Cu(L-L)(*HC\equiv CPh)]^{+} + HC\equiv CPh \quad (5)$$

attributable to the small fraction of the complex present in solution as well as to the weak π -back bonding character of copper(1).

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[†] An increase in activity of unsaturated compounds such as ethylene, ethyl vinyl ether, acetylene and carbon monoxide on the growth of peas can be correlated to the formation constants of their corresponding ternary copper(i) complexes $[Cu(L-L)X]^{+.41}$

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