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**ICA Review**

# Structural Chemistry of Organocopper(I) Compounds

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## Contents

## 1. Introduction

Several organo-copper compounds have been prepared in the last 20 years, but the main interest was centered on their synthesis *in situ* for preparative purposes [1–8a], most of these compounds being thermally unstable and highly reactive. Recently, however, the factors affecting their stability have begun to be understood, so that some fairly stable derivatives are available at present. The aim of this review is to underline the relation between structural and chemical features of those compounds which have been studied by X-ray crystallography in the solid state and by usual spectroscopic and physical techniques in solution. For sake of clarity we shall distinguish the copper organometallic compounds in Cu–C $\sigma$-bonded and Cu–C $\pi$-bonded derivatives.

## 2. $\sigma$-Bonded Compounds

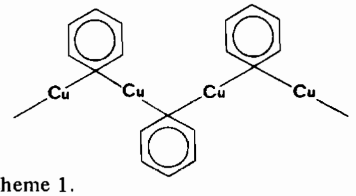
The known $\sigma$-organo-copper(I) compounds are of type CuR or their co-ordination derivatives. The stability of CuR compounds depends upon the nature of R and increases in the order alkyl $<$ alkenyl $\ll$ aryl $\ll$ alkynyl. Perhalogeno alkyl- and aryl-copper derivatives are appreciably thermally more stable and less oxidizable and hydrolyzable than the parent compounds, owing to the stabilizing effect of the halogen (especially fluorine) on the C–Cu $\sigma$-bond. Relatively stable is also the cyanomethylcopper, at high degree of association [8b]. The cyano group has probably a double stabilizing effect, owing to its electron-withdrawing properties and co-ordination ability towards copper. The stability of alkyl copper compounds is considerably enhanced also by replacement of simple alkyl groups by the trimethylsilylmethyl group [9] or by the isoelectronic phosphonium ligand $(CH_3)_3\overset{+}{P}CH_2$ [10]. In these cases the stabilization was attributed to the preclusion of the $\beta$H-elimination route in the decomposition. Attempts to stabilize the copper alkyl bond by coordination with ligands such as 2,2′-bipyridine, which favour low oxidation states in transition metals, have been unsuccessful [11]. Contrasting results have been obtained with triphenylphosphine [12, 13].

A satisfactory stabilization was observed only by further coordination to copper of donor atoms of the same ligand, as for example in some compounds obtained with bis(diphenylphosphino)methane [14] or malonitrile [15].

In the aromatic series the stabilization of the metal–carbon bond is attained by introduction of suitable substituents in appropriate positions of the benzene ring. In fact arylcopper compounds with dimethylamino, (dimethylamino)methyl, methoxy, methoxymethyl, diphenylphosphino and dimethylsulfamoyl groups in *ortho* position with respect to the metal atom are in general thermally stable up to 100–200 °C and are only slowly attacked by water and oxygen [16]. This is probably due to the coordination of the heteroatom of the side group to copper, as suggested by the anomalous strong upfield shift of the methoxy proton resonance in *o*-anisylcopper [17] and then confirmed by the X-ray structure of some of the above compounds [16d] (see later for the structures).

A satisfactory thermal stability was shown also by fluoro- or trifluoromethyl-arylcopper derivatives [18] and by the $\alpha$-cupriobenzylidenamines, obtained by insertion of an isocyanide group in some cuprio-*o*-$(CH_2)nNMe_2$ benzene derivatives [19]. Complexation with CuBr seems to stabilize the carbon–copper bond towards hydrolysis and oxidation [16d], but to decrease its thermal stability [20]. In general the stabilization by complexation did not give satisfactory results. As in the case of the alkyl derivatives, complexes with 2,2′-bipyridine and 1,10-phenanthroline are more unstable than the parent compounds [21], while tertiary phosphines have only a small stabilizing effect [21, 22]. It seems that phosphine ligands act on the polymeric structure of the aryl copper compounds giving smaller aggregates, as already proposed for ethynyl copper compounds [23] and then confirmed by structural studies [24]. The same effect has been suggested for strongly co-ordinating solvents, such as pyridine [16d].

The X-ray analyses so far performed have shown that the Cu–C $\sigma$-bonded compounds have polynuclear structures, if we exclude the case of one carbonyl derivative [25], in which the copper atom is co-ordinatively saturate. Polymeric structures have been proposed also for methyl- and phenyl-copper compounds, because of their insolubility in non co-ordinating solvents. In particular a structure in which the copper atoms are assumed to be two-coordinated, with an almost linear arrangement of the C–Cu–C bonds, has been suggested for the phenylcopper compound [16d] (Scheme 1). Also tolyl- and anisyl-copper compounds, which have low aggregation states in solution [26], must be polymers in the solid state, as demonstrated by autoxidation phenomena [27]. Pentafluorophenyl- and *o*-trifluoromethylphenyl-copper [18] as well as other organocopper derivatives [28, 29] were found to be tetrameric by means of molecular weight measurements in benzene or by mass spectroscopy, whereas for *m*-(trifluoromethyl)-phenylcopper an octameric structure, with a central copper cube and mobile bridging benzotrifluoride groups, was suggested [18a].



Scheme 1.

As above mentioned the unique monomeric structure is that of Cu(CO)(hbpz) (hbpz = hydrotris(1-pyrazolyl)borate) obtained by addition of copper(I) chloride to a solution of K(hbpz) in the presence of carbon monoxide [25]. The copper atoms have a distorted tetrahedral arrangement, in which the hydro-tris-(pyrazolyl)borate anion occupies three positions and the CO molecule occupies the fourth position (Figure 1). The asymmetric unit of the crystal cell contains two molecules, one with a crystallographic $C_3$ symmetry, and the other somewhat distorted from the $C_{3v}$ symmetry, which in turn the molecule could possess. The Cu–N distances range from 2.039(4) to 2.059(3) Å, whereas the mean Cu–C distance is 1.765(14) Å and the $\widehat{CuCO}$ angles are 180° and 176.6(5)°, respectively, in the two crystallographically independent molecules. The Cu–C bond length is the shortest distance so far reported, strongly suggesting a partial double bond character.

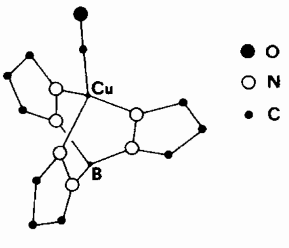


Fig. 1. A sketch of the Cu(CO)(hbpz) molecule, showing the bonding of carbon monoxide to copper(I).

The stability of this compound is noteworthy, since carbonylcopper(I) derivatives are highly unstable, with only a few exceptions [30, 31].

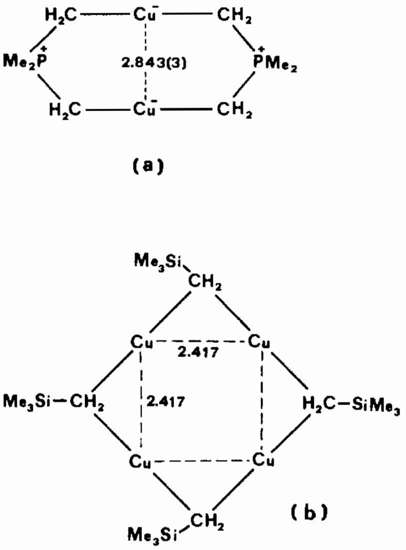


Fig. 2. (a) The dinuclear compound $[Cu(Me_2P(CH_2)_2]_2$. (b) The tetranuclear compound $[Cu(Me_3SiCH_2)]_4$.

The dimeric compound $[CuMe_2P(CH_2)_2]_2$ has been prepared by Schmidbaur *et al.* by treating anhydrous copper(I) chloride with salt-free trimethylmethylenphosphorane (molar ratio 1:2) at room temperature in benzene or toluene under an inert gas [10]. The structure (Figure 2a) proposed by the Authors on the basis of nmr and mass spectra was then confirmed by the X-ray analysis [32]. The Cu atoms have a digonal C–Cu–C arrangement (Cu–C 1.96(2) Å and $\widehat{CCuC}$ 175.8(8)°) and are 2.843(3) Å apart as mainly determined by the bite of the $Me_2P$-$CH_3)_2$ ligand. This compound is one of the two, in which the Cu–C stretching vibrations (557 and 509 cm$^{-1}$)* have been identified in the ir spectrum.

Another stable alkylderivative is the tetranuclear compound $[Cu(Me_3SiCH_2)]_4$ [34], obtained by treatment of CuI in a 1:1 hexane–ether mixture with lithium methyltrimethylsilane at −10 °C. Its crystal structure is built up by discrete centrosymmetric

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*The only other value reported is 630 cm$^{-1}$ for the $(CuMe)_n$ (−60 °C) [33].

units containing a square of copper atoms (Fig. 2b). This arrangement is unusual in clusters of other transition metals, whereas it has been found in tetrakis (1,3-dimethyltriazeno)Cu(I) [35], and is present also in some of the following structures. $Me_3SiCH_2$ acts as a bridging ligand giving a digonal environment ($C\widehat{CuC}$ angle = 164°) of the copper atoms. Each alkyl bridge (Cu–C distances in the range: 1.99–2.04 Å) involves a Cu–C–Cu two-electron–three-centre bond. Although the Cu...Cu distances are particularly short (2.417 Å) the Authors suggest that a copper–copper bonding is relatively unimportant.

An analogous digonal co-ordination geometry has been found also in the structure of the trimeric compound $[Cu(Ph_2PCHPPh_2)]_3$, [14] (Fig. 3). Although the structural non-equivalence of the phosphine ligands suggests a different oxidation state of the Cu atoms, the $Cu\widehat{C}Cu$ angle (158.0(9)°) and the Cu–C bond lengths (1.98(2) Å) are not far from the values reported for the preceding compounds. The overall molecule is stabilized also by efficient phenyl–phenyl intramolecular interactions.

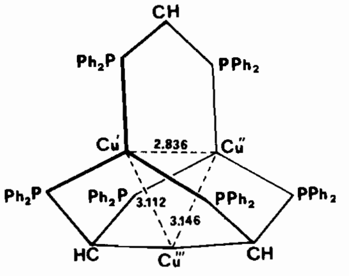


Fig. 3. A sketch of the trinuclear compound $[Cu(Ph_2PCH\text{-}PPh_2)]_3$. Two $Ph_2PCHPPh_2$ groups act as tridentate ligands.

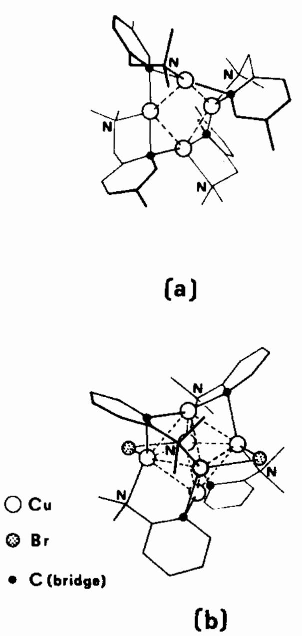
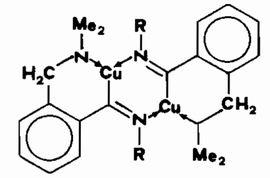


Fig. 4. (a) The "butterfly" arrangement of the copper atoms in 5-methyl-2[(dimethylamino)methyl]phenylcopper(I) and (b) the octahedral arrangement of the copper atoms in [2-dimethylaminophenylcopper(I)]$_2$·CuBr. The bridging atoms of phenyl groups are evidentiated.

A tetranuclear "butterfly" arrangement of copper atoms, intermediate between a square planar and a tetrahedral arrangement, has been established for 5-methyl-2[(dimethylamino)methyl]phenylcopper [28, 36] (Fig. 4a). The most remarkable aspect is the presence of bridging phenyl groups. All the copper pairs are aryl-bridged (Cu–C distances range from 1.97 to 2.16 Å), suggesting a bonding scheme similar to that of the alkyl bridges in $[Cu(Me_3SiCH_2)]_4$. In addition each copper atom achieves the tri-coordination by bonding one nitrogen atom. As far as the bonding scheme is concerned, also in this case direct metal–metal bonding is ruled out, despite the very short Cu...Cu distances (2.389(3) and 2.377(3) Å), because the Raman spectrum does not show strong absorptions in the metal–metal vibration region. The nature of the copper–aryl bonds is thoroughly discussed by the Authors and two-electron–three-center bonding is assumed to be present. The $^1H$ nmr spectrum shows the expected pattern. The benzyl and N-methyl protons appear as singlets, shifted upfield with respect to those of the parent arenes, but the shifts do not give unequivocal information about the arrangement of the aryl ligands around the $Cu_4$ cluster or about the interaction of the ligand with copper, since there are contrasting data in the literature even for compounds in which the M–N coordination takes place surely. Aromatic protons *ortho* to Cu show large downfield shifts (about 1.2–1.4 ppm), whereas the protons *ortho* to the $CH_2NMe_2$ ligand are shifted slightly upfield.

The $Cu_4$ cluster has a considerable stability, as can be deduced by the abundance of the $Cu_4$ containing species in the mass spectrum and by the preferential fragmentation of the ligand with respect to the $Cu_4$ skeleton. The $[Cu_4R_3]^+$ species are more abundant than the $[Cu_4R_4]^+$ ones and this suggests that the removal of one electron from the $Cu_4R_4$ cluster reduces the bonding between R and Cu.

The tetrameric *o*-(dimethylaminomethyl)phenylcopper, which is probably similar to the latter complex, forms a new copper compound by insertion of an isonitrile group into the aryl–copper bond. The following six membered ring structure (Scheme 2),



Scheme 2.

achieved through intermolecular co-ordination of the two Cu–C=N units and intramolecular co-ordination of the Cu–$NMe_2$ groups has been proposed to exist in benzene solutions.

It is possible that $Cu_4R_4$ compounds of the above kind interact also with CuBr, forming new stable complexes of formula $Cu_6Ar_4Br_2$. The X-ray analysis of [2-dimethylaminophenylcopper(I)]$_2$. CuBr [37] has shown that this complex has actually a hexanuclear structure. The octahedral arrangement of the copper atoms is such that the two axial ones are doubly bridged by aryl groups. The resulting C–Cu–C grouping is approximately linear (mean $\widehat{CCuC}$ angle 164°; mean Cu–C distance 1.97 Å). The four equatorial copper atoms, involved in but one aryl bridge (mean $Cu_{eq}$–C distances 2.085 Å) have a trigonal environment, each of them being further co-ordinated by one Br and one N atom. The bromine atoms bridge the *trans*-equatorial edges of the octahedron.

The Cu....Cu distances depend upon the nature of the bridge. They average to 2.48 Å in the four aryl bridges, whereas mean values of 2.70 and 2.64 Å are found for the two Br bridges and for the remaining Cu....Cu distances, respectively. The structure is schematically shown in Fig. 4b.

Mixed complexes of approximately overall composition $Ag_4Cu_2R_4Br_2$ have also been isolated [38]. An interaggregate exchange with presence of species $Ag_{(6-n)}Cu_nR_4Br_2$ has been observed upon dissolving the complexes in benzene.

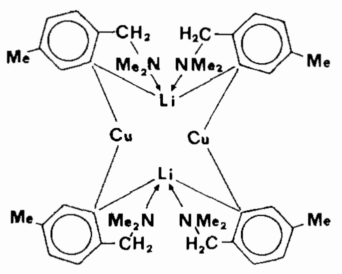
Compounds of the type $Cu_6Ar_4X_2$ (X = halogen) give a new class of polynuclear mixed organocopper derivatives $Cu_6Ar_4R_2$, by reaction with lithium arylacetylides [39]. In the same way also $Cu_6Ar_4(C{\equiv}CSiMe_3)_2$ has been prepared. These compounds maintain the octahedral copper cluster and it is suggested that the –C≡CR group substitutes the Br atoms of the preceding structure, one of the carbon atoms of the acetylide bridging two equatorial copper atoms. The acetylides lose their polymeric structure, as indicated by the absence of significant shifts to lower values of the $\nu(C{\equiv}C)$ frequencies, that is by the absence of important $\pi$-interactions of the metal atom with this bond.

The same overall stoichiometry is present in the $Cu_4MgAr_6$ compounds. They have been obtained by reaction of copper(I) or copper(II) bromide with bis(aryl)Mg in ether or THF [40], and are remarkably thermally stable. Their molecular weights are consistent with the presence of a discrete $Cu_4Mg$ cluster. Furthermore the nmr spectra suggests that there are at least two kinds of aryl group environments. A complex of rough formula $(CuMe)_3CuMgX_3$ has been isolated from the reaction between methyl Grignard and CuBr [41]. It has probably a polymeric nature, given its complete insolubility in non co-ordinating solvents.

Furthermore CuR·CuBr complexes have been described, in which organometallic compound and copper halide are in 1/1 ratio (R = 2[dimethylamino)-methyl]phenylcopper [20]. A polymeric rather than a discrete cluster structure has been suggested for them.

Among the organocopper complexes, of particular interest are the cuprates of the type $CuLiR_2$, so largely used in organic synthesis. Their diffusion with respect to the parent organocopper compounds is due to their higher solubility and especially to their excellent thermal stability. Little is known about their structure. For the lithiumdimethylcuprate, on the basis of low temperature nmr measurements on reaction mixtures, Corey and Posner [42] and Whitesides *et al.* [43] suggested a tetrahedral metal cluster structure with face centered bridging alkyl groups. More recently van Koten and Noltes [44] have studied the bis-[2(methylamino)methylphenyl] copper(I) lithium, obtained as usual by action of the lithium derivative on the organocopper or directly by reaction of two equivalents of the lithium derivative with CuBr in ether at –30 °C. The complex exists in benzene as discrete dimeric units $[Cu_2Li_2R_4]$ and the $^1H$ and $^{13}C$ nmr spectra point out that all four R groups are bonded in the same manner to the metal cluster system, each aryl group bridging a Li and a Cu atom. There are two singlets for the NMe proton resonance pattern (which collapse to one singlet, 1.74 ppm, at 25 °C) and two doublets (which collapse to one singlet, 3.36 ppm, at 80 °C) for the $NCH_2$ grouping, indicating that the four $CH_2NMe$ ligands are co-ordinated to the same metal atom.

The suggested structure, with bridging R groups, is reported in Scheme 3.



Scheme 3.

Afterwards the same Authors [45] have prepared also thermally stable gold–copper cluster compounds $Au_2Cu_2R_4$ with the same dimeric nature and similar nmr spectral characteristics. The spectra show also the presence in solution of species of the type $Au_nCu_{(4-n)}R_4$.

Finally, we include here Cu(I) complexes with cyanide ions. In fact their structures show the presence of Cu–C $\sigma$-bonds, although their chemical behaviour is more similar to that of copper(I) halide complexes than to that of organometallic compounds.

To our knowledge, the first reported structure of such adducts was that of $Cu(NH_3)CN$ [46]. Chains of (Cu–CN) units are arranged along the $C_2$ sym-

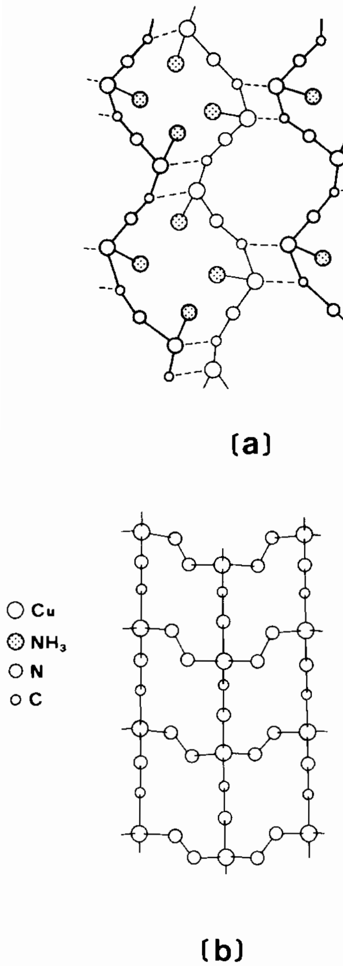


Fig. 5. The polymeric structures of (a) $Cu(NH_3)CN$ and (b) $Cu(N_2H_4)CN$.

metry axes and are linked together to form layers by Cu–C bonds (see Fig. 5a). Thus the basic structural unit of the dark green crystals consists of tetrahedral copper atoms bridged by CN groups. Furthermore these units are linked together by a double bridge $-\mathrm{Cu}{<}^{\mathrm{CN}}_{\mathrm{CN}}{>}\mathrm{Cu}-$ with Cu...Cu distance of 2.418(2) Å and Cu–C bond lengths of 2.09(1) and 2.13(1) Å. The tetrahedral arrangement is completed through co-ordination of $NH_3$ to copper ($Cu-NH_3$, 2.068 Å). It must be stressed, however, that Authors do not rule out the interchange of N and C atoms in the cyanide ligand.

The analogous adduct with hydrazine, of formula $Cu(N_2H_4)CN$ [47] has a solid state structure of puckered layers consisting of infinite zig-zag chains $(CuCN)_n$ lying in parallel mirror planes and bridged together by hydrazine molecules (Fig. 5b).

These structures recall those found in similar adducts of copper(I) halide with nitrogen containing ligands [48]. $[Cu_2{}^{I}Cu^{II}(NH_3)_3(CN)_4]$ [49] consists

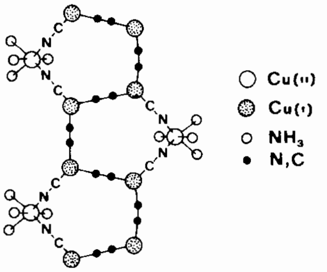


Fig. 6. The polymeric structure of the mixed valence compound $[Cu_2^{I}Cu^{II}(NH_3)_3(CN)_4]$.

of polymeric chains, a segment of which is shown in Fig. 6. They, in turn, are nearly planar pentagons sharing two of their edges with those adjacent. The pentagons are formed by one Cu(II) and four Cu(I) atoms held together by CN bridging groups, three of which are disordered. The octahedral co-ordination of copper(II) is completed by ammonia molecules (some positions might be occupied only partially, *e.g.* three ammonia molecules and one vacancy), whereas the co-ordination about Cu(I) is approximately trigonal planar with Cu–C distances of 1.900(9) Å.

More recently the structures of the 1:1 complexes Cu(paz)CN (paz = pyridazine) and Cu(cp)CN (cp = 4-cyanopyridine) have been determined [50]. Dark red crystals of Cu(paz)CN have been obtained by dissolving a small amount of CuCN in warm pyridazine and allowing the solution to cool. The basic structure of this complex consists of a two-dimensional polymer formed by chains of CuCN groups in a zig-zag conformation, linked by bridges of pyridazine molecules between two copper atoms of opposite chains. Thus hexanuclear rings of copper atoms are formed as shown in Fig. 7a. The Cu–C distances are 1.915(8) and 1.909(12) Å.

In the structure of the Cu(cp)CN, zig-zag nearly planar chains of $(CuCN)_n$ are held together by the two nitrogen atoms of the cp molecules, giving thus the wavy infinite layer shown in Fig. 7b. As in Cu(paz)CN, the copper atoms are approximately tetrahedrally co-ordinated by three nitrogen and one carbon atoms (Cu–C, 1.907(2) Å).

## 3. $\pi$-Bonded Compounds

The greater part of the known $\pi$-bonded organocopper compounds derives from acetylides and olefins.

The structure of acetylides represents a transition term between $\sigma$- and $\pi$-bonded compounds. It is generally assumed that they possess a polymeric structure, where each metal atom is $\sigma$-bonded to a carbon atom and $\pi$-bonded to acetylenic groupings. This fact should decrease the order of the C≡C bond,

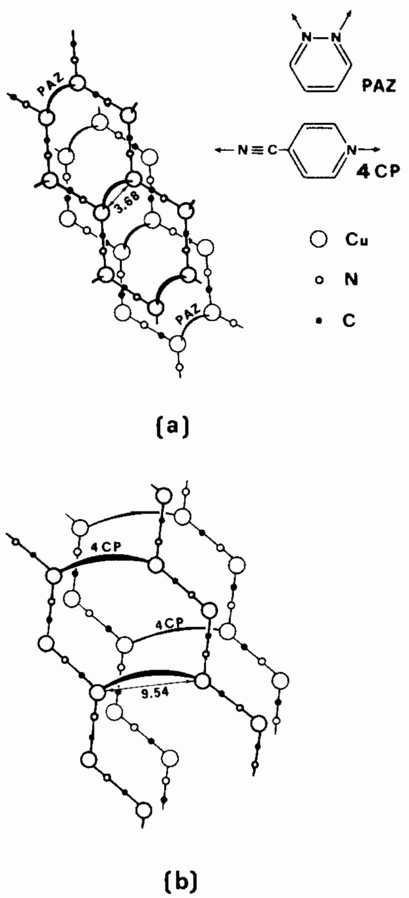


Fig. 7. The layered structures of (a) Cu(paz)CN and (b) Cu(cp)CN.

leading therefore to a decrease of its frequency in the ir spectra with respect to that of the free acetylenes [23].

X-ray diffraction analysis of phenylethynyl copper indicates the presence of infinite zig-zag chains of copper atoms, each of them σ- and π-bonded to three $PhC\equiv C$ groups, lying roughly in the same plane [51]. Although two different types of ethynyl groups are suggested to exist in this structure by different lengths of the $C\equiv C$ bonds (1.33 and 1.24 Å respectively) [51], no evidence for their presence could be obtained by infrared and Raman spectra [52].

The polymeric chain of acetylides is broken down into smaller aggregates by reaction with tertiary alkylphosphine, arsines or stibines. Compounds with a different ligand/metal ratio can be obtained, the maximum value being 3/1. The degree of association in solution of the phosphinic complexes varies within a wide range, depending on the composition of the complex, its concentration and the nature of the solvent [2]. The structure of the phenylethynyl(trimethylphosphine)copper(I) has been studied in detail [24]. The crystals are built up by tetrameric centrosymmetric molecules with four copper atoms in a zig-zag chain. The terminal metal atoms are coordinated by two phosphines and two $RC\equiv C$ groups, whereas the inner ones are bonded to three ethynyl groups. The copper–carbon interactions involve both σ- and π-bonds, as shown in Figure 8a. The distances between the inner and terminal copper atoms are 2.693(4) and 2.450(3) Å, respectively. The overall structure recalls that of the tetrameric $[CuL_4X]$ ($X$ = halide, $L$ = phosphinic ligand) [53], assuming the formal substitution of the halide with the $RC\equiv C$ group. It is worth comparing this structure with that of the analogous silver(I) derivative (Fig. 8b), which consists of infinite almost straight chains of silver atoms, alternately bonded to two ethynyl groups by σ-bond and to two phosphines and two ethynyl groups by weak and unsymmetrical π-bonds [54].

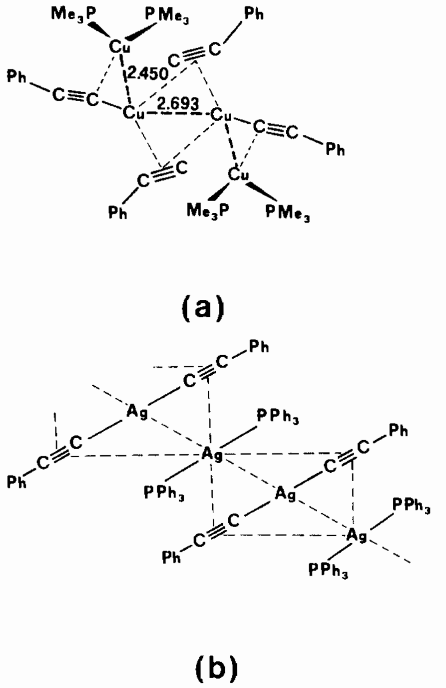


Fig. 8. A comparison between (a) the tetrameric arrangement of copper atoms in phenylethynyl(trimethylphosphine)copper(I) and (b) the linear arrangement of Ag atoms in the analogous silver(I) derivative.

In the last years substituted copper(I) arylacetylides have been largely employed in preparing compounds containing two different metals in the same molecule. Thus mixed metal–copper complexes have been prepared by reaction of copper acetylides with rhenium, iron, ruthenium, rhodium and iridium halide complexes. Usually the copper atom is π-bonded to the acetylenic group, which in turn is σ-bonded to the other metal.

The heteronuclear metal cluster $Cu_4Ir_2(PPh_3)_2(C\equiv CPh)_8$ [55] has four copper atoms in the equatorial plane and two Ir atoms in the axial positions of a distorted octahedron. Each Ir atom is bonded apically to a $PPh_3$ and is σ-co-ordinated to four C≡CPh groups, the Ir–C bonds being in a plane approximately parallel to the copper equatorial plane. Each acetylenic bond forms also an unsymmetrical π-linkage with the copper atoms, (Cu–C(α) and Cu–C(β) distances ranging from 1.87 to 2.08(2) Å and from 2.14 to 2.25(2) Å respectively). Thus the copper atoms are co-ordinated by two acetylenic moieties, which lie one above and the other below the equatorial plane, in an approximate digonal arrangement, if metal–metal bonds are ignored. In fact the metal–metal distances suggest only a weak, if any, direct interaction. Unusual features of the structure are the *trans*-bent conformation of the acetylene moiety and the slight rotation of one $Ir(C_2Ar)_4$ group relative to the other (Fig. 9a).

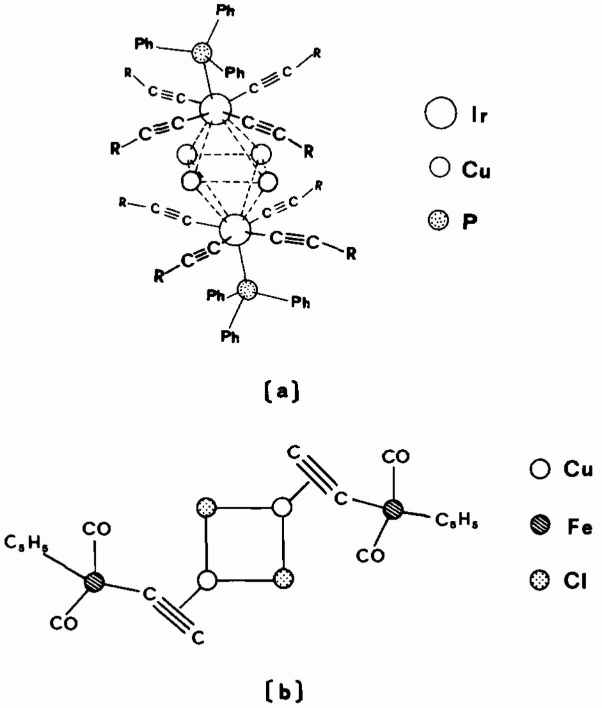


Fig. 9. The structures of the heteronuclear (a) $[Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8]$ and (b) $[CuFe(CO)_2(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)Cl]_2$ compounds.

A series of similar complexes was obtained with other copper arylacetylides [55bis]. It is possible too to replace the triphenylphosphine with methyldiphenylphosphine to increase the solubility of the complexes. All these derivatives have probably structures analogous to that above reported [55b], as suggested from the $^1H$ nmr spectra of the methyldiphenylphosphine derivatives and the $^{19}F$ nmr spectra of the *p*-fluorophenyl complexes, which indicate equivalence of all eight acetylide groups in these compounds. All these complexes show weak broad absorption bands due to ν(C≡C) in the 2000 cm$^{-1}$ region of the ir spectrum. The co-ordinated acetylenic bond is hence reduced by *ca.* 100 cm$^{-1}$ by π-bonding to copper.

These clusters are electron rich, containing six electrons more than those required to fill the metal bonding and non-bonding orbitals. It has been suggested [55b] that these extra electrons are in metal–metal antibonding orbitals, giving a total bond order of 3/4.

The rhodium analogue of Vaska's complex, *trans*-$Rh(CO)(Ph_3)_2Cl$, gave also similar cluster derivatives, $Cu_4Rh_2(C_2Ar)_8(PR_3)_2$, but in much lower yields. No significant structural differences from the corresponding iridium complexes are expected on the basis of their chemico-physical behaviour.

The molecular structure of the air stable reaction product of $Fe(CO)_2(\eta^5\text{-}C_5H_5)Cl$ with $(CuC{\equiv}CPh)_n$, $[CuFe(CO)_2(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)Cl]_2$ [56], is the centrosymmetric chlorine-bridged dimer shown in Figure 9b, where copper atoms have a trigonal geometry. Each Cu atom is symmetrically π-bonded to the $C_2$ unit of the acetylene group, the $Cu_2Cl_2$ ring being coplanar with the $CuC_2$ system.

The same kind of structure is assumed to be present in a series of analogous compounds, in which the phenyl is substituted with other groups ($p$-$MeC_6H_4$, $p$-$FC_6H_4$, $C_6F_5$) [57].

In contrast with the above structures, at first the $[CuRu(PPh_3)_2(C_5H_5)(C{\equiv}CPh)Cl]$ [58] was found to be monomeric, with linear di-co-ordinate Cu(I) (Fig. 10a). Actually a recent more detailed study [59], has shown that the reaction of phenyl-ethynyl copper and $Ru(PPh_3)_2(C_5H_5)Cl$ affords also oligomers, with a probable formation of copper–chlorine bridges.

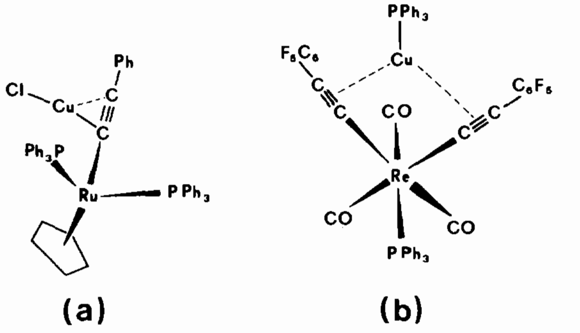
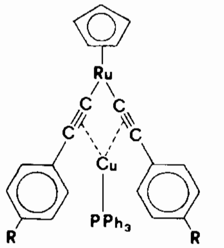


Fig. 10. The monomeric compounds of formula (a) $[CuRe(PPh_3)_2(C_5H_5)(C{\equiv}CPh)]Cl$ and (b) $[CuRe(PPh_3)_2(CO)_3(C{\equiv}CC_6F_5)_2]$.

A 1:1 adduct was obtained also from the reaction between $[Cu(C{\equiv}CPh)]_n$ and *cis*-$Re(CO)_3(PPh_3)_2Cl$ [59]. The crystals were not suitable for an X-ray analysis and, because of their insolubility, it was also impossible to ascertain their degree of polymerization. The proposed structure is similar to that of $[CuFe(CO)_2(C_5H_5)(C{\equiv}CPh)Cl]_2$, in case of a dimer, or to that of $[CuRu(PPh_3)_2(C{\equiv}CPh)Cl]$, in case of a monomer.

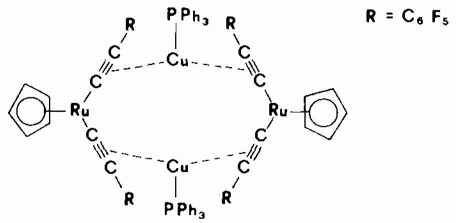
Another common feature of complexes isolated from reactions involving copper arylacetylides and transition metal halides seems to be the formation of zwitterionic aggregates, in which tertiary phosphine copper cations are π-complexed to anionic transition metal arylacetylides. Thus in the reaction of $[Ru(PPh_3)_2(C_5H_5)Cl]$ with copper(I) *p*-tolylacetylide or *p*-fluorobenzenacetylide the main product was a halogen-free complex (I), to which the following formula was attributed (Scheme 4) while the reaction with Cu(I) pentafluoro-phenylacetylide afforded moderate yields of a crimson-red tetranuclear complex, $[CuRu(PPh_3)(C_5H_5)(C_2C_6F_5)_2]_2$. For the latter the following formula, which may be considered a dimeric species of (I), was proposed (Scheme 5).



R = Me, F

(I)

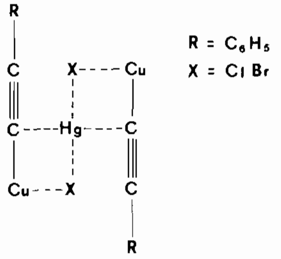
Scheme 4.



Scheme 5.

The same kind of structure is assumed also for the binuclear derivative $CuIr(PPh_3)_3C_2C_6F_5)_4$, obtained as by-product in the reaction between Vaska's complex and copper(I) pentafluorophenyl acetylide [55bis]. These structural hypotheses, advanced on the basis of ir and nmr spectra, are confirmed by the X-ray structure of the pale yellow crystals of $[CuRe(PPh_3)_2(CO)_3(C{\equiv}CC_6F_5)_2]$ [60] obtained among other products by reaction of *cis*-$Re(PPh_3)_2(CO)_3Cl$ with $Cu(C_2C_6F_5)$. The solid state structure is shown in Figure 10b, and consists of zwitterionic associates of $[Cu(PPh_3)]^+$ and $[Re(PPh_3)(CO)_3(C_2C_6H_5)]^-$ additionally held together by π-interactions between copper and acetylide groups. The Cu–C(α) and Cu–C(β) mean distances are 2.05(2) and 2.34(2) Å. The trigonal arrangement around the copper atom is completed by a $PPh_3$ group. The very short Cu–P distance (2.01(1) Å) must be stressed.

Finally complexes of copper acetylides and mercury(II) salts have also been obtained (2). In the ir spectrum of the $(CuC{\equiv}CPh)_2HgBr_2$ two different stretching vibrations, (2000w and 2040m $cm^{-1}$) indicate the presence of triple bonds of different types in the complex. In order to explain this result it has been proposed that the mercury halide is inserted between two molecules of the acetylide and that blocks of such type are linked to one another by π-co-ordination through triple bonds and copper atoms.



Scheme 6.

The copper(I) olefin π-complexes so far studied exhibit copper/olefin stoichiometric ratios 3/1, 2/1, 1/1, 2/3, 1/2 and 1/3 and include derivatives of copper(I) with halides ($Cl^-$, $Br^-$) and other anions. Literature data up to 1968 are available in a review on olefin complexes of transition metals [61].

In general these complexes are not very stable: they lose the olefin slowly at room temperature or on prolonged washing with organic solvents, while oxidation of Cu(I) occurs. Recently, however, cationic olefin compounds of copper(I) with trifluoromethanesulphonate ($OTf^-$) have been obtained [62]. They have high thermal stability and low tendency to dissociation also in solution. Furthermore, in contrast with the well known insolubility of the complexes with halides, they are readily soluble in polar organic solvents.

The nmr spectrum of the olefin changes with co-ordination to copper(I), the nature of the olefin–metal bond varying predictably with the number and the geometric arrangement of the co-ordinated C=C bonds [62b, 63]. However, owing to the scarce solubility, structural hypotheses for these complexes have been advanced mainly on the basis of ir spectra, studying the lowering of the C=C stretching frequency of the olefin upon co-ordination and/or the shifts of the more intensive bands due to the transverse CH-deformation in the 1000–700 $cm^{-1}$ region [64].

The only X-ray structures so far determined for copper(I) olefin complexes are those of some chloride derivatives. The first determined structure was that of CuCl·COD (COD = 1,5-cyclooctadiene) [65], a rather questioned complex, which has been obtained by direct reaction of the olefin with CuCl dissolved in HCl [65, 66] or acrylonitrile [67], or by reduction of Cu(II) chloride in the presence of the ligand [61, 64].

This compound has been found to be a centrosymmetric dimer with two bridging chlorine atoms inserted between the metal atoms, which are at a 2.944 Å distance (Figure 11a). Two double bonds of the boat shaped COD molecule complete the *quasi*-tetrahedral co-ordination around the copper atoms [65]. The formation of the complex involves a lowering of the C=C stretching frequency from 1660 to 1612 cm$^{-1}$. The X-ray structure is in contrast with that previously suggested on the basis of the ir spectrum [66], where the cuprous ions were considered to be linked at COD molecules in the chair conformation.

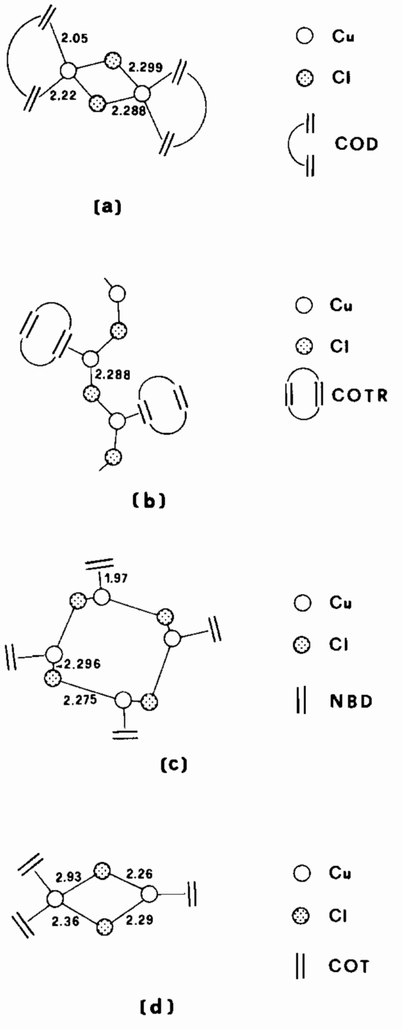
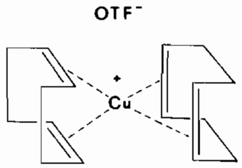


Fig. 11. A sketch of the structures of the copper(I) chloride olefinic complexes (a) [CuCl·COD]$_2$; (b) [CuCl·COTR]$_n$; (c) [CuCl·NBD]$_4$; (d) $(CuCl)_2(COT)_3$.

There are also COD complexes of different stoichiometries, for example $(CuO_2CCF_3)_2$·COD [68] and $(CuO_2CCH_3)_2$·COD [69], or complexes containing two COD molecules for each copper atom [64, 70]. In the $CuClO_4$·$(COD)_2$ the band at 1660 cm$^{-1}$ of the diene is replaced by two bands at 1638 and 1595 cm$^{-1}$, suggesting a non equivalent co-ordination of the double bonds. Cook *et al.* [64] failed to observe them and reported instead that both the perchlorate and the tetrafluoroborate derivatives show a C=C absorption at 1590 cm$^{-1}$, similar to that of the halide complexes. In the Cu(OTf)·$(COD)_2$ complex, Solomon and Kochi [62a] propose that 1,5-COD acts as a tetrahapto-ligand (Scheme 7).

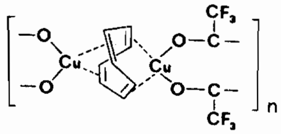


Scheme 7.

[CuCl·COD·$HgCl_2$]$_n$ and [(CuBr·COD)$_2$$HgBr_2$]$_n$ obtained by reaction of mercury(II) halides with (CuX·COD)$_2$ or by direct combination of CuX, $MgX_2$ and olefin in ethylacetate [71] show ir spectra very different from those of (CuCl·COD)$_2$ and (CuBr·COD)$_2$. Their low solubility did not allow to determine their aggregation state.

A 1/1 CuCl complex has been prepared also with 1,4-COD [72]. Its ir spectrum shows two $\nu$(C=C) absorptions at 1615 and 1495 cm$^{-1}$, suggesting an asymmetry of the two double bonds with respect to the metal atom. The copper bonding with 1,4-COD is considered weaker than that with the 1,5 isomer. 1,3-COD gives a $(CuCl)_3$·1,3-COD complex, which is the only known with such a stoichiometry [73].

Other complexes that have been thoroughly investigated are those with cyclo-octatetraene (COTR). The CuCl·COTR structure consists of continuous $(CuCl)_n$ chains with one double bond of the olefin closely bound to each copper atom. The carbon atoms of the bonded olefinic group are approximately coplanar with the $CuCl_2$ unit (Figure 11b) [74]. CuBr·COTR has probably an analogous structure. It is interesting to note, however, that the 1:1 stoichiometry is the only found with CuBr, while also a $(CuCl)_2$·COTR complex has been obtained with CuCl [64, 67]. In the latter complex the infrared spectrum indicates the presence of both free (1613 cm$^{-1}$) and complexed (1525 cm$^{-1}$) double bonds. On the contrary a full coordination of the double bonds is assumed in the $(CuX)_2$·COTR (X = trifluoroacetate ion [69a] (Scheme 8).



Scheme 8.

No evidence for this hypothesis may be obtained by ir spectroscopy, because the intense carboxyl band interferes with the bands of the double bonds. On the contrary the $^{13}$C nmr spectrum shows that only one double bond is bound to each copper atom in solution, where the complex is dimeric at high concentration [69b]. The ir spectrum of $(CuO_2CCH_3)_2$·COTR [69a] suggests a bridging feature of the tetraene, which forms two strong and two weak bonds with each of the two copper atoms of a $(CuO_2CCH_3)_2$ unit.

Also in the cationic [Cu(I)COTR]OTf the ir spectrum indicates the presence of non equivalent carbon–carbon double bonds (1630 and 1520 cm$^{-1}$ with respect to 1635 cm$^{-1}$ in the free ligand). The complex is monomeric and molecular weight demonstrates the absence of appreciable dissociation in organic polar solvents. However, in the nmr spectrum the protons, not magnetically equivalent at −100 °C, are all equivalent at room temperature, which indicates a rapid exchange of cyclooctatetraene in solution [62a].

A tetranuclear structure has been found for the CuCl·NBD complex (NBD = 1,5-norbornadiene) [75] (Figure 11c). The copper atoms, arranged in a $\bar{4}$ symmetry, are bridged by chlorine atoms to form an eight-membered tub shaped ring, the third co-ordination position of copper being occupied by one double bond of the olefin, which lies in the plane defined by the $CuCl_2$ moiety. The second double bond is not co-ordinated, in agreement with the ir spectrum of the compound, which shows two ν(C=C) stretching frequencies at 1563 and 1473 cm$^{-1}$. The first one, close to that of the double bond in the free NBD (1547 cm$^{-1}$), is attributed to an un-co-ordinated C=C bond [67]. Also thermodynamic data [76] indicate that the Cu(I)Cl complex of NBD is not chelated. The distorted trigonal co-ordination around copper is similar to that present in the above COTR complex, as well as in the CuCl·2-butyne complex [77]. On the contrary NBD seems to act as chelating ligand in $CuO_2CCH_3$·NBD [69].

NBD forms also 1/2 adducts with copper halides [64, 67, 78]. $(CuCl)_2$NBD shows only fully co-ordinated C=C groups, with an absorption at 1470 cm$^{-1}$. Also the bands at 730 and 660 cm$^{-1}$, present in the uncomplexed NBD, are absent [64]. The same kind of co-ordination is reported for the CuBr derivative [67] (only one C=C absorption at 1456 cm$^{-1}$), while Cook *et al.* [64] suggest that one double bond is not co-ordinated in this complex, because strong absorptions occur at 1555 and 690 cm$^{-1}$. It is possible that the two complexes, obtained by different methods, are different.

Polymeric structures with bridging chlorine atoms have been proposed also for the $(CuCl)_2$ olefin complexes with cyclic allenes (1,2,6-cyclononatriene, 1,2,6-cyclodecatriene and 1,2,6,7-cyclodecatetraene). Their ir spectra show two frequencies in the C=C stretching region at about 1840 (uncomplexed allenic double bond) and 1660 cm$^{-1}$ (weak, co-ordinated allenic double bond) [79].

A low degree of polymerization is suggested also for compounds of formula $CuCl{\cdot}Me_3MCH{=}CH_2$ and $(CuCl)_2Me_2M(CH{=}CH_2)_2$ (M = Si, Sn) [80]. The divinyl complexes are among the most stable CuCl olefin complexes yet described. Their ir spectra do not show stretching frequencies of un-co-ordinated double bonds. The ΔνC=C upon co-ordination is 80–90 cm$^{-1}$, greater than that usually observed for the CuCl–olefin complexes.

A rather unusual stoichiometry for the Cu(I) halide olefin complexes was found in crystals of $(CuCl)_2(COT)_3$ (COT = *trans*-cyclo-octene) [81] (Figure 11d).

The copper and chlorine atoms form a non planar and asymmetric bridged system with three nearly equal Cu–Cl distances (2.3–2.4 Å) and a fourth one considerably longer (2.9 Å). Both copper atoms present sp$^2$ hybridization. The co-ordination around one of the copper atoms is trigonal with the apical positions completely free, while the other copper atoms linked to a chlorine atom and to two COT molecules (Cu–double bond distance 1.93–2.09 Å), may be considered as trigonal pyramidal. The cyclo-olefin molecule bonded to the first copper atom has a conformation different from that of the other two, but in any case the double bond is orthogonal within 2–3° to the line joining the copper atom with the centre of the double bond and lies in the co-ordination plane.

There are also π-organocopper complexes with olefins where the other constituent is a neutral ligand, for example $Cu(PEt_3)(C_5H_5)$ [82] (Fig. 12a) and $Cu(PPh_3)(C_5H_5)$ [83] (Fig. 12b). As already

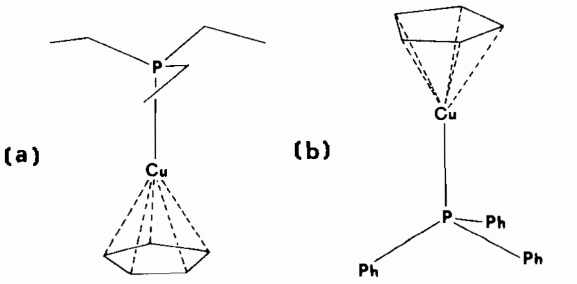


Fig. 12. A sketch of π-organocopper complexes containing a neutral ligand: (a) $Cu(PEt_3)C_5H_5$ and (b) $Cu(PPh_3)C_5H_5$.

suggested by ir spectra [84] these compounds contain a pentahaptocyclopentadienyl ring. The Cu atom lies at 1.90(3) Å from the cyclopentadienyl plane, with Cu–C distances ranging from 2.24 to 2.25(3) Å in the triethylphosphine derivative. The corresponding values in the triphenylderivative are 1.862(3) and 2.190(3)–2.232(2) Å. Short Cu–P bond lengths (2.139(6) and 2.135(1) Å, respectively), have been observed in these compounds. The difference with respect to the normal values found for "one phosphine" Cu–P bonds (2.194(2) Å [85, 86] has been attributed mainly to a lower crowding of ligands around the metal atom.

Also cyclopentadienyl and indenyl-butylisocyanide complexes of Cu(I) are known. The first is undoubtedly isostructural with the tertiary phosphine complexes, whereas the [Cu(indenyl)-(Bu$^t$NC)$_3$], which has also a different stoichiometry, is almost certainly σ-bonded, on account of its ir and nmr spectra [87]. There are no indications on the structure of other organocopper isonitrile complexes with "active" hydrogen compounds, such as acetylacetone, acetoacetate, malonate and cyanoacetate [88].

An unusual Cu–benzene bonding has been found in $C_6H_6Cu^IAlCl_4$ [89], prepared from dry benzene and anhydrous resublimed cuprous and aluminium chlorides. The structure may be considered as built up by $AlCl_4^-$ anions and $[Cu(C_6H_6)]^+$ cations. Distorted tetrahedral Cu(I) atoms are bonded to chlorine atoms of three different anions, the fourth coordination position being occupied by a π-bonded benzene molecule. The Cu(I) is located almost exactly above one C–C bond of the benzene ring with Cu–C distances of 2.15 and 2.30(3) Å.

Later, Rodesiler and Amma [90] have reported the structure of another unusual polynuclear Cu(I) aromatic complex, the $Cu_4(F_3CCO_2)_4 \cdot 2C_6H_6$, obtained by reaction of trifluoroacetic anhydride with $Cu_2O$ in dry benzene at 60 °C. The complex (Fig. 13) is a planar parallelogram of four copper atoms, held together by bridging trifluoroacetate groups, alternating above and below the $Cu_4$ plane. Each benzene molecule is weakly π-bonded (shortest Cu–C distances 2.7–3.0 Å) to two copper atoms. In this way the metal atoms reach a co-ordination number of three. The aromatic molecules are situated on opposite sides of the parallelogram and each of them can be readily replaced by two indene, 1,4-cyclohexadiene or 1,3-cyclohexadiene molecules, probably leaving the $Cu_4(TFA)_4$ (TFA = trifluoroacetate) polynuclear species intact.

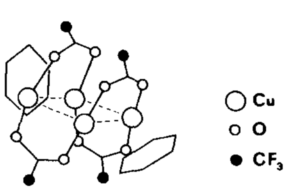
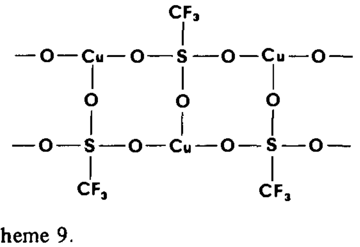


Fig. 13. The square-planar arrangement of the copper atoms in $Cu_4(F_3CCO_2)_4 \cdot 2C_6H_6$. The weakly π-bonded benzene molecules are also shown.

Among this kind of complexes with aromatic molecules must be considered also the benzene complex $(CuOTf)_2 \cdot C_6H_6$ [62b]. Its structure consists of infinite chains of CuOTf units (Scheme 9) cross-linked in sheets by the benzene molecules [91]. Two copper atoms are π-bonded to each ring in a *meta*-relationship (Cu–C distances vary from 2.09(2) to 2.30(2) Å). Benzene molecules can be selectively substituted by suitable aromatic compounds.



Scheme 9.

## 4. Conclusion

As already pointed out, practically all the σ-bonded and most of the π-bonded organocopper compounds are polymeric.

The σ-bonded compounds present nearly always structures characterized by copper clusters, whereas only in one case has a copper cluster been found in the known acetylides derivatives. On the other hand in the π-olefin organocopper compounds the polymeric structure is due either to a skeleton of $(CuX)_n$ (X = Cl, Br) chains or to dimeric species of bridged copper halides or carboxylates.

In spite of the very short copper–copper distances found in the σ-organocopper compounds (about 2.40 Å), all the Authors have ruled out significant metal–metal bonding interactions. If Cu–Cu bonding is excluded, the most commonly found co-ordination numbers are two and three whereas four is the preferred one for the cyanide compounds.

Digonal co-ordination seems to require a high σ-donor power of the σ-C ligands and the absence of mobile hydrogens on β-carbon atoms. Tri-co-ordination implies, besides two carbon atoms, a donor atom different from carbon. A two-electron–three-center bonding scheme, similar to that proposed for organo aluminium dimers [92] and some osmium trinuclear clusters [93], is assumed in compounds having carbanionic bridging ligands.

The digonal σ-Cu–alkyl bond lengths range from 1.96(2) to 2.04(2) Å and are very similar both in bridged and unbridged bonds. Similar values have been found for bridging aryl ligands (1.97–2.16(2) Å). The values reported for $Cu_{dig}$ and $Cu_{trig}$ are different, however, averaging to 1.97 and 2.09 Å, respectively. It is worth noting that the aryl ring is always almost perpendicular to the axis of the bridged copper atom.

Cu–C bond lengths shorter than the above values are found for unbridged σ-Cu–cyanide bonds (1.900(9)–1.915(8) Å), but they increase significantly (2.09(1)–2.13(1) Å) when cyanide acts as C-bridging ligand between two tetrahedral copper atoms [47].

Tri-co-ordination is usually found in olefin copper complexes. Only one or two mono-olefins are co-ordinated to the metal atom, which achieves its co-ordination number by other ligands. The bonding of the olefin to the copper atom in these compounds is interpreted in terms of the usual σ-π-bonding scheme of Dewar–Chatt–Duncanson. The stoichiometry of these complexes with mono-olefinic ligands appears to be dominated by steric effects, that is by their crowding. Analogously steric effects may be invoked to explain why, with potentially chelating polyenes, the copper forms more than one bond only with ligands of particularly favourable conformation. The stoichiometry depends largely also upon the type of anion present in the compound [69a]. In general, anions of low co-ordinating ability (*e.g.* $ClO_4^-$, $B(Ph)_4^-$) favour a low Cu/L ratio; otherwise there is competition between olefin and anion for the available co-ordination sites around the copper. Thus carboxylates and halides form preferentially complexes of $(CuX_2)L$ type. The highest known Cu/L ratio is found in the complex $(CuCl)_3 \cdot$1,3-COD [74].

Organocopper, organocuprate and catalytic reactions by Cu(I) salts, often related to intermediate formation of organocopper compounds, are increasingly diffuse in preparative organic chemistry, but till a few years ago their use was based mainly on empirical facts [4]. The recent development of the structural chemistry of copper(I) compound demonstrates that the interest of Authors is now moving to clarify their role in these reactions. This review shows that a further insight is needed into the nature of the organocopper compounds bonding, as well as a systematic approach to their structure, although a good number of chemico-physical and structural results on the subject is available at present. In particular a better knowledge is required about cluster formation. Probably the better shielding of the copper atoms by ligands contributes to the stabilization of clusters. However, since the distance between two atoms is usually taken as strongly indicative of bonding, the reported Cu...Cu distances, which are shorter than the Cu–Cu distance in the metal (2.56 Å), could suggest that a metal–metal interaction must be present in these complexes. Furthermore, since compounds of this kind were found to be diamagnetic, one should assume the presence of multiple bonding between the metal atoms [94]. We believe that further studies on the nature of copper–copper interaction are necessary in order to clarify this problem.

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