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Copper(I) complexes with conjugated dienes

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Abstract

Three copper(I) complexes containing conjugated dienes and one containing the acetylenic analogue of isoprene, 2-methyl-1-butene-3-yne (isopropenylacetylene), have been prepared and characterised by means of crystal-structure determination. Direct reaction between isoprene (2-methylbutadiene) and copper(I) trifluoromethylsulfonate, using triphenylphosphine as a stabilising ligand, results in $[Cu_2(PPh_3)_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}(O_3SCF_3)_2]$ (**1**), whereas reaction between copper(I) chloride and isopropenylacetylene, dimethylbutadiene, and *trans*-1,3-pentadiene yields the labile compounds $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}CHC(CH_3){\equiv}CH)\}]$ (**2**), $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}C(CH_3)C(CH_3){=}CH_2)\}]$ (**3**) and $[Cu_2Cl_2\{\mu\text{-}(\textit{trans}\text{-}H_2C{=}CHCH{=}CH(CH_3))\}]$ (**4**), respectively. All four compounds are polymeric. Thus, the organic ligands bridge two copper(I) centres via the alkene or alkyne bonds, the conjugated dienes all assuming the *s-trans* conformation. Further bridging is effected by the trifluoromethylsulfonate ligands in **1** and by the chloride ligands in **2**, **3** and **4**. In **1**, copper(I) has distorted tetrahedral geometry, whereas in **2**, **3** and **4**, copper(I) exhibits tetrahedral or trigonal pyramidal geometry with the C=C/C≡C linkage in the trigonal plane and an apical Cu–Cl bond. The nearly planar carbon skeleton of isoprene in **1** bonds to two copper(I) atoms from opposite faces of the diene. The Cu–C distances range from 2.085(6) to 2.220(6) Å [$C(CH_3)$] and the C=C bond lengths are 1.360(8) and 1.353(8) Å. Trifluoromethylsulfonate ligands bridge adjacent $[Cu_2(PPh_3)_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}(O_3SCF_3)_2]$ units leading to the formation of chains, containing internal chair-shaped $Cu_2S_2O_4$ rings alternating with isoprene ligands, with peripheral triphenylphosphine ligands. The carbon skeleton of the isopropenylacetylene ligand in **2** and those of dimethylbutadiene in **3** and of *trans*-1,3-pentadiene in **4** are also approximately planar, but, unlike the situation in **1**, in compounds **2**–**4**, two copper(I) atoms are coordinated by C=C/C≡C from the same face of the ligand. In **2**, Cu–C distances range from 2.005(11) to 2.158(9) Å [$C(CH_3)$] and the C=C and C≡C bond lengths are 1.373(13) and 1.200(14) Å, respectively. In **3**, Cu–C distances range from 2.06(1) to 2.17(1) Å [$C(CH_3)$] and both C=C bonds are 1.35(1) Å. Dimeric $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}CHC(CH_3){\equiv}CH)\}]_2$ and $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}C(CH_3)C(CH_3){=}CH_2)\}]$ units are linked by long Cu–Cl bonds leading to the formation of chains with peripheral isopropenylacetylene (**2**) and dimethylbutadiene (**3**) ligands. The crystal structure of **4** could be determined only with low precision, but can be described in terms of copper(I) chloride layers with peripheral *trans*-1,3-pentadiene ligands. Shifts in the infrared absorptions on coordination of the conjugated dienes (including butadiene and *cis*-1,3-pentadiene) to copper(I) are discussed in the light of the crystal structures of **2**–**4**.

Keywords: Isoprene; Isopropenylacetylene; Butadiene; Dimethylbutadiene; 1,3-Pentadiene; Alkene; Alkyne; Copper(I); Infrared spectroscopy; Crystal structure

1. Introduction

Several structures of π-olefinic complexes of copper(I) have now been characterised and analysed [1,2]. Despite this, there is still relatively little information available on the mode of bonding of conjugated dienes to copper(I), and this is restricted to isoprene (2-methylbutadiene), namely the coordination of this ligand in $[Cu_2Cl_2(\mu\text{-}C_5H_8)]$ [3] and in $[Cu_2\{(C_6H_5CH_2N(C_5H_4N)_2\}_2((\mu\text{-}C_5H_8)(O_3SCF_3)_2]$ [4]. It was here shown that the conjugated diene does not complex the metal in the more usual η^4, *tetrahapto*, mode [5,6] but acts essentially as an η^2 donor, bridging two copper(I) centres [2,3]. In these two compounds, the ligand thus retains the *s-trans* conformation, demonstrated to be the more stable for the free isoprene ligand and its non-methylated analogue butadiene [7].

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The present investigation was undertaken in order to provide more information on the bonding of conjugated dienes to copper(I), and encompasses butadiene, isoprene, dimethylbutadiene and *cis*- and *trans*-piperylene. In addition, we were interested in preparing an acetylenic analogue of the isoprene complex described earlier, [$Cu_2Cl_2(\mu\text{-}C_5H_8)$] [3], in order to facilitate comparison of π-ethylenic and π-acetylenic coordination within the same ligand. To our knowledge, the only previous such example is divinylacetylene complexed to copper(I) chloride [2,8]. In this compound the organic ligand bridges three copper(I) centres [2,8].

2. Experimental

2.1. General

All operations were carried out under argon using standard Schlenk or special low-temperature techniques [9]. Copper(I) triflate (trifluoromethylsulfonate) was prepared using the method of Salomon and Kochi [10]. Triphenylphosphine was recrystallised from ethanol, and copper(I) chloride was purified according to the method of Keller and Wycoff [11]. Solvents and ligands were dried with 3 or 4 Å molecular sieves, deoxygenated by means of freeze–pump–thaw cycles and distilled immediately prior to use.

2.2. Preparation of [$Cu_2(PPh_3)_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}(O_3SCF_3)_2$] (**1**)

A solution of triphenylphosphine (0.11 g, 0.44 mmol) in 1 ml of isoprene was added slowly under stirring to a suspension of copper(I) triflate [$Cu(O_3SCF_3)]_2\cdot C_6H_6$ [10] in 2 ml of isoprene. The dark-brown suspension rapidly changed colour, forming a beige precipitate and a pale-yellow solution. A further 5 ml of isoprene was added and stirring was continued for a few hours. After centrifugation, the clear, pale-yellow solution was separated from the precipitate and cooled to 5°C, pale-yellow plates of **1** being deposited, in low yield, overnight. Crystals of **1** are relatively stable, decomposing only after 1–2 h exposure to the atmosphere.

2.3. Preparation of [$Cu_2Cl_2\{\mu\text{-}(H_2C{=}CHC(CH_3){\equiv}CH)\}$] (**2**)

Copper(I) chloride (0.1 g, 1.0 mmol) was dissolved in 1 ml of isopropenylacetylene at room temperature yielding a yellow solution. Almost immediately, a bright yellow, flocculant precipitate (presumably the copper(I) acetylide [12]) separated. The clear solution was removed from the precipitate and stored at −18°C, pale-yellow rods of **2** being deposited, in low yield, after a few days. Crystals of **2** are unstable in air decomposing with loss of the organic ligand within a few seconds of exposure to the atmosphere. Attempts to suppress acetylide formation by the addition of a small amount of hydrochloric acid [13] were not successful and yielded a dark suspension of decomposition products.

2.4. Preparation of [$Cu_2Cl_2\{\mu\text{-}(H_2C{=}C(CH_3)C(CH_3){=}CH_2)\}$] (**3**)

The compound was prepared according to the general method described previously [9]. Thus, ca. 2.0 mmol (0.2 g) copper(I) chloride was added to 10 ml of ethyl vinyl ketone at ambient temperature, yielding a clear solution upon stirring. Dimethylbutadiene (10 ml) was added slowly to the solution at ambient temperature. The solution was stored at −25°C, yellow crystals of **3** being deposited, in quantitative yield, overnight. The mother liquor was withdrawn at low temperature and fresh dimethylbutadiene added. Crystals of **3** decompose instantaneously, with loss of dimethylbutadiene, on exposure to the atmosphere.

2.5. Preparation of [$Cu_2Cl_2\{\mu\text{-}(trans\text{-}H_2C{=}CHCH{=}CH(CH_3))\}$] (**4**)

The compound was prepared according to the general method described previously [9]. Thus, ca. 2.0 mmol (0.2 g) copper(I) chloride was added to 10 ml of ethyl vinyl ketone at ambient temperature, yielding a clear solution upon stirring. *trans*-1,3-Pentadiene (4.0 ml) was added very slowly to the solution at ambient temperature, yellow crystals of **4** being deposited overnight, in quantitative yield. The mother liquor was withdrawn at low temperature and fresh *trans*-1,3-pentadiene was added. *trans*-1,3-Pentadiene is lost from **4** instantaneously on exposure of the compound to the atmosphere.

2.6. Preparation of a complex between *cis*-1,3-pentadiene and copper(I) chloride (**5**)

Yellow crystals of **5** were obtained by an identical procedure to that described above for **4**, using *cis*-1,3-pentadiene instead of *trans*-1,3-pentadiene. The compound was obtained in quantitative yield. Crystals of **5** were, however, not of sufficiently good diffracting quality to permit even an approximate structure determination of the compound; they decompose instantaneously with loss of diene ligand on exposure to the atmosphere.

2.7. Preparation of a complex between butadiene and copper(I) chloride (**6**)

Ca. 2.0 mmol (0.2 g) copper(I) chloride was added to 10 ml of ethyl vinyl ketone at ambient temperature, yielding a clear solution upon stirring. Introduction of gaseous butadiene caused immediate precipitation of microcrystalline **6**, in quantitative yield. The mother liquor was withdrawn at low temperature with a syringe and 10 ml of cyclohexane, saturated with butadiene was added. The compound decomposes immediately, with loss of butadiene, on exposure to the atmosphere.

Table 1
Crystallographic data for [$Cu_2(PPh_3)_2${μ-(H_2C=CHC(CH_3)=CH_2)}(O_3SCF_3)$_2$] (**1**) and [Cu_2Cl_2{μ-(H_2C=CHC(CH_3))CH)}] (**2**) [a]

Compound	**1**	**2**
Formula	$C_{43}H_{38}Cu_2F_6O_6P_2S_2$	$C_5H_6Cu_2Cl_2$
M_r	1017.9	264.1
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	13.109(5)	7.162(1)
b (Å)	17.629(4)	8.772(2)
c (Å)	10.658(5)	6.369(1)
α (°)	96.58(3)	108.13(2)
β (°)	107.62(4)	90.83(2)
γ (°)	70.70(2)	102.80(1)
V (Å^3)	2215(1)	369.5(1)
Z	2	2
D_{calc} (g cm^{-3})	1.526	2.373
μ(Mo–K$_\alpha$) (cm^{-1})	11.93	64.08
Temperature (°C)	22	−120
No. observed reflections	3709	1003
No. parameters refined	550	106
R	0.038	0.048
R_w	0.043	0.060

[a] $R = \Sigma||F_o| - |F_c|/\Sigma|F_o|$; $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

Table 2
Crystallographic data for [Cu_2Cl_2{μ-(H_2C=C(CH_3)C(CH_3)=CH_2)}] (**3**) and [Cu_2Cl_2{μ-(*trans*-H_2C=CHCH=CH(CH_3))}] (**4**) [a]

Compound	**3**	**4**
Formula	$C_6H_{10}Cu_2Cl_2$	$C_5H_8Cu_2Cl_2$
M_r	280.1	266.1
Crystal system	Orthorhombic	Monoclinic
Space group	$Pbcn$	$P2_1/a$
Unit cell dimensions		
a (Å)	16.048(4)	6.543(6)
b (Å)	8.709(2)	12.981(3)
c (Å)	12.154(3)	8.994(3)
β (°)	90	95.07(3)
V (Å^3)	1699(1)	760.9(8)
Z	8	4
D_{calc} (g cm^{-3})	2.19	2.32
μ(Mo-K$_\alpha$) (cm^{-1})	55.8	62.2
Temperature (°C)	−140	−144
No. observed reflections	904	825
No. parameters refined	121	82
R	0.036	0.11
R_w	0.040	0.14

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

2.8. Infrared spectrometry

Measurements were performed on crystalline samples of **1** and **2**, mixed with Fluorolube®, and also on the pure ligands placed between KBr discs, using a Mattson Polaris FTIR spectrometer. Solid samples of **3–6** were prepared at low temperature as described in Ref. [9] and CaF_2 mull windows were employed. Spectra were recorded with a resolution of 2 cm^{-1}, varying the number of scans from 10 to 100. For **1** the C=C stretching frequencies were masked by stretches associated with the phenyl groups, thus precluding observation of shifts caused by coordination of isoprene to copper(I). For **2**: ν(C≡C) 1962 cm^{-1}, ν(C=C) 1525 cm^{-1} (tentative assignment). Corresponding frequencies for isopropenylacetylene: 2103 and 1615 cm^{-1}. For **3**: ν(C=C–C=C) 1551, 1514 cm^{-1}; for dimethylbutadiene: ν(C=C–C=C) 1601 cm^{-1}; For **4**: ν(C=C–C=C) 1579, 1517 cm^{-1}; corresponding frequencies for *trans*-1,3-pentadiene: 1650, 1603 cm^{-1}. For **5**: ν(C=C–C=C) 1567, 1502 cm^{-1}; corresponding frequencies for *cis*-1,3-pentadiene: 1646, 1595 cm^{-1}. For **6**: ν(C=C–C=C) 1564, 1506 cm^{-1}. For butadiene ν(C=C–C=C) 1595 cm^{-1}.

2.9. NMR spectrometry

Rapid loss of ligand from **2** to **5** on attempted dissolution, prevented measurement of spectra for these compounds. ^{1}H-NMR spectra (400 MHz) for **1** and for uncoordinated isoprene were recorded on a Varian XL 400 spectrometer, using TMS as internal standard (s, singlet; d, doublet; dd, doublet of doublets). For **1** δ (ppm): methylic 1.84 (s, 3H); non-methylated olefinic bond, internal vinylic 6.39 (dd, 1H), terminal vinylic 5.06 (d, 1H), 4.97 (d, 1H); methylated olefinic bond, terminal vinylic 4.99 (s, 1H), 4.96 (s, 1H). For free isoprene: methylic 1.84 (s, 3H); non-methylated olefinic bond, internal vinylic 6.45 (dd, 1H), terminal vinylic 5.18 (d, 1H), 5.07 (d, 1H); methylated olefinic bond, terminal vinylic 5.00 (s, 1H), 4.98 (s, 1H).

2.10. X-ray crystallography

Crystal and experimental data are summarised in Tables 1 and 2. Crystals of **1**–**4** were mounted in glass capillaries, **2–4** were mounted under argon, at −155°C [9] and transferred at the same temperature to a Rigaku AFC6R diffractometer. Diffracted intensities were measured with a Rigaku AFC6R diffractometer, using graphite-monochromated Mo–K$_\alpha$ (λ = 0.710 73 Å) radiation from a RU200 rotating anode operated at 9 kW (50 kV; 180 mA). The ω–2θ scan mode was employed, and stationary background counts were recorded on each side of the reflection, the ratio of peak counting time to background counting time being 2:1. Weak reflections ($I < 10.0\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. The intensities of three reflections were monitored regularly after measurement of 150 reflections and indicated crystal stability in all cases. Cell constants were obtained by least-squares refinement from the setting angles of 25 reflections.

For **1**, data were measured at 22°C for $5 < 2\theta < 50.1°$ from a pale-yellow plate-shaped crystal with dimensions ca. $0.35 \times 0.30 \times 0.20$ mm, using the ω–2θ scan mode with an ω scan rate of 16° min^{-1} and a scan width of $(1.15 + 0.30 \tan \theta)°$. Correction was made for Lorentz and polarisation effects; an empirical correction based on azimuthal scans for several reflections was made for the effects of absorption (minimum/maximum transmission factors = 0.88/1.00). Of the 7784 unique reflections measured ($+h$, $\pm k$, $\pm l$), 3709 had $I > 3.0\sigma(I)$ and were considered observed. The structure was solved by direct methods (MITHRIL [14]) and refined using full-matrix least-squares calculations on F for 3709 observed $[I > 3.0\sigma(I)]$ reflections and 550 parameters, with anisotropic thermal displacement parameters for all the non-hydrogen atoms and with the hydrogen atoms included as a fixed contribution in calculated positions. Final R: 0.038 ($R_w = 0.043$); maximum and minimum residual electron density: 0.63, -0.38 e Å^{-3}.

For **2**, data were measured at -120°C for $5 < 2\theta < 50.1°$ from a pale-yellow plate-shaped crystal with dimensions ca. $0.30 \times 0.30 \times 0.10$ mm, using the ω–2θ scan mode with an ω scan rate of 32° min^{-1} and a scan width of $(1.42 + 0.30 \tan \theta)°$. Correction was made for Lorentz and polarisation effects; an empirical correction for the effects of absorption was made as for **1** (minimum/maximum transmission factors = 0.76/1.00). Of the 1306 unique reflections measured, ($+h$, $\pm k$, $\pm l$), 1003 had $[I > 3.0\sigma(I)]$ and were considered observed. The structure was solved by direct methods (MITHRIL [14]) and refined by means of full-matrix least-squares calculations on F for 1003 observed $[I > 3.0\sigma(I)]$ reflections and 106 parameters, including anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. Final R: 0.048 ($R_w = 0.060$); maximum and minimum values in the final difference map were 1.38 and -1.63 e Å^{-3}, respectively.

For **3**, data were measured at -140°C for $5 < 2\theta < 50°$ from a pale-yellow rod with dimensions ca. $0.20 \times 0.10 \times 0.05$ mm, using the ω–2θ scan mode with an ω scan rate of 16° min^{-1} and a scan width of $(1.42 + 0.30 \tan \theta)°$. Correction was made for Lorentz and polarisation effects but not for absorption. Of the 1746 unique reflections measured, ($+h$, $+k$, $+l$), 904 had $[I > 3.0\sigma(I)]$ and were considered observed. The structure was solved by direct methods (MITHRIL [14]). Full-matrix least-squares refinement on F including anisotropic thermal displacement parameters for the non-hydrogen atoms and positional parameters for the hydrogen atoms gave $R = 0.036$ ($R_w = 0.040$) for 121 parameters and 904 reflections. The maximum and minimum values in the final difference map were 0.63 and -0.59 e Å^{-3}, respectively.

For **4**, data were measured at -144°C for $5 < 2\theta < 50°$ from a pale-yellow cube with dimensions ca. $0.15 \times 0.15 \times 0.15$ mm, using the ω–2θ scan mode with an ω scan rate of 16° min^{-1} and a scan width of $(1.52 + 0.30 \tan \theta)°$. Correction was made for Lorentz and polarisation effects; an empirical correction for the effects of absorption was made as for **1** (minimum/maximum transmission factors = 0.72/1.00). Of the 1408 unique reflections measured, ($+h$, $+k$, $\pm l$), 825 had $[I > 3.0\sigma(I)]$ and were considered observed. Full-matrix least-squares refinement on F, including anisotropic thermal displacement parameters for the non-hydrogen atoms, gave $R = 0.11$ ($R_w = 0.14$) for 82 parameters. The hydrogen atoms could not be located.

All calculations on **1**–**4** were carried out with the TEXSAN program package [15]. Atomic scattering factors and anomalous dispersion correction factors were taken from Ref. [16]. Structural illustrations have been drawn with ORTEP [17]. Selected interatomic distances and angles are given in Tables 3–5. Owing to the poor precision of the structure determination of **4**, despite numerous attempts to collect better quality data, the partial structure has been deposited (see below) and the structural results will not be discussed in detail here.

3. Results and discussion

The general preparative method described previously [9], and also used to prepare the labile complexes $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}]$ [3], [Cu(CO)Cl] [18] and $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}CH{-}CH_2{-}CH{=}CH_2)\}]$ [19], has been exploited to obtain novel complexes between copper(I) chloride and the conjugated dienes butadiene, dimethylbutadiene and *cis*- and *trans*-piperylene. Of these compounds, $Cu_2Cl_2\{\mu\text{-}(H_2C{=}C(CH_3)C(CH_3){=}CH_2)\}]$ (**3**) and $[Cu_2Cl_2\{\mu\text{-}(trans\text{-}H_2C{=}CHCH{=}CH(CH_3))\}]$ (**4**) have been subjected to crystal-structure determination, whereas the complexes between copper(I) chloride and butadiene and *cis*-piperylene, **6** and **5**, respectively, have been investigated solely by means of infrared (IR) spectroscopy. By means of direct reaction between copper(I) trifluoromethanesulfonate and copper(I) chloride with isoprene and isopropenylacetylene, respectively, two further complexes, **1** and **2** have been prepared and their crystal structures deter-

Table 3
Selected bond distances (Å) and angles (°) for $[Cu_2(PPh_3)_2(\mu\text{-}C_5H_8)(O_3SCF_3)_2]$ (**1**) [a]

Cu(1)–C(1)	2.114(6)	Cu(2)–C(3)	2.220(6)
Cu(1)–C(2)	2.179(6)	Cu(2)–C(4)	2.085(6)
Cu(1)–X(1)	2.036	Cu(2)–X(2)	2.045
C(1)–C(2)	1.360(8)	C(3)–C(4)	1.353(8)
C(2)–C(3)	1.440(8)	C(3)–C(5)	1.543(9)
Cu(1)–P(1)	2.262(2)	Cu(2)–P(2)	2.278(2)
Cu(1)–O(1)	2.079(4)	Cu(2)–O(2)	2.091(4)
Cu(1)–O(3^{i})	2.370(5)	Cu(2)–O(6^{ii})	2.297(4)
O(1)–S(1)	1.444(4)	O(2)–S(2)	1.450(4)
S(1)–O(3)	1.424(4)	S(2)–O(5)	1.424(4)
S(1)–O(4)	1.421(4)	S(2)–O(6)	1.440(4)
S(1)–C(6)	1.828(8)	S(2)–C(7)	1.810(6)
C(6)–F(1)	1.337(8)	C(7)–F(4)	1.326(7)
C(6)–F(2)	1.308(8)	C(7)–F(5)	1.310(7)
C(6)–F(3)	1.288(8)	C(7)–F(6)	1.324(7)
O(1)–Cu(1)–C(1)	95.5(2)	O(2)–Cu(2)–C(4)	99.1(2)
O(1)–Cu(1)–C(2)	129.6(2)	O(2)–Cu(2)–C(3)	133.8(2)
P(1)–Cu(1)–C(1)	156.2(2)	P(2)–Cu(2)–C(4)	156.2(2)
P(1)–Cu(1)–C(2)	119.5(2)	P(2)–Cu(2)–C(3)	121.2(2)
O(3^{i})–Cu(1)–C(1)	95.6(2)	O(6^{ii})–Cu(2)–C(4)	95.1(2)
O(3^{i})–Cu(1)–C(2)	102.2(2)	O(6^{ii})–Cu(2)–C(3)	102.9(2)
P(1)–Cu(1)–O(1)	105.2(1)	P(2)–Cu(2)–O(2)	99.0(1)
P(1)–Cu(1)–O(3^{i})	93.7(1)	P(2)–Cu(2)–O(6^{ii})	100.3(1)
O(1)–Cu(1)–O(3^{i})	96.7(2)	O(2)–Cu(2)–O(6^{ii})	89.9(1)
C(1)–C(2)–C(3)	127.2(7)	C(2)–C(3)–C(4)	121.0(6)
C(2)–C(3)–C(5)	116.8(5)	C(4)–C(3)–C(5)	121.4(6)
Cu(1)–O(1)–S(1)	139.4(3)	Cu(2)–O(2)–S(2)	137.2(3)
S(1)–O(3)–Cu(1^{i})	129.5(3)	S(2)–O(6)–Cu(2^{ii})	132.8(2)
O(1)–S(1)–O(3)	112.4(3)	O(2)–S(2)–O(5)	115.9(3)
O(1)–S(1)–O(4)	116.8(3)	O(2)–S(2)–O(6)	113.8(2)
O(3)–S(1)–O(4)	116.2(3)	O(5)–S(2)–O(6)	115.3(3)
O(1)–S(1)–C(6)	101.2(3)	O(2)–S(2)–C(7)	101.3(3)
O(3)–S(1)–C(6)	103.2(3)	O(5)–S(2)–C(7)	105.1(3)
O(4)–S(1)–C(6)	104.4(4)	O(6)–S(2)–C(7)	102.9(3)

[a] Symmetry code: (i) $-x$, $1-y$, $-z$; (ii) $1-x$, $-y$, $-z$.

mined. Although two isoprene complexes of copper(I), namely $[Cu_2Cl_2(\mu\text{-}C_5H_8)]$ [3] and $[Cu_2\{(C_6H_5CH_2N(C_5H_4N)_2\}_2((\mu\text{-}C_5H_8)(O_3SCF_3)_2]$ [4] have been fully characterised previously, to the best of our knowledge, complex **2** represents the first compound in which copper(I) is coordinated by an isopropenylacetylene ligand.

All the conjugated dienes adopt the *s-trans* conformation on coordination to copper(I), as has been observed previously for isoprene [3,4]. This property of copper(I) is unusual since the most prevalent bonding mode of conjugated dienes to transition metals is the *tetrahapto*, with the ligand in the *s-cis* conformation [5,6], notable exceptions being the butadiene derivatives: $[\{Ni(C_4H_6)(C_{10}H_8N_2)\}_2(C_4H_6)]$ [20], $[\{Mn(C_5H_5)(CO)\}_2(C_4H_6)]$ [21], $[N(CH_3)_3(C_2H_5)]_2[Pt_2Cl_6(C_4H_6)]$ [22] and $[Os_3(CO)_{10}(C_4H_6)]$ [23]. In $Cp_2Zr(C_4H_6)$, the butadiene ligand is, however, coordinated to zirconium in the *tetrahapto* mode, despite *transoid* ligand conformation [24].

In **1**, the isoprene ligand bridges two copper(I) centres via η^2 coordination involving both C=C bonds. Coordination occurs from opposite faces of the diene (Fig. 1). This resembles the structure found for bridging isoprene in $[Cu_2\{(C_6H_5CH_2)N(C_5H_4N)_2\}_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}(O_3SCF_3)_2]$ [4], in which, as in **1**, there are bulky ligands on copper(I), hindering η^2 coordination from the same face of the diene. Further bridging is effected by the trifluoromethanesulfonate ligand, leading to the formation of chains in which isoprene and trifluoromethanesulfonate alternate as linkages, the latter ligand participating in chair-shaped $Cu_2S_2O_4$ rings (Fig. 2). In contrast to the chloride-containing compounds, the diene in **1** is embedded in the chain, the carbon skeleton of the ligand (C(1)–C(4)) being planar to within 0.03 Å. The copper(I) centres are approximately tetrahedrally coordinated by phosphorus of a triphenylphosphine, C=C and two triflate oxygen donors from different anions (see Fig. 2 and Table 3). The Cu–C bond lengths range from 2.085(6) to 2.220(6) Å [C(CH$_3$)] and are very similar to those in $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}]$ [3], whereas corresponding distances in the more stable compound, $[Cu_2\{(C_6H_5CH_2)N(C_5H_4N)_2\}_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}(O_3SCF_3)_2]$, are ca. 0.1 Å shorter [4], which may indicate a stronger interaction between isoprene and copper(I) in the latter compound. As in the two other isoprene-containing copper(I) complexes [3,4], the metal is closer to the terminal carbons of both double bonds, the asymmetry in coordination being more pronounced for the olefinic ligand carrying the methyl group. In solution, **1** shows a net magnetic shielding, as indicated by upfield ^{1}H-NMR shifts, of all the vinylic protons in comparison with the free ligand. The somewhat larger

Table 4
Bond distances (Å) and angles (°) for the non-hydrogen atoms in $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}CHC(CH_3){\equiv}CH)\}]$ (**2**) [a]

Cu(1)–C(1)	2.048(10)	Cu(2)–C(3)	2.056(9)
Cu(1)–C(2)	2.158(9)	Cu(2)–C(4)	2.005(10)
Cu(1)–X(1)	1.989	Cu(2)–X(2)	1.940
C(1)–C(2)	1.373(13)	C(3)–C(4)	1.200(14)
C(2)–C(3)	1.473(13)	C(2)–C(5)	1.480(13)
Cu(1)–Cl(1)	2.274(3)	Cu(2)–Cl(1^{ii})	2.255(2)
Cu(1)–Cl(2)	2.322(2)	Cu(2)–Cl(2)	2.293(3)
Cu(1)–Cl(2^{i})	2.766(3)	Cu(2)–Cl(2^{ii})	3.239(3)
Cl(1)–Cu(1)–C(1)	105.6(3)	Cl(2)–Cu(2)–C(4)	137.9(3)
Cl(1)–Cu(1)–C(2)	143.3(3)	Cl(2)–Cu(2)–C(3)	105.1(3)
Cl(2)–Cu(1)–C(1)	138.5(3)	Cl(1^{ii})–Cu(2)–C(4)	113.1(3)
Cl(2)–Cu(1)–C(2)	104.6(3)	Cl(1^{ii})–Cu(2)–C(3)	146.5(2)
Cl(2^{i})–Cu(1)–C(1)	108.2(3)	Cl(2^{ii})–Cu(2)–C(4)	105.8(4)
Cl(2^{i})–Cu(1)–C(2)	98.9(3)	Cl(2^{ii})–Cu(2)–C(3)	97.8(3)
Cl(1)–Cu(1)–Cl(2)	107.0(1)	Cl(1^{ii})–Cu(2)–Cl(2)	108.3(1)
Cl(1)–Cu(1)–Cl(2^{i})	98.4(1)	Cl(1^{ii})–Cu(2)–Cl(2^{ii})	82.4(1)
Cl(2)–Cu(1)–Cl(2^{i})	91.9(1)	Cl(2)–Cu(2)–Cl(2^{ii})	86.0(1)
C(1)–C(2)–C(3)	119.6(9)	C(2)–C(3)–C(4)	168.0(10)
C(1)–C(2)–C(5)	124.7(9)	C(3)–C(2)–C(5)	114.5(8)

[a] Symmetry code: (i) $-x$, $-y$, $1-z$; (ii) $-x$, $-y$, $2-z$.

Table 5
Bond distances (Å) and angles (°) for the non-hydrogen atoms in $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}C(CH_3)C(CH_3){=}CH_2)\}]$ (**3**) [a]

Cu(1)–C(1)	2.07(1)	Cu(2)–C(3)	2.17(1)
Cu(1)–C(2)	2.12(1)	Cu(2)–C(4)	2.06(1)
Cu(1)–X(1)	1.98	Cu(2)–X(2)	2.00
C(1)–C(2)	1.35(1)	C(3)–C(4)	1.35(1)
C(2)–C(3)	1.48(1)	C(3)–C(6)	1.51(1)
C(2)–C(5)	1.52(1)		
Cu(1)–Cl(1)	2.319(2)	Cu(2)–Cl(1)	2.448(2)
Cu(1)–Cl(2)	2.307(3)	Cu(2)–Cl(1^{ii})	2.455(2)
Cu(1)–Cl(2^{i})	2.750(2)	Cu(2)–Cl(2^{ii})	2.319(2)
Cl(1)–Cu(1)–C(1)	138.2(3)	Cl(1)–Cu(2)–C(4)	120.7(3)
Cl(1)–Cu(1)–C(2)	100.5(2)	Cl(1)–Cu(2)–C(3)	105.0(3)
Cl(2)–Cu(1)–C(1)	118.2(3)	Cl(1^{ii})–Cu(2)–C(4)	132.2(3)
Cl(2)–Cu(1)–C(2)	147.9(2)	Cl(1^{ii})–Cu(2)–C(3)	104.8(2)
Cl(2^{i})–Cu(1)–C(1)	95.6(3)	Cl(2^{ii})–Cu(2)–C(4)	109.1(3)
Cl(2^{i})–Cu(1)–C(2)	107.8(2)	Cl(2^{ii})–Cu(2)–C(3)	145.4(2)
Cl(1)–Cu(1)–Cl(2)	100.28(8)	Cl(1)–Cu(2)–Cl(2^{ii})	101.77(8)
Cl(1)–Cu(1)–Cl(2^{i})	98.18(8)	Cl(1^{ii})–Cu(2)–Cl(2^{ii})	96.07(8)
Cl(2)–Cu(1)–Cl(2^{i})	93.13(8)	Cl(1)–Cu(2)–Cl(1^{ii})	91.38(8)
C(1)–C(2)–C(3)	121.1(8)	C(2)–C(3)–C(4)	121.2(8)
C(1)–C(2)–C(5)	119.7(9)	C(2)–C(3)–C(6)	117.2(8)
C(3)–C(2)–C(5)	117.7(8)	C(4)–C(3)–C(6)	120.0(9)
Cu(1)–Cl(1)–Cu(2)	82.83(7)	Cu(1)–Cl(2)–Cu(2^{ii})	80.02(8)
Cu(1)–Cl(1)–Cu(2^{ii})	77.03(7)	Cu(1)–Cl(2)–Cu(1^{i})	85.56(8)
Cu(2)–Cl(1)–Cu(2^{ii})	88.62(8)	Cu(1^{i})–Cl(2)–Cu(2^{ii})	106.86(8)

[a] Symmetry code: (i) $1-x$, y, $1.5-z$; (ii) $1-x$, $1-y$, $1-z$.

shifts for the terminal vinylic protons associated with the non-methylated olefinic bond suggest the presence of a somewhat larger back-bonding component for this bond, as compared with the methylated linkage, which would be consistent with electron release from the methyl group tending to reduce the back-bonding component to the latter. The bending back of C(3) from the C(1)–C(2) bond (C(1)–C(2)–C(3) = 127.2(7)°) is also more pronounced than that of C(5) and C(2) from C(3)–C(4) (121.4(6) and 121.0(6)°), respectively).

The C=C bond lengths do not differ significantly from one another and are similar to those determined previously for isoprene coordinated to copper(I) [3,4]. The lengthening on coordination is slight and corresponding reduction in the IR absorption frequencies impossible to ascertain, owing to the interference from aromatic ring stretches in this crucial region.

Triflate is normally assumed to be a non-coordinating or a very weakly coordinating anion. In $[Cu_2\{(C_6H_5CH_2)N(C_5H_4N)_2\}_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}(O_3SCF_3)_2]$ [4], it is weakly coordinating and, as a result, both copper(I) centres attain trigonal pyramidal coordination with an apical triflate oxygen donor. Triflate bridges containing two short Cu–O bonds, viz. 2.101(4) and 2.135(4) Å, are, however, present in the compound with a chelating 1,5-hexadiene ligand, in which copper(I) is approximately tetrahedrally coordinated [25]. In **1**, the bridging Cu–O bonds indicate one strong (2.079(4) and 2.091(4) Å, respectively) and one weaker (2.370(5) and 2.297(4) Å, respectively) for each copper(I) centre. This leads to distorted tetrahedral coordination geometry for the metal, which geometry

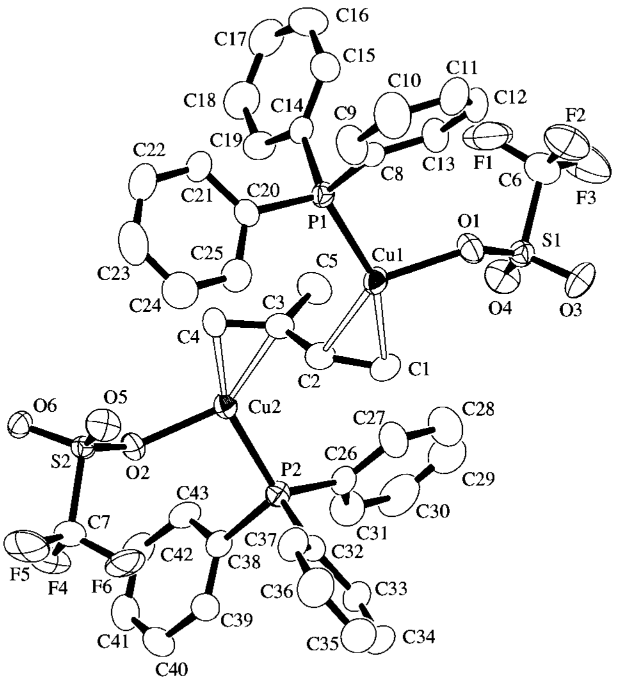

Fig. 1. View of $[Cu_2(PPh_3)_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}(O_3SCF_3)_2]$ (**1**), showing the crystallographic numbering. Thermal ellipsoids enclose 50% probability. In addition, Cu(1) is coordinated by O(3) of a neighbouring triflate group and Cu(2) likewise by O(6) of a neighbouring triflate ligand (see Table 3).

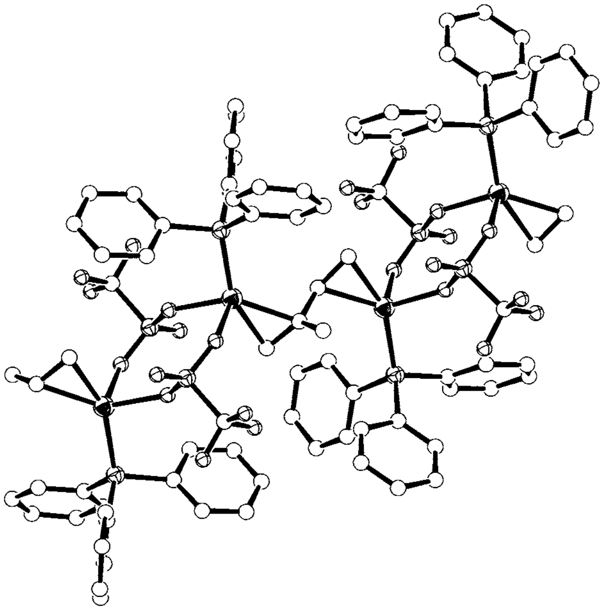

Fig. 2. Part of a chain in $[Cu_2(PPh_3)_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}(O_3SCF_3)_2]$ (**1**), showing the alternate bridging of copper(I) by isoprene and triflate (participating in eight-membered $Cu_2S_2O_4$ rings).

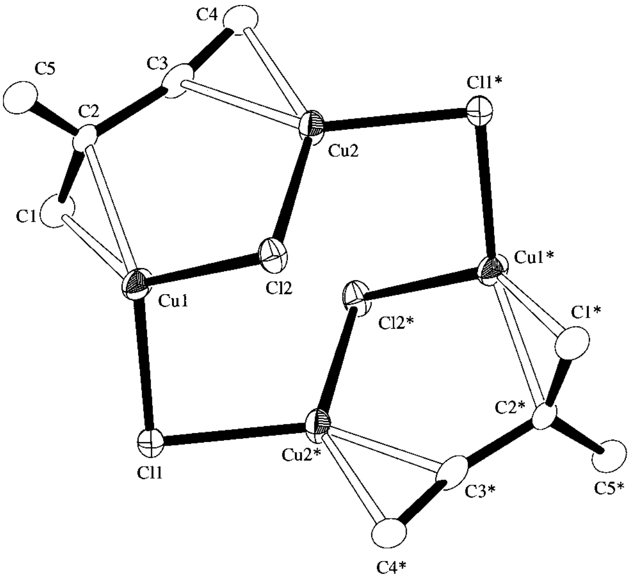

Fig. 3. The basic dimeric $[\{Cu_2Cl_2\{\mu\text{-}(H_2C{=}CHC(CH_3){\equiv}CH)\}\}_2]$ unit in **2**, showing the crystallographic numbering. Starred atoms are related to the non-starred counterparts by $-x$, $-y$, $2-z$ (see Table 4). Thermal ellipsoids enclose 50% probability.

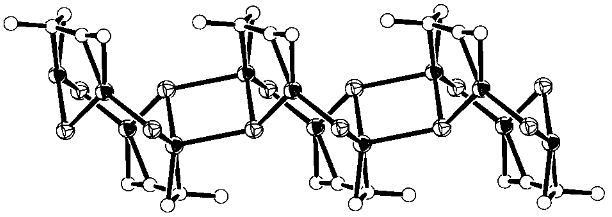

Fig. 4. Part of a chain of $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}CHC(CH_3){\equiv}CH)\}]$ (**2**), showing the connection of the dimers depicted in Fig. 3, which contain chair-shaped Cu_4Cl_4 rings, by longer Cu···Cl contacts of 2.766(3) Å (see Table 4). Note that the isopropenylacetylene ligands are situated on the periphery of the copper–chloride framework.

more closely approaches that of a trigonal pyramid for Cu(2) than is the case for Cu(1).

The copper(I) chloride complexes, **2**–**4** are similar in that the basic copper(I) units bridged by the conjugated diene in the *s-trans* conformation (**3**, **4**) or by isopropenylacetylene (**2**) are further linked by long Cu···Cl interactions to form chains (**2**, **3**) or layers (**4**) in which the organic ligands are positioned on the periphery. These basic units, which are dimeric in **2** and **3**, and their linking to form chains are illustrated in Figs. 3 and 4 and Figs. 5 and 6, respectively. The basic dimeric units in **2** and **3** are seen to be very similar if the long Cu(2)–Cl(2^{ii}) and Cl(2)–Cu(2^{ii}) contacts of 3.239(3) Å are visualised as bonds. The linking of these dimeric units to form chains differs, however. Thus in **2**, the chains are composed of alternate four-membered and chair-shaped Cu_4Cl_4 eight-membered rings, whereas the copper–chloride linking in **3** results in a pleated ribbon-like chain. Part of a chain of **5** is shown in Fig. 7, these chains being further linked by long Cu···Cl interactions (ca. 3 Å) to form layers. Contrary to the situation in **1** and in $[Cu_2\{(C_6H_5CH_2)N(C_5H_4N)_2\}_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}(O_3SCF_3)_2]$ [4], the conjugated dienes in **3** and **4**, bond to two copper(I) centres from the same face of the ligand, as in $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}CHC(CH_3){=}CH_2)\}]$ [3].

A trigonal pyramid in which the trigonal plane comprises the C=C linkage and two chloride ligands with an additional chloride forming the apex is the prevalent coordination geometry for copper(I) in **2**–**4**, but some copper(I) centres exhibit tetrahedral coordination geometry. Thus, in **2** both Cu(1) and Cu(2) are trigonal pyramidally coordinated by two chloride ligands and a

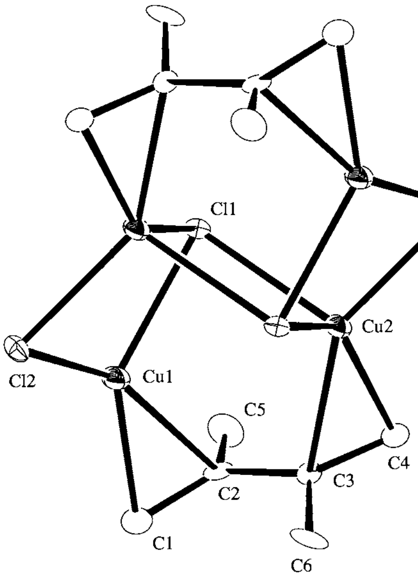

Fig. 5. The basic dimeric unit of $[\{Cu_2Cl_2\{\mu\text{-}(H_2C{=}C(CH_3)C(CH_3){=}CH_2)\}\}_2]$ (**3**), showing the crystallographic numbering. Thermal ellipsoids enclose 50% probability. For clarity only the asymmetric unit has been labelled, the remaining atoms are related by a centre of symmetry ($1-x$, $1-y$, $1-z$).

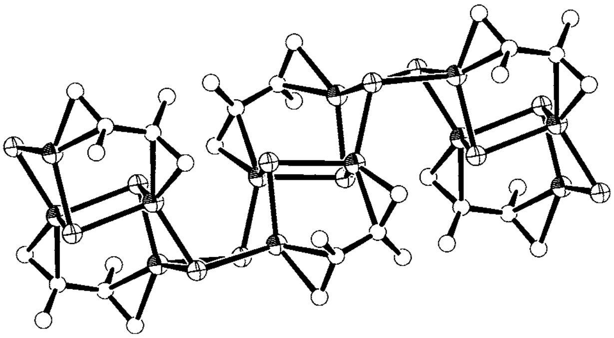

Fig. 6. Part of a chain in $[Cu_2Cl_2\{\mu\text{-}(H_2C{=}C(CH_3)C(CH_3){=}CH_2)\}]$ (**3**), illustrating the pleated ribbon-like copper–chloride chain with peripheral dimethylbutadiene ligands.

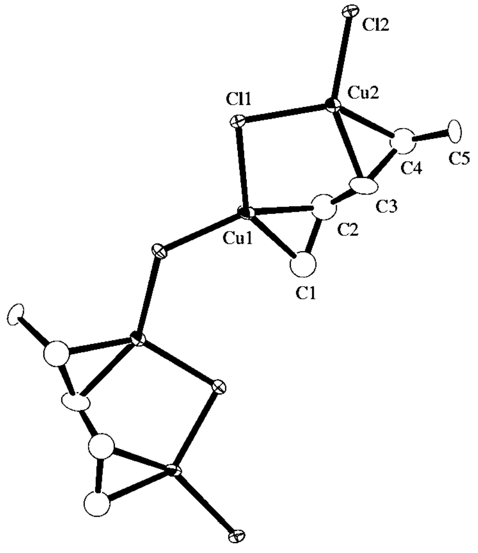

Fig. 7. Part of chain in $[Cu_2Cl_2\{\mu\text{-}(\textit{trans}\text{-}H_2C{=}CHCH{=}CH(CH_3))\}]$ (**4**) showing the overall structural features and the crystallographic numbering. Such chains are further connected by long Cu···Cl contacts to form layers with peripheral *trans*-1,3-pentadiene ligands.

C=C or C≡C linkage comprising the basal plane with long apical Cu···Cl contacts of 2.766(3) and 3.239(3) Å, respectively, copper(I) being displaced 0.32 and 0.02 Å towards the apices. The carbon skeleton (C(1)–C(4)) of the ligand is planar to within 0.04 Å. There is little olefin sliding [26], and the midpoint of the C=C bond is symmetrically placed with respect to the chloride ligands in the trigonal plane (Cl–Cu–X(1) = 121 and 125°). The C≡C linkage is, however, less symmetrically coordinated, with corresponding angles of 121 and 130°. The deviation of the C(2)–C(3)–C(4) angle (168(1)°) from linearity is similar to values determined previously for π-acetylenic complexes of copper(I) chloride [13,27]. Slight bending back of the methyl group from the C=C bond is evident from the C(1)–C(2)–C(5) and C(3)–C(2)–C(5) angles (Table 4).

In **3**, Cu(2) has distorted tetrahedral coordination, whereas Cu(1) is trigonal pyramidally coordinated, the metal being displaced 0.31 Å from the trigonal plane towards the apical chloride situated at 2.750(2) Å from Cu(1). The discrepancy between the X(1)–Cu(1)–Cl(1) and X(1)–Cu(1)–Cl(2) angles (119 and 134°, respectively), indicate olefin sliding [26] in the trigonal plane. There would not appear to be any appreciable bending back of the methyl groups from C=C linkages (Table 5). The diene backbone of the ligand (C(1)–C(4)) is planar to within 0.05 Å. In **4**, both copper(I) centres exhibit trigonal pyramidal coordination geometry, Cu(1) with two chloride ligands at 2.283(7) Å and a third at 2.905(9) Å towards which the metal is displaced by 0.16 Å and Cu(2) with two chloride ligands at 2.287(7) and 2.308(7) Å and a third at 2.793(8) Å towards which the metal is displaced by 0.27 Å. The Cu(1)–C(1) and Cu(1)–C(2) distances are 2.06(3) and 2.07(3) Å, respectively, while Cu(2)–C(3) and Cu(2)–C(4) = 2.11(4) and 2.12(2) Å. The C=C bonds are unrealistically long at 1.46(4) and 1.50(4) Å, which artefact is attributable to the low precision and accuracy of the structure determination, since such lengthening is not mirrored by extraordinary shifts in IR absorption frequencies (see below).

IR absorption frequencies for compounds **2**–**6** are compared with those of the free ligands in Table 6. As has been noted previously, the conjugated dienes assume the *s-trans* conformation and coordinate to copper(I) in the η^2 mode. The dienes are essentially unchanged in geometry on coordination with marginal lengthening of the C=C bonds, which is in accordance with previous studies (see Refs. [1–4,19,25,27] and Refs. therein). Weak interaction between the dienes and copper(I) is evident from the magnitudes of the observed shifts (70–100 cm^{-1}), each diene acting essentially as if it were composed of two localised η^2 donors. In the complex with the analogous non-conjugated 1, 4-pentadiene $[Cu_2Cl_2(\{\mu\text{-}(H_2C{=}CH{-}CH_2{-}CH{=}CH_2)\}]$ [19], where the ligand is a true localised η^2 donor, bridging two copper(I) centres via the two C=C functionalities, marginally greater shifts are observed (Table 6), which are reflected in a reduced lability of $[Cu_2Cl_2(\{\mu\text{-}(H_2C{=}CH{-}CH_2{-}CH{=}CH_2)\}]$ [19] in comparison with **2**–**6**. The similarity in the C=C–C=C shifts for **5** and **6** to those of the other compounds suggest that these are likely to possess similar structures with the ligand in the *s-trans* conformation: **5** is therefore tentatively formulated as '$[Cu_2Cl_2(C_5H_8)]$' where C_5H_8 = *cis*-1,3-pentadiene and **6** as '$[Cu_2Cl_2(C_4H_6)]$' where C_4H_6 = 1,3-butadiene. The vibrations at 1564 and 1506 cm^{-1} for **6** correspond well, moreover, to those of the compound prepared from copper(I) chloride and liquid butadiene (1570 and 1507 cm^{-1}) [30] and that prepared by reducing cupric chloride with organic phosphites in the presence of butadiene (1565 and 1500 cm^{-1}) [31], suggesting that these butadiene complexes of copper(I) chloride are identical, independent of the preparative method. It is interesting that in the complex between 1,5 hexadiene and copper(I) trifluoromethanesulfonate the hexadiene ligand is chelating, rather than bridging [25]; yielding a compound in which the Cu:diene stoichiometry is 1:1, in contrast to the 2:1 stoichiometry exhibited by the compounds **1**–**4**. The copper(I) trifluoromethanesulfonate–1,5 hexadiene complex is relatively stable [25], which indicates that once a diene can be induced to bond to a single copper(I) centre as a chelating ligand, enhanced stability results.

It has, thus, now been further established that the preferential bonding mode of a conjugated diene to copper(I) is as an η^2 bridge between metal centres, the diene assuming the *s-trans* conformation. Similar bonding is also observed for the acetylenic analogue of isoprene: isopropenylacetylene. While it is unlikely that back-bonding effects in such compounds are negligible [2,19,32], particularly since the trigonal pyramidal coordination geometry relies on this component for its stabilisation [19], the ready loss of organic ligand, if positioned on the peripheries of chains or layers, thus occupying unprotected or vulnerable structural sites, is suggestive of a weak overall π-interaction between the ligand and copper(I).

It is also possible to compare the effect on lability of bridging chloride *contra* bridging trifluoromethanesulfonate in copper(I) complexes containing conjugated dienes: when isoprene is embedded in the chain, as in **1**, or protected by bulky ligands, as in $[Cu_2\{(C_6H_5CH_2N(C_5H_4N)_2\}_2((\mu\text{-}C_5H_8)(O_3SCF_3)_2]$ [4], relatively stable compounds are obtained. When the diene (or isopropenylacetylene) is situated on the periphery of a copper(I)–chloride chain or layer, the organic ligand is lost instantaneously on exposure to the atmosphere. A rationale for this has been proposed to account for the resistance of $[(Cu(O^tBu)(CO))_4]$ to decarbonylation [33]: namely, the unfavourable pyramidal coordination geometry for copper(I) which would result from the initial decarbonylation product [33]. Similar reasoning can be used to account for instantaneous loss of carbon monoxide from [Cu(CO)Cl] (s) [18], which contains carbonyl groups peripherally bonded to copper(I) centres participating in a copper(I) chloride layer. Here tetrahedral coordination of copper(I) by chloride following loss of carbon monoxide is favoured by the proximity of chloride ligands, the decomposition product being copper(I) chloride. Similarly, in **2**–**4**, the organic ligands are unprotected on the periphery of a copper(I) chloride framework, and initial loss of an organic ligand can therefore result in rapid formation of copper(I) chloride.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 138841 for compound **1**, CCDC no. 138842 for compound **2**, CCDC no. 138843 for compound **3** and CCDC no. 138844 for compound **4**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Rd., Cambridge CB2 1EX, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 6
Comparison of the shifts in IR absorption frequencies observed on coordination of some conjugated and non-conjugated dienes and 2-methyl-1-butene-3-yne to copper(I) [a]

Compound	Free ligand		Complex			
	ν_s	ν_{as}	ν_s	ν_{as}	$\Delta\nu_s$	$\Delta\nu_{as}$
'$[Cu_2Cl_2(C_4H_6)]$' (Butadiene, **6**)	1643 [a,b]	1595	1564	1506	89	89
$[Cu_2Cl_2(C_5H_8)]$ (Isoprene [1])	1640	1598	1569	1520	71	78
$[Cu_2Cl_2(C_5H_8)]$ (*trans*-1,3-pentadiene, **4**)	1650	1603	1579	1517	71	86
'$[Cu_2Cl_2(C_5H_8)]$' (*cis*-1,3-pentadiene, **5**)	1646	1595	1567	1502	79	93
$[Cu_2Cl_2(C_6H_{10})]$ (dimethylbutadiene, **3**)	1654 [a,c]	1601	1551	1514	103	87
	$\nu_{C=C}$		$\nu_{C=C}$		$\Delta\nu_{C=C}$	
$[Cu_2Cl_2(C_5H_8)]$ (1,4-pentadiene [22])	1639		1542	1532	97	107
	$\nu_{C=C}$	$\nu_{C\equiv C}$	$\nu_{C=C}$	$\nu_{C\equiv C}$	$\Delta\nu_{C=C}$	$\Delta\nu_{C\equiv C}$
$[Cu_2Cl_2(C_5H_6)]$ (2-methyl-1-butene-3-yne, **2**)	1615	2103	1525	1962	90	141

[a] R, Raman.

[b] See Ref. [28].

[c] See Ref. [29].

Acknowledgements

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