Russian Chemical Reviews, 37 (10), 1968

U. D. C. 547.255.61 : 547.314.2,13

Copper and Silver Acetylides in Organic Synthesis

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A review of the reactions of copper, silver, and gold acetylides with halides, aryl halides, unsaturated halogen compounds, diazonium salts, halides of organic acids, and organometallic compounds. Information on the structure of copper and silver acetylides and their physical properties is given. The mechanisms of the reactions of copper acetylides with the above types of compounds and the mechanism of the oxidative condensation of acetylenes are considered. The properties of copper and silver acetylides are compared with the properties of the cyanides of these metals. Bibliography of 127 references.

CONTENTS

I.	Introduction	748
II.	Acetylides of acetylene	748
III.	Structure of acetylides	750
IV.	Chemical properties of acetylides	751

I. INTRODUCTION

In 1955, Braude, in considering the progress reached in organometallic synthesis, noted two important stages—the discovery of the organomagnesium compounds by Grignard and the development by Ziegler of the chemistry of organolithium compounds. Approximately 25 years after the discovery of the organolithium compounds, Ziegler investigated the organic compounds of aluminium and introduced them into the practice of organometallic synthesis.

And now these three classes of organoelemental compounds are of importance in organometallic synthesis. In addition the unceasing search in the field of reactions of other organoelemental compounds is evidence that the use of organic compounds of other elements is necessary to solve many particular and some general problems of synthetic organic chemistry.

Even as long ago as 1959 at the VIIIth Mendeleev Conference on General and Applied Chemistry, A. N. Nesmeyanov noted that the intensive investigations of the last decade had allowed almost all the known types of organoelemental compounds to be introduced into the practice of organic synthesis; organoelemental chemistry, which had been separated as an independent branch of organic chemistry was reunited with it again on another, more modern, level.

The impression is created that there is now an accumulation of experimental material and of its generalisation in the field of the reactions and properties of many organoelemental compounds. It must be expected that the development of the chemistry of certain of these compounds will lead to the emergence of a new stage in the development of organometallic synthesis.

Of such compounds the organic compounds of copper merit attention. An investigation of the aryl and alkyl compounds of copper showed the possibility of their use in organic synthesis. However, the ethynyl compounds of copper were of the most interest, owing to their relative stability and promise of application. Copper acetylides have already come to be regarded as common reagents in organic synthesis. Oxidative condensation of acetylenes was recently examined in several extensive reviews. Information published recently about certain reactions of the copper acetylides reflects the great interest in these compounds. Evidently the acetylides of the bisacetylene derivatives present a unique possibility for the synthesis of individual poly-ynes and of polymers, the chain of which consists of conjugated carbon–carbon groupings with triple bonds.

Because of this we thought it timely to review the information on the synthesis, structure, and reactions of the copper and silver acetylides.

II. ACETYLIDES OF ACETYLENE

The first information on copper acetylides was published by Böttger[1] in 1859. On passing illuminating gas through an ammoniacal solution of copper(I) chloride he observed the formation of a cinnabar-red precipitate, explosive when dry. Some of the reactions of copper acetylide led the author to suggest that he had obtained a substance containing copper, carbon, and very little hydrogen. In particular it was found that under the action of potassium cyanide and hydrochloric acid the precipitate is decomposed with evolution of a gaseous hydrocarbon burning with a very smoky flame. Analogous compounds were obtained with salts of silver(I) and gold(I). A year later Berthelot[2] purified the hydrocarbon obtained from the copper acetylide, investigated it, and named it acetylene.

From the moment of discovery of the acetylides their intensive investigation began. Finding the composition and structure of the acetylides became the theme of a series of investigations, but immediately a large number of contradictions arose, both in the results of the experiments and also in their treatment. A detailed review of the work at the end of the XIXth century and the beginning of the XXth century was given in a monograph[3]. It seems desirable in the present review to pay attention mainly to the latest studies in this field, referring to the older studies mainly as illustrative material.

The most widespread of the methods for obtaining the copper acetylides, including also those for analytical purposes, was developed by Ilosvay[4]. He proposed reagents which stored well, prepared by the reduction with hydroxylammonium chloride of ammoniacal solutions of copper(II) chloride, sulphate, or nitrate. Keiser[5] showed that copper acetylides, unlike the silver acetylides, always contain a certain amount of elemental carbon and explained its formation by the oxidising action of atmospheric oxygen. He obtained the purest specimen of copper acetylide in the reaction of acetylene with copper hydroxide (CuOH)

suspended in water. The analyses were in complete agreement with the formula Cu_2C_2 for copper acetylide and Ag_2C_2 for silver acetylide.

Klement and Ködermann-Gros[6], who obtained copper acetylide in the absence of oxygen, consider that ammoniacal solution first deposits a non-explosive red acetylide of composition $Cu_2C_2.H_2O$, which in air is partly oxidised and loses water, being converted into a black, extremely explosive acetylide. Brameld and coworkers[7] obtained acetylides from various copper(I) salts in alkali and acid media in an atmosphere of nitrogen. The acetylides obtained in an ammoniacal medium from Cu_2Cl_2 and dried in a vacuum over H_2SO_4 and P_2O_5 had a C/Cu ratio in the range 0.94–1.2, depending on the alkalinity of the ammoniacal solution.

In Easterbrook and Erskine's comprehensive review[8] it was noted that slight variations in the method of preparation are reflected in the composition of the acetylide. The time of passing (or the flow rate) of the acetylene and the possibility of oxidation had a considerable effect. Even the dry acetylide is slowly changed on storage in the air with normal humidity, $Cu(OH)_2$ and a carbonaceous substance being formed. The authors[8] found that the copper acetylide obtained by passing acetylene into an ammoniacal solution of copper(I) salt contains on average 91–93% of an acetylide of the empirical formula $(Cu_2C_2)_2.H_2O$, 4–6% $Cu(OH)_2$, and 3–5% of a carbonaceous substance. On raising the acetylene flow rate the proportion of the carbonaceous substance is raised to 5–6%, but that of $Cu(OH)_2$ falls.

The above investigations were carried out with acetylides obtained in alkaline solutions. This is a comparatively simple example, where in the main the process is always the replacement of the acetylenic hydrogen by the metal. The reactions of acetylene with copper and silver salts in neutral or acid media are much more complicated.

The first indications of the formation of insoluble acetylenic compounds in dilute neutral aqueous solutions of Cu_2Cl_2 is in Bertholet's work[9]. Chevastelon[10] obtained the acetylide $C_2Ag_2.AgNO_3$ from neutral silver nitrate solution. The passage of acetylene into an acidified aqueous or alcoholic solution of copper(I) chloride led to the formation of colourless crystals, the composition of which was close to the formula $C_2H_2.Cu_2Cl_2$.[11] Chevastelon also isolated more complex compounds: white $C_2H_2.2Cu_2Cl_2.KCl$ and yellow $C_2H_2.4Cu_2Cl_2.2KCl$.[12]

Manchot and coworkers[13,14] found that on treatment of a hydrochloric acid solution of copper(I) chloride with acetylene a transparent solution of an addition product is formed initially, which is then converted into a violet precipitate of composition $Cu_2C_2.CuCl.H_2O$, with liberation of acetylene.

Various authors have described a large number of compounds isolated from neutral and acid solutions of silver salts but the formulae proposed for some of them (for example, $4Ag_2S_2O_3.Na_2S_2O_3.86Ag_2C_2.13C_2H_2$ [15]) raise doubts as to the individuality of the products.

The variety, and often the contradiction, in the results on the composition and structure of the acetylides reflects the complexity of the work with these substances. The explosive tendency and low solubility often do not permit the usual methods of purification to be used. At the same time the voluminous precipitates which are formed can absorb and retain firmly various impurities on the surface. The sensitivity of the acetylides to the action of oxidants and also the possibility of the conversion of the compounds formed in the presence of an excess of one of the reagents creates additional difficulties for investigators. All this evidently led in a series of instances to mixtures being described as pure substances and the adsorbed impurities being included in the composition of the acetylides.

In this connection a series of studies by Vestin and coworkers[16-24], in which the authors examine the acetylene compounds of silver and copper as analogues of sparingly soluble inorganic salts and determine the conditions of formation and existence of various compounds by measurement of equilibria, is of interest. This was usually possible. For example, by starting from the equation for the formation of silver acetylide

$$C_2H_2 + 2\,Ag^+ \rightleftarrows C_2Ag_2\,(solid) + 2\,H^+ \quad K_1 \qquad (1)$$

an expression can be written for the equilibrium constant:

$$K_1 = \frac{[H^+]^2}{[C_2H_2]\cdot[Ag^+]}.$$

When Eqn. (1) is written in the form

$$H^+ + {}^1/_2\,C_2Ag_2\,(solid) \rightleftarrows {}^1/_2\,C_2H_2 + Ag^+ \qquad (2)$$

then

$$K = \frac{[Ag]\cdot[C_2H_2]}{[H^+]} = \frac{1}{K_1}.$$

Hence

$$\lg K = \lg[Ag^+] + {}^1/_2\,\lg[C_2H_2] - \lg[H^+]$$

$$pK = -\lg K = -\lg[Ag^+] - {}^1/_2\,\lg[C_2H_2] - \lg[H^+],$$

or

$$pK = (pAg - pH) + {}^1/_2\,pP_A,$$

where P_A is the partial pressure of acetylene in the gas mixture and (pAg – pH) the difference in potentials between silver and glass electrodes. All these three quantities can be measured directly. As a result of the investigations it was shown that in ammoniacal aqueous solutions of silver salts Ag_2C_2 is precipitated but usually complexes are not formed. It is suggested that the yellow and white silver acetylides are modifications distinguished by size of the colloidal particles. Ag_2C_2 was also obtained by the reaction between dry silver acetate and acetylene:

$$2\,CH_3COOAg + HC{\equiv}CH \rightarrow 2\,CH_3COOH + AgC{\equiv}CAg.$$

Of the complex silver acetylides described earlier the individuality of the following were confirmed: $C_2Ag_2.AgNO_3$, $C_2Ag_2(AgNO_3)_6$, $C_2Ag_2.AgCl$, $C_2Ag_2.Ag_2SO_4$, and another two were obtained $C_2Ag_2.HPO_4$ and $C_2Ag_2.(AgClO_4.H_2O)_2$. All the compounds are colourless and crystallise well. The perchlorate and nitrate (1 : 1) detonate with considerable force, the others weakly.

Some authors[16-24] suggested the existence of soluble acetylene compounds of silver $(C_2Ag_2)_n.(Ag^+)_m$. The dissolution of a certain amount of acetylene in concentrated solutions of silver salts without the formation of a precipitate was noted, whereas an increase in the pH suggested the chemical bonding of acetylene. It was noted[25] that not a single silver complex is known in which the acetylene would retain both hydrogen atoms. Neither could a non-symmetrical silver acetylide be obtained[16,24]; it was shown[16] that information about the existence of complexes containing such an acetylide is unreliable. Any asymmetric copper compound of the type $HC{\equiv}CCu$ has also not been identified. The red copper acetylide obtained from ammoniacal solutions of copper salts or from dilute solutions of CuCl in an aqueous solution of alkali metal chloride

was found to have the composition Cu_2C_2 and reports of the existence of the hydrate $Cu_2C_2.H_2O$ were considered erroneous by these authors.

The complexity and variety of the compounds formed in neutral and acid media is shown by the example of the C_2H_2–CuCl–KCl–H_2O system from which no less than six solid and four dissolved compounds of acetylene can be prepared. Österlöf's[25] results on the existence of the colourless crystalline compounds $C_2H_2(CuCl)_3$ and $C_2H_2(CuCl)_2$ were confirmed.

An investigation of the violet complex, to which Chevastelon ascribed the formula $C_2H_2.Cu_2Cl_2.Cu_2O$ but Manchot and coworkers[14] $C_2Cu_2.CuCl.H_2O$, showed that this complex contains Cu_2C_2, and the ratio Cu_2C_2 : CuCl equals unity, which supports the Manchot formula. The existence of several compounds of the type $(C_2Cu_2).(CuCl)_m$ was suggested.

It was found that in a neutral concentrated solution of KCl (or NH_4Cl) and CuCl acetylene forms a yellow crystalline precipitate for which the formula $M_2[C_2(CuCl)_8]$, where $M^+ = K^+$, NH_4^+, was proposed[19]. There are grounds for considering that the violet and yellow complexes are in equilibrium:

$$Cu_2C_2 \cdot CuCl\ (solid) + 5\ CuCl + 2\ KCl \rightleftarrows K_2[C_2(CuCl)_8]\ (solid).$$

It was found subsequently that both in solution and in the solid phase compounds of two types can be formed—acetylides (bright yellow) and molecular (colourless)[20], the first in alkaline solutions, the second in neutral and acid. The results obtained suggest that in the HCl–CuCl–H_2O and HCl–$HClO_4$–CuCl–H_2O systems there are soluble complexes $CH_2.CuCl$, $C_2H_2.CuCl_2$, and $C_2H_2Cu^+$. In aqueous solutions CuCl–MCl (M = alkali metal) which contain an insignificant amount of the base, a small quantity of acetylene brings about an intense yellow coloration. The concentration of the yellow product is determined by the equilibrium, which can be written in the form:

$$C_2H_2 + n\,CuCl \rightleftarrows C_2(CuCl)_n^{-2} + 2\,H^+$$

where n lies in the range 6–8.

These results are correlated with the existence of solid complexes $M_2[C_2(CuCl)_8]$, which are readily soluble for Na^+ and Li^+, and poorly soluble for K^+ and NH_4^+.

In connection with the nature of the acetylene–metal bond it was shown[21] that copper molecular compounds of acetylene are probably close to the corresponding alkenic compounds, that is, they are π-complexes. As for the acetylenic complexes, there is only the general view that they should contain a special type of C–M bond.

The first report of the synthesis of a copper(II) acetylide belongs to Söderbaum[26]. By passing acetylene into ammoniacal solutions of various copper(II) salts he obtained a black explosive substance with the approximate molar ratio C : Cu = 2. The formulae proposed on the basis of the analytical results—the approximate $nC_6Cu_3.H_2O$ and the more accurate $nC_{17}Cu_8H_4O_3$, make it extremely doubtful that the substance is an individual and the fact that only a little acetylene is liberated under the action of hydrochloric acid, most of the carbon being converted into a humus-like substance—suggest that the product obtained is not a copper(II) acetylide.

Easterbrook and Erskine showed[8] that the precipitate obtained on passing acetylene into an ammoniacal solution of $CuCl_2$ does not contain copper(II) but is a mixture of Cu(I) acetylides and poly-ynes.

Nast and Pfab[27] obtained copper(II) acetylide in liquid ammonia by the reaction:

$$[Cu(NH_3)_4](NO_3)_2 + 2\,KC_2H \rightarrow CuC_2 + C_2H_2 + 2\,KNO_3 + 4\,NH_3.$$

The authors consider that they had isolated the compound described earlier by Söderbaum. With acid a carbonaceous residue is also formed. The only analysis for copper, made a day after obtaining the precipitate, gave a 2.7% difference from theory. We think that the results given are completely insufficient for drawing a definite conclusion about the nature of the product obtained.

By the reaction of acetylene with aqueous solutions of copper(II) salts Brameld and coworkers[7] obtained a precipitate whose composition and appearance varied with the anion, the pH of the medium, and the nature of the alkali. For products formed in ammoniacal solutions the C : Cu ratio was 2.7–2.8, for those formed in NaOH solutions, 1.99–2.07. Silvery grey, extremely explosive plates with ratio C : Cu = 2.18 separated from concentrated ammoniacal and acetic acid solutions of copper(II) acetate.

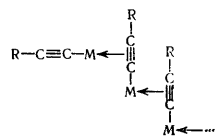
However, not one of the compounds described corresponds to the formula CuC_2—the discrepancy between the analyses and theory is always < 20%, hence here also there is also either a mixture or a compound of more complicated structure containing other components as well as C and Cu.

Feitknecht and Hugi-Carmes[28] made a detailed study of the conditions for the formation of red and black copper acetylides and even attempted to investigate the structure of these products by an X-ray diffraction method. The authors found that the acetylide precipitates obtained by Brameld and coworkers[7] from ammoniacal solutions of copper(II) sulphate and acetate, give identical X-ray diagrams, irrespective of their appearance. They did not observe bivalent copper in the acetylides obtained from solutions of copper(II) salts.

III. STRUCTURE OF ACETYLIDES

Favorskii[29] first made a cryoscopic determination of the molecular weight of copper t-butylacetylide and found that it is an octamer in benzene. The same result was obtained by ebullioscopy[30].

Calvin and coworkers[31,32] suggested that copper(I), silver(I), and gold(I) acetylides are coordination polymers in which each metal atom is π-bound with at least two acetylenic groupings. The electrons are drawn from the π_u-bonding acetylenic orbitals to the metal and from the filled d-orbitals of the metal to the unoccupied π_g-antibonding orbitals of the acetylene:



where $M^+ = Cu^+$, Ag^+, Au^+.

Both these effects should decrease the order of the C≡C bond and lead to a decrease in its frequency. Coates and Parkin[30,33] investigated the infrared spectra of copper and silver acetylides. It is known that disubstituted acetylenes absorb light in the range 2190–2260 cm^{-1}, owing to the stretching vibrations of the C≡C bond[34].

The characteristic frequency of the triple bond in the π-complex of di-t-butylacetylene with platinum is decreased[35] by 200 cm^{-1} and analogous effects are noted in transition metal complexes with alkenes[36]. In confirmation of the fact that copper acetylides are coordination polymers it was found[30,33] that these compounds absorb light in the range 1920–1960 cm^{-1}, that is, the frequency of the C≡C stretching vibrations lies 270–300 cm^{-1} lower

than in disubstituted acetylenes. The depression of the frequency is somewhat less appreciable in silver and gold acetylides (by 150–200 cm^{-1}).

The X-ray diffraction investigation of the acetylides of acetylene showed that they were crystalline but the smallness of the particles prevented any decisions concerning structure. Thus, according to the X-ray powder diagram Ag_2C_2 is a distinctly crystalline substance consisting of agglomerates of particles with a size of $> 0.1\ \mu$.[24] X-Ray diffraction data for the acetylides have also been published elsewhere[28,33].

Copper(I) and silver acetylides and cyanides have much in common. The electrons which form the coordinate bond in acetylides are the π-electrons of the acetylene groups, and in cyanides, the free pair of p-electrons of the nitrogen atom. Unfortunately, there is no information about the value of the characteristic frequency of the stretching vibrations $\nu_{C\equiv N}$ for the complexes of copper cyanide with electron-donating ligands, for which evidently an effect opposite to that observable in the infrared spectra of acetylide complexes can be expected.

Terenin and coworkers[37] showed that $\nu_{C\equiv N}$ in nitriles is increased in the formation of complexes with Lewis acids ($SnCl_4$, $AlCl_3$, etc.), copper in the cyanide can be regarded as a Lewis acid in relation to the nitrogen of the other molecule; if such an analogy is correct the release of the pair on the nitrogen should lead to a decrease in $\nu_{C\equiv N}$.

Brune and Zeil[38] consider that in nitriles the carbon of the C≡N bond group is in an sp-hybrid state, as in the acetylenes, but the nitrogen is not hybridised. In confirmation of the pair on the nitrogen having an s-character and not participating in the hybridisation as in amines the authors refer to the low basicity of the nitriles and the absence of $n \rightarrow \pi^*$ transitions in their ultraviolet spectra. Hence the σ-bond in the C≡N group will be formed by the sp-hybrid orbital of the carbon and one p-orbital of the nitrogen, but the π-bond from the C π-electrons and the N p-electrons. During coordination sp-hybridisation also appears at the nitrogen.

From quantum-chemical considerations the sp–sp bond is more stable than the sp–p bond. This is due to an increase in the strength of the bond inside the C≡N group on going from free nitrile to coordination-bound, and to the increase in $\nu_{C\equiv N}$.

However, the difference in the structure of the copper(I) acetylides and cyanide has more effect on the reactivity than on the nature of the processes which take place—copper cyanide is usually more active than acetylides in the various reactions.

IV. CHEMICAL PROPERTIES OF ACETYLIDES

1. Reactions with Formation of Acetylide Ions

The investigation of the chemical properties of the acetylides was begun by Böttger[1], who found that on treating copper acetylide with potassium cyanide a hydrocarbon is liberated, which burns with a very smoky flame. The reaction is:

$$Cu_2C_2 + 2\,KCN + 2\,H_2O \rightarrow 2\,CuCN + HC\equiv CH + 2\,KOH\,. \qquad (3)$$

In this reaction copper acetylide behaves as a sparingly soluble salt which is characterised by a definite solubility product. The bonding of the copper ions by the cyanide ions leads to a shift of the equilibrium to the right but the hydrolysis of the acetylide ion makes this process irreversible. Since the solubility product of the acetylide is scarcely greater (and usually much less) than of copper cyanide (10^{-14})[39] the occurrence of the reaction is evidently due to the formation of complex cyanides of copper $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$. The instability constants of these ions are each[40] 5×10^{-28}. An approximate calculation shows that the copper ion concentration thus created in 1 M solutions is approximately seven orders of magnitude below the Cu^+ concentration in saturated CuCN solutions. Hence, Eqn. (3) is the overall process for the following reactions:

$$Cu_2C_2 \rightleftarrows 2\,Cu^+ + C_2^{2-}, \qquad (a)$$

$$2\,Cu^+ + 6\,CN^- \rightleftarrows 2\,[Cu\,(CN)_3]^{2-}, \qquad (b)$$

$$C_2^{2-} + K^+ + H_2O \rightleftarrows C_2H_2 + 2\,KOH\,. \qquad (c)$$

Like copper cyanide, acetylides are capable of the formation of ionic complexes with acetylenic groups as ligands. Nast and coworkers obtained several such compounds by the action of alkali metal acetylides on the acetylides of copper(I),[27] silver(I),[41] and gold(I),[42] in liquid ammonia:

$$M_2\,[Cu\,(C\equiv CR)_3] \text{ and } M\,[Cu\,(C\equiv CR)_2]\,,$$

where M = Na, K; R = H, CH_3, C_6H_5;

$$K\,[Ag\,(C\equiv CH)_2] \text{ and } K\,[Ag\,(C\equiv CR)_2]\,,$$

where R = CH_3, C_6H_5; and

$$K\,[Au\,(C\equiv CH)_2],\ K\,[Au\,(C\equiv CPh)_2]\,.$$

The bifunctionality of acetylene imparts a singularity to this class of acetylide complexes, making possible the existence of μ-complexes, unknown for cyanides:

$$K_2\,[HC\equiv C—Au—C\equiv C—Au—C\equiv CH]\,.$$

An interesting complex acetylide of Cu^0 was obtained[43] by the reduction of $K_2[Cu(C\equiv CPh)_3]$ with metallic lithium in liquid ammonia and precipitation with $Ba(CNS)_2$. The infrared spectrum and diamagnetism of this compound $Ba_3[Cu(C\equiv CPh)_3]_2$ allowed its anion to be ascribed the dinuclear structure:

$$[(PhC\equiv C)_3\,Cu—Cu\,(C\equiv CPh)_3]^{6-}.$$

Whereas cyanide ions stabilise copper(II) cyanide, by forming the anionic complexes $[Cu(CN)_4]^{2-}$ the complex acetylides of copper(II) are evidently even less stable than its simple acetylenic compounds. Attempts to obtain complex acetylides of copper(II) ended in failure. In the reaction of $[Cu(NH_3)_4].(NO_3)_2$ with KC≡CH in liquid ammonia instead of the expected complex acetylide a black, very explosive precipitate is formed, which the authors consider[27] to be copper(II) acetylide, CuC_2:

$$[Cu\,(NH_3)_4]\cdot(NO_3)_2 + KC\equiv CH \rightarrow 2\,CuC_2 + C_2H_2 + 2\,KNO_3 + 4\,NH_3\,.$$

Quantitative reduction of Cu^{II} to Cu^{I} takes place with potassium methylacetylide and phenylacetylide:

$$2\,[Cu\,(NH_3)_4]^{2+} + 4\,(C\equiv C—CH_3)^- \rightarrow 2\,CuC\equiv C—CH_3 + H_3C—C\equiv C—C\equiv C—CH_3\,.$$

The reaction takes place in stages. A mixed salt of copper(I) and copper(II) is formed as an intermediate:

$$3\,[Cu\,(NH_3)_4]^{2+} + 6\,(C\equiv CPh)^- + NH_3 \rightarrow [(Cu\,(NH_3)_4]\cdot[Cu\,(C\equiv CPh)_2]_2\cdot x\,NH_3 + \\ + PhC\equiv C—C\equiv C—Ph + 8\,NH_3$$

which decomposes on distilling off the solvent, with reduction of the copper(II) and dimerisation of the acetylene radicals:

$$[Cu\,(NH_3)_4]\cdot[Cu\,(C\equiv CPh)_2]_2\cdot x\,NH_3 \rightarrow \\ \rightarrow 3\,CuC\equiv CPh + (x+4)\,NH_3 + {}^1/_2\,Ph—C\equiv C—C\equiv C—Ph\,.$$

All the complex acetylides of Cu copper(I), unlike the cyanide complexes, are extremely sensitive to moisture, which is due to the acidic properties of the alkynes being much weaker than those of even such a weak acid as HCN ($K = 4.8 \times 10^{-10}$).

2. Complexes with Electron-Donating Molecules

Like most of the compounds of copper(I), the acetylides tend to form complexes with molecules which are donors of a free pair of electrons. However, these complexes are usually considerably less stable than the corresponding derivatives of inorganic copper(I) compounds.

In liquid ammonia many acetylides form colourless insoluble ammines, stable only at low temperatures. Thus, copper phenylacetylide[27] forms the compound $C_6H_5C{\equiv}CCu.NH_3$. The analogous compound of copper cyanide, $CuC{\equiv}N.NH_3$, on being dried in a vacuum, is completely stable in dry air under ordinary conditions[44]. Copper phenylacetylide can be slowly extracted with isopropylamine[33].

Silver phenylacetylide dissolves in various amines and with isopropylamine it forms the complex $Pr^iNH_2.AgC{\equiv}C-Ph$, which rapidly loses the amine in air[31].

Gold acetylides form much more stable ammines. In the reaction of a solution of AuI in liquid ammonia—polymeric $(AuI)_n$ dissolves in liquid ammonia to form $AuI.6NH_3$—with potassium acetylide a yellow-white explosive ammine complex $Au_2C_2.xNH_3$ is precipitated, which after 4 h in a vacuum at room temperature is converted into a black-brown $Au_2C_2.xNH_3$, insensitive to moisture but extremely explosive[42]. With phenylacetylene, an aqueous ammoniacal solution of $Na_3[Au(S_2O_3)_2].2H_2O$ forms white, diamagnetic, light-sensitive $AuC{\equiv}C-C_6H_5.NH_3$, sparingly soluble only in liquid NH_3.[44]

It has been noted[27] that a suspension of dry Cu_2C_2 in liquid NH_3 is indifferent to CO. On passing dry, pure carbon monoxide into a suspension of copper methylacetylide or phenylacetylide in liquid ammonia a colourless solution of an adduct of the acetylide with CO is formed. The vaporisation of ammonia leads to the decomposition of the compound into the acetylide and carbon monoxide[45].

The copper(I) carbonyl cyanide is also unstable. With the similarly obtainable carbonyl acetylides at −79°C it decomposes with liberation of CO, even at the boiling point of liquid ammonia. Carbon monoxide is displaced from it even on blowing nitrogen through the solution[44].

A suspension of gold phenylacetylide in liquid ammonia, unlike copper phenylacetylide, does not react with CO, that is, it behaves analogously to copper acetylide[42].

On adding *p*-toluisonitrile to an ether–pyridine suspension of copper phenylacetylide at −10°C a colourless crystalline complex

$$(CH_3C_6H_4{-}N{\equiv}C)_3{\cdot}Cu{-}C{\equiv}C{-}C_6H_5$$

is formed rapidly[46]. The compound is extremely labile, is decomposed by water and organic solvents, whereas it is completely stable thermally (it decomposes at ~ 100°C). Keeping in air leads to a decomposition of the complex in a few hours. The loss of isonitrile molecules takes place even under the action of dry ether at room temperature. In aqueous pyridine at 0°C the complex dissolves with liberation of CO, since hydration of the isonitrile molecule takes place simultaneously with the decomposition:

$$C_7H_7{-}N{\equiv}C \xrightarrow{H_2O} CO + C_7H_7{-}NH_2 \xrightarrow{C_7H_7N{\equiv}C} C_7H_7{-}NH{-}CH{=}N{-}C_7H_7 .$$

It is especially interesting that there is an analogy between the other complexes of the acetylides, the reaction of the isonitrile complex of the phenylacetylide with chloroform, dissolution in which is accompanied by rapid replacement of the phenylacetylene residue by chlorine:

$$(Ar{-}N{\equiv}C)_3\,Cu{-}C{\equiv}C{-}C_6H_5 \xrightarrow{CHCl_3} (Ar{-}N{\equiv}C)_3 \cdot CuCl .$$

Copper, silver, and gold acetylides form stable complexes with tertiary phosphines, arsines, and stilbines. Coates and coworkers[30,31,33,47] synthesised and studied a large number of such complexes. The stability of these complexes, which is sharply contrasted with the instability of the ammine and amine complexes, was attributed by the authors to the ability of phosphorus and its analogues to back coordination owing to the vacant *d*-orbitals. Depending on the ratio of the components, compounds with a different number of ligands belonging to one metal atom can be obtained. The maximal number is three but the only complex of this composition:

$$PhC{\equiv}C{-}Cu\cdot(PMe_3)_3$$

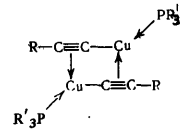
was unstable in solution, which did not allow its molecular weight to be determined. As the cryoscopic investigations showed, complexes with two ligands,

$$Bu^t{-}C{\equiv}CCu\cdot(PMe_3)_2 \text{ and } Ph{-}C{\equiv}C{-}Cu\cdot(PMe_3)_2$$

are monomeric in benzene, but the monophosphinic complexes:

$$Bu^t{-}C{\equiv}CCu\cdot PMe_3,\ Ph{-}C{\equiv}CCu\cdot PMe_3,\ Ph{-}C{\equiv}CCu\cdot PEt_3 \text{ etc.}$$

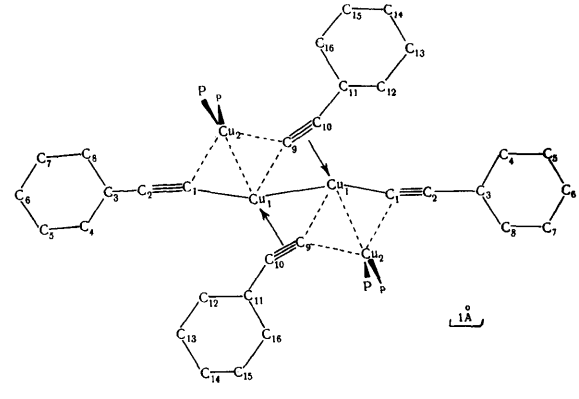
are dimeric in nitrobenzene. The authors suggest that the dimeric complexes are constructed in the following manner:



Coates and Parkin[30] give the results of an X-ray structural investigation of the complex

$$(PhC{\equiv}C{-}Cu\cdot CuPMe_3)_4.$$

Each tetrameric cell contains a zig-zag of four copper atoms. With the exception of phosphinic groups lying above and below the plane of the diagram, the structure of the tetramer is almost planar. Atoms $C_{(4)}$ and $C_{(5)}$ remain 0.2 Å from the *X*–*Y* plane of the diagram, but $C_{(7)}$, $C_{(8)}$, $C_{(15)}$, and $C_{(16)}$, 0.3 Å. The departure of all the other atoms along the *Z*-coordinate averages 0.06 Å. The benzene ring is only slightly inclined to the *X*–*Y* plane. The Cu–Cu distance ($Cu_{(1)}$–$Cu_{(1)}$ = 2.7 Å, $Cu_{(1)}$–$Cu_{(2)}$ = 2.45 Å) is almost the same as in metallic copper.



The monophosphinic complexes of silver acetylides are also not monomeric. For example, $Rh-C\equiv CAg.PEt_3$ is dimeric in nitrobenzene, and for it a structure analogous to that given above is proposed. Unlike the compounds of copper and silver the monophosphinic derivatives of gold acetylides are monomeric, which is explained by the relatively low tendency of Au^+ to an increase in the coordination number above 2. The degree of association of the phosphinic complexes can be varied within wide limits, depending on the composition of the complex, its concentration, and the nature of the solvent. Thus $Ph-C\equiv CCu.PEt_3$ is trimeric in nitrobenzene and has a degree of association from 3.3 to 3.8 (depending on the concentration) in benzene.

Unexpected properties destroying the concept of the monophosphinic complexes as coordination unsaturated compounds and therefore associated in solutions, were displayed by $p\text{-}O_2NC_6H_4-C\equiv CCuPPh_3$. It was monomeric in nitrobenzene. In the solid state it could be obtained in two different forms—bright red and orange, having identical composition. In benzene it is dimeric, that is, behaves similarly to many other complexes of similar structure. Monomeric diphosphinic complexes are usually coloured more than weakly associated compounds. For example, the octamer $Bu^t-C\equiv C-Cu$ is orange-red[29], the dimeric $Bu^t-C\equiv CCu.PMe_3$ is yellow-green[30], but the monomeric $Bu^t-C-CCu.(PMe_3)_2$ is colourless[30]. The phosphinic complexes of copper acetylides are completely stable thermally (most of them melt without decomposition at temperatures up to 150°C) but gradually decompose on storage in air. The complexes of the diacetylenes seemed unexpectedly stable in this respect. Whereas $Ph-C\equiv CCu.PEt_3$ is converted into yellow amorphous $Ph-C\equiv CCu$ after standing in air for 1-2 days, $Ph-C\equiv C-C\equiv CCu.PEt_3$ remains unchanged after a week.

The complexes of silver acetylides with phosphines decompose more rapidly on access of air and also in the light.

3. Reactions with Halogens and Halogenoacetylenes

Even Böttger[1] in studying the chemical properties of copper acetylide found that the reaction with chlorine is explosive, $CuCl_2$, HCl, and carbon being formed. In reacting with Br_2, or on grinding with I_2, copper acetylide ignites and carbon is liberated. On reacting silver acetylide with iodine in ether, Berend[48] obtained di-iodoacetylene. Bayer[49] found that a mixture of di-iodoacetylene and di-iododiacetylene is obtained from copper acetylide under these conditions. By the reaction of an aqueous suspension of copper acetylide of propargyl alcohol with iodine, Lespieau[50] obtained iodopropargylic alcohol:

$$HO-CH_2-C\equiv C-Cu + I_2 \rightarrow HO-CH_2-C\equiv CI + CuI .$$

It is interesting to compare the reaction of halides with acetylenic derivatives of various metals and the reaction of halides with copper acetylides. It is known that during the action of halides on the acetylenic derivatives of various metals the metal is replaced by halogen[48,51-57]:

$$BrMgC\equiv CMgBr + 2\,X_2 \rightarrow XC\equiv CX + 2\,MgBrX, (X=I, Br),$$
$$RC\equiv CMgBr + X_2 \rightarrow RC\equiv CX + MgBrX, (X=I, Br),$$
$$(RC\equiv C)_2Hg + 2\,Br_2 \rightarrow 2\,RC\equiv CBr + HgBr_2,$$
$$AgC\equiv CAg + 2\,I_2 \rightarrow IC\equiv CI + 2\,AgI,$$
$$RC\equiv CNa\ (K, Li) + Cl_2 \rightarrow RC\equiv CCl + NaCl\ (KCl, LiCl).$$

In all these instances the interaction proceeds as a competition of the halogen with the metal for the redistribution of electrons of the existing metal-carbon bond since the metals (excluding silver) are found in their highest oxidation states.

For copper acetylides, in addition to the analogous process:

$$R-C\equiv C-Cu + X_2 \rightarrow R-C\equiv C-X + CuX$$

there is another possibility—oxidation of Cu^+ to Cu^{2+}. Unlike univalent copper, bivalent copper is a typical transition metal. It could be expected that the Cu-C σ-bond in the compounds being formed, as in most compounds of metals with an incomplete *d*-level, will be weak and easily broken with formation of a new compound of Cu^+ or Cu^{2+} and an acetylenic radical:

$$RC\equiv CCu \longrightarrow [RC\equiv C\overset{\cdot}{\frown}Cu^+\ X^{\cdot-}] \longrightarrow RC\equiv C^{\cdot} + CuX + X^{\cdot}, (\text{or } CuX_2)$$

$$2RC\equiv C^{\cdot} \longrightarrow RC\equiv C-C\equiv CR .$$

The weakness of such σ-bonds is explained by the similarity in energy of the electrons of the bond and the *d*-electrons of the metal[58]. The ease of interaction here must depend on the properties of the acetylide as a base and the halogen as a Lewis acid. The strengths of the halogens as Lewis acids change in the order

$$F_2 > Cl_2 > Br_2 > I_2.$$

This is well illustrated by the relative rates of addition of the halogens and interhalogen compounds at a double bond[59]:

I—I	1	I—Br	3000	I—Cl 100 000
		Br—Br	10 000	Br—Cl 4 000 000 .

In the molecule of the acetylide the electron-accepting groupings at the C≡C bond should hinder the removal of the *d*-electron of copper and electron-donating ones facilitate it.

Actually it was found[60,61] that in the reaction of copper acetylide with iodine—a weak Lewis acid, at room temperature only iodoacetylenes are formed. The reactions evidently proceed through a four-centre state of the type:

$$R-C\equiv C-Cu$$
$$\delta^+X\ \ X^{\delta-} .$$

The simplicity of the experiment, the possibility of using acetylides with different functional groups and the high yields of iodoacetylenes allow this reaction to be regarded as a convenient preparative method for making iodoacetylenes.

By introducing iodine monobromide into the reaction it was shown that the final product is determined by the initial polarisation of the reacting molecules:

$$C_6H_5-\overset{\delta-}{C}\equiv\overset{\delta+}{C}-Cu + \overset{\delta+}{I}\,\overset{\delta-}{Br} \rightarrow C_6H_5C\equiv C-I + CuBr .$$

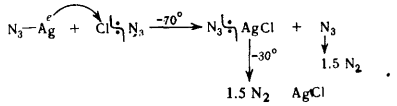
Actually, iodophenylacetylene acetylene was obtained in 60% yield.

Even at low temperatures, bromine oxidises more than half copper phenylacetylide to diphenylbutadiyne—the yield of bromophenylacetylene is ⩾ 40%. Copper *p*-nitrophenylacetylide gives under these conditions ~ 70% *p*-nitrobromophenylacetylene and only traces of di-(4-nitrophenyl)-butadiyne[61-63]. Hence acetylides with electron-withdrawing substituents at the triple bond can give bromoacetylenes in high yields.

The yield of chlorophenylacetylene from the action of a carbon tetrachloride solution of chlorine on copper phenylacetylide does not exceed 20%.

The possibility of an oxidation is also not ruled out for silver acetylides. It is known, for example, that silver

azide reacts with chlorine azide at −70°C with the formation of silver(II) azide chloride, which decomposes when the temperature is raised to −30°C to give silver chloride and molecular nitrogen[64]. The reaction is interesting in that with an obvious analogy with the oxidising action of halogens on copper acetylides an intermediate compound of the bivalent metal is fixed:



However, the bivalent state is not very characteristic for silver and is achieved only in the reaction of its compounds with very strong oxidants.

Since the ethynyl group exhibits a strong *I*-effect, the appearance of quasi-halide properties can be expected from the halogenoacetylenes, in particular the ability to play the part of strong electrophilic reagents. The dipole moments of the monohalogenoacetylenes[65] show that the electron-withdrawing properties of ethynyl and the halogens in these compounds are of the same order of magnitude:

$$HC{\equiv}CF \quad 0.75\ D\ ,$$
$$HC{\equiv}CCl \quad 0.44\ D\ ,$$
$$HC{\equiv}CBr \quad 0.00\ D\ .$$

The result of the electrophilic substitution, as for the halogens and interhalogen compounds, will be determined by the initial polarisation of the halogen derivative, for example[66,67]:

$$2\,R{-}C{\equiv}C{-}MgX + \overset{\delta+}{I}C{\equiv}Cl \rightarrow 2\,R{-}C{\equiv}C{-}I + XMgC{\equiv}CMgX\ ,$$
$$R{-}C{\equiv}C{-}MgX + \overset{\delta-}{Cl}C{\equiv}CCl \rightarrow R{-}C{\equiv}C{-}C{\equiv}C{-}Cl + MgXCl\ .$$

Actually, it was found[68] that di-iodoacetylene reacts with copper acetylides in the same way as with organomagnesium compounds:

$$2\,R{-}C{\equiv}C{-}Cu + IC{\equiv}CI \rightarrow 2\,R{-}C{\equiv}C{-}I + CuC{\equiv}CCu\ .$$

It was also shown[68] that the copper is replaced by iodine in reactions of the acetylides with di-iodoacetylene and iodonitroform $IC(NO_2)_3$.

The reaction of bromoacetylenes with acetylenes in the presence of catalytic amounts of CuCl, dissolved in the primary amine, and of a small quantity of reductant ($NH_2OH.HCl$) was proposed by Chodkiewicz and Cadiot[69] as a method for the synthesis of non-symmetrical diacetylenic compounds. Although the overall process is expressed by the equation:

$$R{-}C{\equiv}CH + BrC{\equiv}CR' \rightarrow R(C{\equiv}C)_2R' + HBr$$

the reaction actually proceeds between bromoacetylene and the acetylide[70]:

$$R{-}C{\equiv}CH + Cu^{+} \rightarrow R{-}C{\equiv}C{-}Cu + H^{+}\ , \qquad (4)$$
$$R{-}C{\equiv}C{-}Cu + Br{-}C{\equiv}C{-}R' \rightarrow R{-}C{\equiv}C{-}C{\equiv}C{-}R' + CuBr\ . \qquad (5)$$

There is also the side-process of condensation of the bromoacetylene under the action of Cu^{+} ions:

$$2\,R'{-}C{\equiv}C{-}Br + 2\,Cu^{+} \rightarrow R'{-}C{\equiv}C{-}C{\equiv}C{-}R' + 2\,Br^{-} + 2\,Cu^{2+} \qquad (6)$$

which is thought to proceed through the following two stages:

$$R'{-}C{\equiv}C{-}Br + 3\,Cu^{+} \rightarrow R'{-}C{\equiv}C{-}Cu + Br^{-} + 2\,Cu^{2+}\ (\text{slow})\ , \qquad (7)$$

$$R{-}C{\equiv}C{-}Cu + Br{-}C{\equiv}C{-}R' \rightarrow R'{-}C{\equiv}C{-}C{\equiv}C{-}R' + Cu^{+} + Br^{-}\ (\text{fast})\ . \qquad (8)$$

The formation of the dimer ($R'{-}C{\equiv}C{-}C{\equiv}C{-}R'$) from the acetylide can be explained by the oxidising action of the Cu^{2+} ions which are produced in reaction (6), or by the replacement of the copper in the acetylide by halogen under the action of the halogenoacetylene. The halogenoacetylene obtained can undergo condensation (6) just like the initial one. It is possible for both these processes to proceed simultaneously. A thorough survey of the Cadiot–Chodkiewicz condensation and also extensive data on its practical application have been given in a review[70].

It was found[68] that in the reaction of bromoacetylenes and iodoacetylenes ($R{-}C{\equiv}C{-}X$) with copper acetylides ($R'{-}C{\equiv}C{-}Cu$), introduced in stoichiometric amounts, a mixture of three diynes is formed:

$$R{-}C{\equiv}C{-}C{\equiv}C{-}R',\quad R{-}C{\equiv}C{-}C{\equiv}C{-}R \quad \text{и} \quad R'{-}C{\equiv}C{-}C{\equiv}C{-}R'.$$

For example, from a reaction mixture of bromophenylacetylene with copper *p*-bromophenylacetylide in dimethylformamide the products diphenylbutadiyne, 1-*p*-bromophenyl-4-phenylbutadiyne, and di-(*p*-bromophenyl)butadiyne were isolated.

The similarity in the chemical properties of copper cyanide and acetylides is observed in the reaction of CuCN with iodo- and bromo-phenylacetylenes. It was shown[62] that this results in the formation of phenylpropiolonitrile in ~ 40% yield. When the iodophenylacetylene was used, diphenylbutadiyne was also isolated from the reaction mass. The formation of diphenylbutadiyne during the synthesis of phenylpropiolonitrile from iodophenylacetylene and copper cyanide could be the result not only of condensation under the action of Cu^{+}, but also of the exchange of copper and halogen between the initial components.

4. Reactions with Aromatic and Unsaturated Halogen Derivatives

Friedman and Schlechter[71] found that aryl chlorides and bromides in boiling dimethylformamide react with copper(I) cyanide to form nitriles in yields from 80% to quantitative:

$$ArX + 2\,CuCN \rightarrow (ArCN)_2{\cdot}CuX + CuX\ ,$$
$$(ArCN)_2\,CuX \xrightarrow{H^{+}} 2\,ArCN + CuX\ .$$

The similarity between the copper acetylides and cyanide led the authors of the present review to investigate the possibility of the introduction of acetylenic groups into the aromatic nuclei in an analogous way. It was found[60] that when aryl iodides are boiled with copper acetylides in dimethylformamide for 8–16 h disubstituted acetylenes are formed in 30–70% yield:

$$ArC{\equiv}C{-}Cu + Ar'I \rightarrow Ar{-}C{\equiv}C{-}Ar' + CuI\ .$$

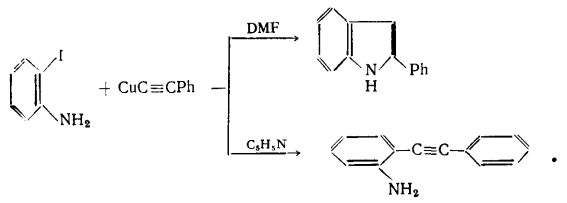
Aryl iodides with various functional groupings (nitro-, amino-, hydroxy-, etc.) can be used in the synthesis. In di-iodoaryl compounds one or both of the iodine atoms can be replaced by acetylenic radicals. Boiling a suspension of copper *p*-iodophenylacetylide in dimethylformamide leads to its autocondensation into the acetylide of 4-iodo-4-ethynyltolane.

This reaction was described simultaneously and independently by Castro and Stephens[72,73], who synthesised several tolanes in yields of 70–90% by the reaction of *para*- and *ortho*-substituted derivatives of iodobenzene with copper phenylacetylide in boiling pyridine:

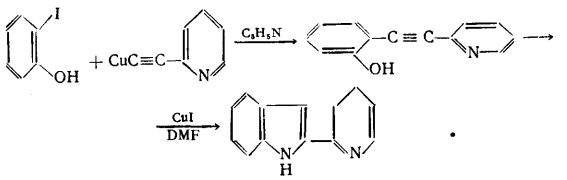
$$ArI + CuC{\equiv}CPh \rightarrow Ar{-}C{\equiv}C{-}Ph + CuI\ .$$

Heterocyclic compounds were obtained from some of the *ortho*-substituted derivatives in the same high yields. Further investigations[74] showed that this reaction is a general method for the synthesis of tolanes, indoles,

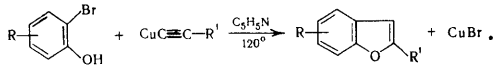
benzofurans, and phthalides. For the *ortho*-amino-derivatives the direction of the reaction is determined by the solvent: in dimethylformamide an indole is formed; in pyridine, either only an *o*-aminotolane, or a mixture of both products, depending on the acetylide:



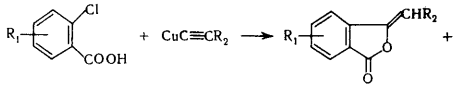
The reaction proceeds in two stages: substitution and cyclisation. The second stage takes place only in the presence of copper salts:



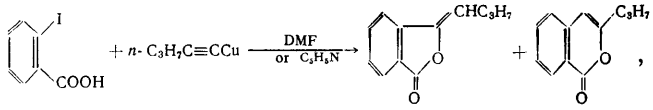
The synthesis of benzofurans proceeds easily in pyridine. Halogenophenols react more vigorously than the corresponding anilines. This allows the more stable *o*-bromophenols to be used as starting compounds:



Halogenobenzoic acids are a group of most reactive substances. Here the use of even chloro-derivatives is possible and the formation of phthalides occurs even at room temperature both in dimethylformamide and in pyridine:

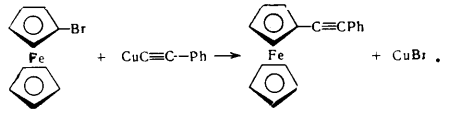


Only in one instance was the formation of isocoumarin noted as well as the phthalide:



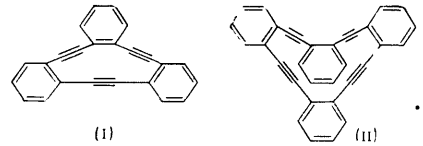
The simplicity of the behaviour and the high yields of the final products made this reaction a convenient preparative method for obtaining various acetylenic derivatives with aromatic substituents.

Nesmeyanov and coworkers[75] extended it to halogen derivatives of ferrocene. Whereas aryl bromides do not react with copper acetylides, on boiling bromoferrocene for three hours with copper phenylacetylide in a medium of dimethylformamide, ethynylphenylferrocene was formed in 48% yield:

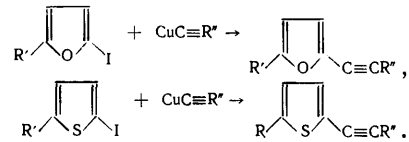


By starting from iodoferrocene, Rausch and coworkers[76] obtained the same product in 84% yield.

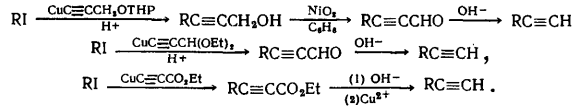
Campbell and coworkers[77] isolated cyclic condensation products from the pyridine solution after heating copper *o*-iodophenylacetylide—mainly the trimer (I) and a little tetramer (II):



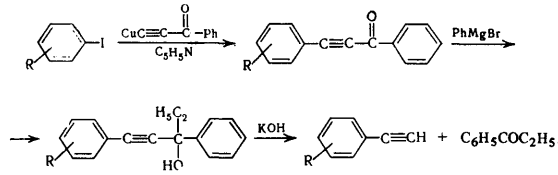
The work of Atkinson and coworkers[78,79] was devoted to the production of the acetylene derivatives of furan and thiophen:



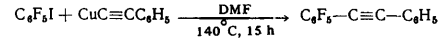
Monosubstituted arylacetylenes were also synthesised. The authors used the tetrahydropyranyl group (THP) for the protection of the hydroxyl group in the acetylides of propargyl alcohol:



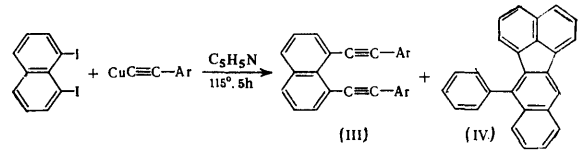
Shvartsberg and coworkers[80] developed another way of obtaining the monosubstituted arylacetylenes:



Filler and Heffern[81] carried out the reaction with pentafluoroiodoacetylene:

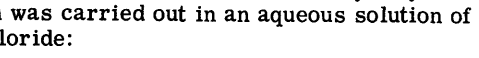


By studying the intramolecular reaction of closely situated triple bonds, Ipaktschi and Staab[82] synthesised a series of 1,8-substituted naphthalenes from 1,8-di-iodonaphthalene and copper acetylides:



Here in addition to the colourless product (III) its yellow isomer (IV) was formed. The yield of (IV) from the copper phenylacetylide was 19.5% and rose to almost quantitative on continuing boiling.

Colonge and Falcotet[83] obtained acetylenic and ethylenic alcohols by the reaction of allyl chloride and bromide or propargyl chloride (and their alkylated derivatives) with acetylides of propargyl alcohol or methylbutynol. The reaction was carried out in an aqueous solution of ammonium chloride:



where R = CH_2OH.

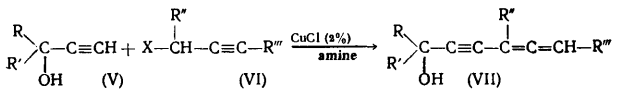
Somewhat later Kurtz[84] reproduced the same reaction but in an aqueous alcoholic solution of sodium chloride:

$$H_2C{=}CR{-}CH_2Cl + HC{\equiv}C{-}R' \xrightarrow[NaCl]{Cu^+,\ H_2O} H_2C{=}CR{-}CH_2{-}C{\equiv}CR' + HCl$$

a	*b*	*c*	*d*
R=H	$R=CH_3$	R=H	$R=CH_3$
$R'=CH_3$	$R'=C_2H_5$	R'=H	R'=H

Hepta-5-en-2-yn-1-ol and 5-methylhepta-6-en-2-yn-1-ol were obtained from the acetylide of propargyl alcohol. The yields were from 29 to 90% at 70–80°C and a reaction time of 7–8 h.

On using amines as a medium for the same reaction and ethynyl carbinols as the acetylenic component, Sevin[85] employed catalytic quantities of CuCl, and observed the isomerisation of the propargyl group into allenyl:



(V) (VI) (VII)

(X = Cl or Br)

(V)	*a*	*b*	*c*	(VI)	*a*	*b*	*c*
R	H	CH_3	CH_3	R″	H	CH_3	H
R′	H	H	CH_3	R‴	H	H	CH_3

The activity of amines in reactions for the condensation of propargyl halides with ethynylcarbinols in the presence of copper(I) chloride falls in the order NH_3 > primary > > secondary > tertiary. The author suggests that the reaction proceeds by a six-centre cyclic mechanism.

Allyl halides also react with copper acetylides in boiling dimethylformamide, forming a substitution product with yields of up to 40% on the acetylide taken[60].

$$CH_2{=}CH{-}CH_2X + Cu{-}C{\equiv}C{-}R \rightarrow CH_2{=}CH{-}CH_2{-}C{\equiv}C{-}R + CuX\,.$$

For the acetylide to react completely, a large excess (up to 100%) of the allyl halide is necessary. In the presence of a catalytic amount of copper powder the reaction takes 5–15 min. The reaction proceeds readily with high yields in liquid ammonia at −33°C.

Propargyl chloride reacts no less vigorously with copper acetylide[68] on heating in dimethylformamide above 70°C. However, the products formed under these conditions are polymerised and low-molecular-weight individual substances cannot be isolated. The use of liquid ammonia instead of dimethylformamide in the reaction of copper phenylacetylide with propargyl chloride allowed a little of a hydrocarbon of composition $C_{11}H_8$ to be obtained in subsequent high vacuum distillation. On the basis of the infrared spectra it was ascribed the cumulene structure $C_6H_5{-}CH{=}C{=}C{=}C{=}CH_2$.

The ability of halogen as an isolated double bond to react with copper acetylides was studied by the example of *trans*-di-iodoethylene[86]. Copper acetylides react with di-iodoethylene more readily than with aryl iodides. Depending on the ratio of the reagents and the duration of the reaction, mono- or di-substituted products can be isolated in yields up to 65%.

$$R{-}C{\equiv}C{-}Cu + ICH{=}CHI \rightarrow RC{\equiv}C{-}CH{=}CHI + CuI\,,$$
$$2\,R{-}C{\equiv}C{-}Cu + ICH{=}CHI \rightarrow R{-}C{\equiv}C{-}CH{=}CH{-}C{\equiv}C{-}R + 2\,CuI\,.$$

The reaction takes place without change in the configuration of the *trans*-di-iodoethylene. To replace the first iodine atom it is sufficient to boil the reagents for 10–15 min. About 2 h is needed to replace the second atom.

Copper(I) cyanide also reacts analogously to the acetylides with di-iodoethylene, forming fumarodinitrile.

Burdon and coworkers[87] also reacted dihalogenoethylenes with copper acetylides in dimethylformamide or pyridine and obtained enyne and endiyne compounds in yields of up to 90%:

$$R{-}C{\equiv}C{-}Cu \xrightarrow[1\text{–}12\ h;]{40\text{–}100^\circ} \begin{cases} \xrightarrow{ICH{=}CHCl} R{-}C{\equiv}C{-}CH{=}CHCl \\ \xrightarrow{ICH{=}CHI} R{-}C{\equiv}C{-}CH{=}CH{-}C{\equiv}C{-}R\,. \end{cases}$$

The activity of the halogen at an sp^2-carbon atom increases in the order I > Br > Cl; fluorine does not react.

It can be assumed that the reaction of copper acetylides with iodoaryl and halogen derivatives containing multiple bonds takes place through an intermediate complex. The bond with the metal in this complex can be effected by the π-electrons of the halogen derivative molecules. The absence of an interaction between alkyl halides and copper acetylides supports this assumption.

The reactivity of a halogen derivative can be determined by its basicity in relation to the copper atom of the acetylide. Only indirect data can be produced to explain the results from this viewpoint.

It is known that alkylalkenes exhibit in relation to a proton much more basic properties than aromatic hydrocarbons or conjugated alkenes[88]. If this dependence is also valid for the complex formation of halogeno-derivatives with a transition metal the drop in reactivity in the sequence

$$ICH{=}CHI > ICH{=}CH{-}C{\equiv}C{-}R > ArI$$

is completely regular.

The polarisability of the halogen atom can also play a significant part in reactions of this type. From the Table it is clear that the least reactive allyl halides, aryl chlorides and bromides have the highest dipole moments, that is, they are more difficult to polarise.

The possibility of a change in the valency of copper during the interaction also cannot be excluded. Silver phenylacetylide, for which a change in the valency of the metal under these conditions is improbable, dissolves when heated in pyridine with di-iodoethylene, but does not react.

5. Reaction with Acid Chlorides

Nef[89] reported that on dissolving silver phenylacetylide in benzoyl chloride and boiling the resulting solution, phenylpropiolophenone is formed. The reaction cannot be performed with large quantities of materials since it can take place very violently.

Davis and Scheiber[90] observed that some silver alkylacetylides dissolve in CCl_4, $CHCl_3$ or benzene. By the interaction of such acetylides with various acid chlorides in carbon tetrachloride they obtained the corresponding ketones in yields of up to 72%. It appeared that these reactions are catalysed by Lewis acids. For example, silver n-butylacetylide does not react with benzoyl chloride without a catalyst, but in the presence of $AlCl_3$ n-butylpropiolophenone is formed in 72% yield:

$$n\text{-}C_4H_9{-}C{\equiv}C{-}Ag + Cl{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \xrightarrow[CCl_4]{AlCl_3} n\text{-}C_4H_9{-}C{\equiv}C{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 + AgCl\,.$$

Crombie and Griffin[91] used this method for obtaining intermediates in the synthesis of certain derivatives of

unsaturated acids. The reaction was carried out with the acid chlorides of the partial esters of dicarboxylic acids:

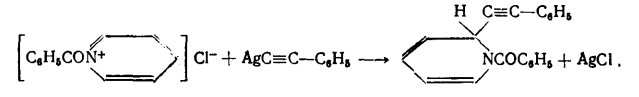
$$R{-}C{\equiv}C{-}Ag + ClCO[CH_2]_n COOMe \rightarrow R{-}C{\equiv}C{-}\overset{\overset{O}{\|}}{C}[CH_2]_n COOMe + AgCl.$$

The yields of the ketones were 30–35%.

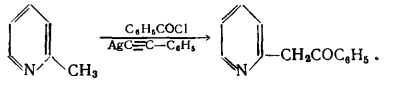
Additional moments of halogen derivatives.

X	Dipole moment, D		
	CH_3CH_2X	$CH_2{=}CHX$	C_6H_5X
Cl	2.05	1.44	1.73
Br	2.02	1.41	1.71
-	1.90	1.26	1.50

Interesting work by Agawa and Miller [92] disclosed new synthetic possibilities of reaction of silver acetylides with acid chlorides. These authors found that pyridine introduced into the reaction medium (CCl_4) becomes, in the form of an acylpyridinium salt, the main object of the nucleophilic attack of the silver acetylide. As a result of the reaction α-ethynyl derivatives of *N*-acyl-1,2-dihydropyridines are formed in yields of up to 70%:



Analogous products were also obtained with quinoline. The acetylenic ketones present as impurity did not exceed 15%. Reaction between 2-picoline, benzoyl chloride, and silver phenylacetylide takes place with the formation of 2-phenacylpyridine, AgCl, and probably phenylacetylene:



The first report of the synthesis of α-ethynylketones from acid chlorides and copper arylacetylides was published recently [93]; the yields were 40–60%:

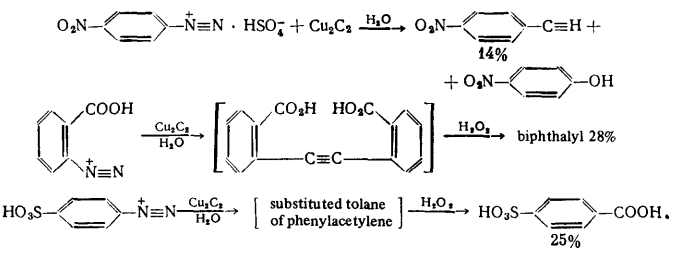
$$R{-}COCl + Cu{-}C{\equiv}C{-}C_6H_5 \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}C{\equiv}C{-}C_6H_5 + CuCl$$

where R = C_6H_5, *p*-BrC_6H_4, *p*-$O_2NC_6H_4$, *m*-$O_2NC_6H_4$, mesityl.

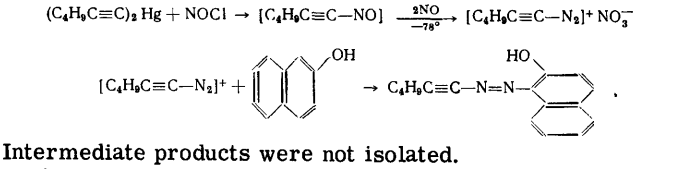
Bifunctional acid chlorides (terephthalyl chloride and isophthalyl chloride) react analogously. The reaction was carried out with the successive action of triethylamine, and then pyridine in a medium of dioxan, dichloroethane, or benzene. In the presence of only triethylamine, or only pyridine, and also in a medium of pyridine or dimethylformamide the formation of acetylenic ketones was not observed.

6. Reactions with Diazonium Salts

Sandmeyer [94] studied the reaction of copper acetylide with phenyldiazonium chloride and found that chlorobenzene is formed and acetylene does not take part in the reaction. Sharvina and Plakhuta [95] isolated tetraphenylethane from the products of the reaction of copper acetylide with phenyldiazonium sulphate, showing in this way that acetylene takes part in the reaction to an insignificant extent. Sokol'skii and Nikolenko [96] found that the presence of an electron-withdrawing substituent at the *para*- and especially the *ortho*-positions of the diazonium salt facilitates the entry of the acetylenic radical into the aromatic nucleus:



Robson and Tedder [97,98] first reported the production of compounds containing an azoethynyl grouping. The reaction proceeded thus:



Intermediate products were not isolated.

A new method for the synthesis of azoethynyl compounds by the reaction of aqueous solutions of aryldiazonium chlorides with silver acetylides [99,100] was developed:

$$Ar\overset{+}{N}_2Cl + AgC{\equiv}C{-}Ar' \rightarrow Ar{-}N{=}N{-}C{\equiv}C{-}Ar' + AgCl.$$

All the compounds except one were obtained from diazonium salts containing electron-withdrawing groupings in the *para*- or *ortho*-positions. The simplest compound of this series with two unsaturated phenyl radicals could not be synthesised. 4-Hydroxyazobenzene and bisphenylazophenol were isolated from the products of the reaction of phenyldiazonium chloride with silver phenylacetylide. The competitive formation of phenol with subsequent azocoupling makes the part of the substituents in the nucleus of the diazonium salt understandable.

It is known that the decomposition of diazonium compounds is unimolecular. There are many facts supporting an S_N1 mechanism [101,102]:

$$(Ar{-}\overset{+}{N}{\equiv}N{:})\,\bar{X} \xrightarrow{\text{slow}} Ar^+ + {:}N{\equiv}N{:} + X^-,$$

$$Ar^+ + H_2O \xrightarrow{\text{fast}} Ar{-}\overset{+}{O}H_2 \rightleftarrows ArOH + H^+.$$

$-M$- and $-I$-groupings in the *ortho*- and *para*-positions should hinder the removal of nitrogen (by impeding the displacement of the electrons $Ar{-}\overset{\curvearrowright}{N}{}^+{=}N$) but $+M$- and $+I$-groups should facilitate it. At the azo-coupling stage the substituent will exert an opposite influence on the components.

In the diazonium ion substituents which increase the positive charge on account of an inductive or mesomeric effect will increase its reactivity in relation to aromatic compounds, but $+I$- and $+M$-substituents will decrease it [59]. In the phenol being formed, on the other hand, $-I$- and $-M$-groups, by withdrawing electrons from the aromatic ring, reduce its basicity, and consequently its capability for azo-coupling. Hence the rate of decomposition of the diazonium salts with electron-withdrawing substituents and the tendency to coupling with the phenols being formed will be reduced. At the same time the rate of electrophilic replacement of silver should increase with increase in the electrophilic nature of the diazonium ion. Azoethynyl

compounds can also be obtained from diazonium salts with electron-donating substituents in the nucleus. However, as the example of tolyldiazonium chloride showed, the yields here are very small.

The known similarity of copper and silver acetylides with sparingly soluble salts suggests the possibility of their existing in aqueous medium in equilibrium with the solid a definite concentration of acetylide ions and metal ions:

$$L = [R{-}C{\equiv}C^-][Ag^+]$$

where L is the solubility product. Reaction with diazonium salts could then proceed as a simple exchange:

$$Ag^+ + R{-}C{\equiv}C^- + R'{-}\overset{+}{N}_2 \rightleftarrows R{-}C{\equiv}C{-}N{=}N{-}R' + Ag^+ .$$

The factor displacing the equilibrium to the right is the formation of the C–N covalent bond.

One of the significant objections against this mechanism is the weakness of the acid properties of acetylene and its homologues. The acetylide ions would be completely hydrolysed under the reaction conditions (weakly acid medium):

$$R{-}C{\equiv}C^- + H^+ \rightarrow R{-}C{\equiv}CH .$$

Interaction would lead to a combination of the diazonium salt with acetylene, which, as shown by the example of phenylacetylene[103], proceeds as follows:

$$C_6H_5{-}C{\equiv}CH + Ar\overset{+}{N}_2 \rightarrow (C_6H_5{-}\overset{+}{C}{=}CH{-}N{=}N{-}Ar) \xrightarrow{+H_2O}$$

$$C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}CH{=}N{-}NH{-}Ar \rightleftarrows C_6H_5{-}\underset{\underset{OH}{|}}{C}{=}CH{-}N{=}N{-}Ar .$$

It is also difficult to explain the dependence of the results of the reaction for a single acetylide on the electrophilic nature of the diazonium ion.

The reaction of silver acetylides with diazonium salts can evidently be regarded as an electrophilic substitution similar to the reactions of diazonium fluoroborate with organozinc and organomagnesium compounds[104,105]:

$$R{-}ZnCl + \overset{+}{N}_2{-}Ar \rightarrow R{-}N{=}N{-}Ar + Zn^{2+} + Cl^- .$$

The presence in the reacting molecule of an acetylenic group does not rule out the possibility of yet another reaction mechanism—two-stage addition–splitting. The carbonium ion produced would differ from that obtained from phenylacetylene by the presence of a =C–Ag bond of comparatively low stability. The elimination of the Ag^+ ion in this instance would also lead to an azoethynyl compound.

$$R{-}C{\equiv}CAg + N{\equiv}\overset{+}{N}{-}R \rightarrow [R{-}\underset{\underset{Ag}{|}}{\overset{+}{C}}{=}C{-}N{=}N{-}R'] \xrightarrow{-Ag^+} R{-}C{\equiv}C{-}N{=}N{-}R'$$

However, such a mechanism seems to us much more probable for the following reasons.

It is known[106] that styrylsilver $Ag{-}CH{=}CH{-}C_6H_5$ is insoluble, brightly coloured, and—unlike the alkylethynyl derivatives of silver, for example, $Ag{-}CH{=}C(CH_3)_2$ [107]—is a rather stable compound, stable in air at room temperature for several hours. A comparatively high stability could also be expected from the product of the addition of a diazonium salt to silver phenylacetylide, similar in structure to styrylsilver. Furthermore, in all the examples investigated[106,108] compounds with an Ag–C bond decompose homolytically with liberation of metallic silver.

7. Interaction of Copper Acetylides with Inorganic Compounds

The interaction of $HgCl_2$, $HgBr_2$, and $Hg(OOCCH_3)_2$ with various acetylides has been studied in tetrahydrofuran, dioxan, alcohol, and water[109]. The formation of insoluble compounds was always observed. With an aqueous solution of ammonia the compound decomposes with separation of bisacetylene derivatives of mercury.

An investigation of the product of the reaction of two moles of copper phenylacetylide with one mole of mercury(II) bromide showed that it has the composition $HgBr_2 \cdot 2C_6H_5C{\equiv}CCu$. The complex is insoluble in ordinary organic solvents, soluble in pyridine but in dissolving it decomposes (as under the action of ammonia) into bis-(phenylethynyl)mercury and copper halide. An aqueous alcoholic solution of potassium iodide also decomposes the complex on heating, with liberation of the initial copper acetylide:

$$K_2(HgX_2I_2) + 2\,CuC{\equiv}CR \xleftarrow{2KI} HgX_2 \cdot 2\,CuC{\equiv}CR \xrightarrow{NH_3} Hg(C{\equiv}CR)_2 + 2[Cu(NH_3)_n] + 2\,X^- .$$

It is extremely probable that the reaction of HgX_2 with $R{-}C{\equiv}CCu$ takes place in the coordination sphere of the metals in the solid phase, however, it is also possible to postulate the existence of a double equilibrium between the solid and the solution:

$$HgX_2 + 2\,CuC{\equiv}CR \rightleftarrows HgX_2 \cdot 2\,CuC{\equiv}CR \rightleftarrows Hg(C{\equiv}CR)_2 + 2\,CuX .$$

Potassium iodide can shift the equilibrium only to the side of the formation of the acetylide. Both directions are possible for ammonia in principle, and the result will be determined by the ratio of the reaction rates.

In the infrared spectrum of the complex there are two bands in the range of the stretching vibrations of the triple bond: a weak one at 2000 cm^{-1} and a medium at 2040 cm^{-1}, which evidently shows the presence in the complex of triple bonds of different type. The decrease in the frequencies of the triple bonds compared with the monomeric bis-(phenylethynyl)mercury ($\nu_{C{\equiv}C}$ = 2143 cm^{-1}) suggests their interaction with the copper atoms, but less strongly than in copper phenylacetylide ($\nu_{C{\equiv}C}$ = 1930 cm^{-1}). The position of the bands of the stretching vibrations of the triple bonds and their relative intensities are reminiscent of the same parameters of the infrared spectra described by Coates and Parkin[30] for the tetrameric complex of copper phenylacetylide with trimethylphosphine.

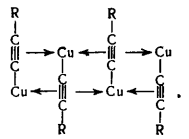
The absence of interaction between bis-(*C*-methylbarenyl)mercury and copper phenylacetylide[109] suggests that a significant part in the formation of such complexes is played by the difference in electronegativity associated with the mercury halide and the ethynyl group of the acetylide. The capability of the more electronegative ethynyl group to withdraw part of the electron density of the readily polarisable mercury atom can lead to the formation of a four-centre structure with bridging halogen atom:

$$\begin{array}{l} Br{-}Hg{-}Br \\ \quad\vdots\quad\vdots \\ R{-}C{\equiv}C{-}Cu \end{array} .$$

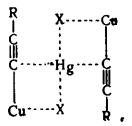
With bis-(*C*-methylbarenyl)mercury the formation of such a cyclic structure is also impossible because of the (already unusually high) coordination saturation of the barene carbon atom, which here should increase the coordination number from six to seven.

The formation of the complex $HgBr_2 \cdot 2CuC{\equiv}CR$, even in the presence of 100% excess of a mercury salt, can be explained by first assuming that oligomeric fragments of

acetylene are constructed from molecules oriented "head to tail":



On p. 1760 a structure was given for the complex $[CuC{\equiv}C\text{-}Ph.PMe_3]_4$, in which the phenyl rings of the acetylide were directed to opposite sides. The same orientation is proposed for the dimeric complexes of the copper[30] and silver[31] acetylides. It has also been suggested[31] that in the copper acetylides every metal atom is π-bonded with not less than two acetylene groupings, resulting in the coordination saturation of these compounds. Hence the structure given above for the mercury complex (not necessarily planar)—is one of the possible variants corresponding to these ideas. In this orientation in the blocks of the acetylide each molecule of the mercury halide can be inserted in the ready "matrix" of two molecules of acetylide:



If the complex is constructed from such fragments linked to one another by the coordination of the π-electrons of the triple bonds with the copper atoms, then even for the dimer an explanation is found for the two bands of the stretching vibrations of the triple bond in its infrared spectrum.

Like mercury, thallium forms two extremely stable covalent bonds with organic radicals. Grignard reagents alkylate thallium(III) chloride to stable and sparingly soluble dialkylthallium chlorides[110]:

$$TlCl_3 + 2\,RMgX \rightarrow R_2TlCl + 2\,MgXCl\,.$$

The significant difference of the Tl^{3+} salts from the Hg^{2+} salts is the tendency to the formation of ions with an electron cloud containing an "inert pair" determining the strong oxidising properties of the thallium(III) compounds. From the value of the oxidation potential of Tl^{3+} in the reaction $Tl^{3+} + 2e \rightarrow Tl^{+}$ (1.25 $E°$, V), clearly the Tl^{3+} ion occupies a position intermediate between bromine and chlorine (+1.066 and 1.358 $E°$, V respectively).

This feature of the thallium(III) salts was also determining in the reaction between $TlCl_3.4H_2O$ and copper phenylacetylide. The reaction can be represented by the following equation:

$$TlCl_3 \cdot 4\,H_2O + 2\,CuC{\equiv}C{-}C_6H_5 \rightarrow TlCl + 2\,CuCl + C_6H_5C{\equiv}C{-}C{\equiv}C{-}C_6H_5 + 4\,H_2O\,.$$

Dry copper phenylacetylide in a medium of phosphorus trichloride forms a colourless insoluble complex. An aqueous solution of ammonia or pyridine destroys the complex with the liberation of tri(phenylethynyl)phosphine $(C_6H_5C{\equiv}C)_3P$.

The same course for the reaction is evidently determined by the structure of the reactants, which permits intermediate coordination of one molecule of phosphorus trichloride with three molecules of the acetylide. The zig-zag arrangement of the copper atoms in the oligomeric blocks of the acetylide should facilitate such interaction, bearing in mind the pyramidal structure of the PCl_3 molecule.

It is also known that in many instances an increase in the polarity of the element–halogen bond hinders alkynylation[111]. As the phenylethynyl group is a stronger acceptor of electrons than chlorine its introduction into the molecule should decrease the polarity of the remaining P–Cl bonds and facilitate the subsequent stage of alkylation.

8. Oxidative Condensation of Copper Acetylides

The reactions most widely employed in synthetic organic chemistry are those connected with the oxidation of acetylenic derivatives of copper(I), and above all there is the oxidative condensation of copper acetylides into diacetylene derivatives, discovered by Glaser[112]:

$$2\,R{-}C{\equiv}CCu \xrightarrow{\text{oxidant}} R{-}C{\equiv}C{-}C{\equiv}C{-}R\,.$$

The extensive reviews of the reactions for oxidative condensation of acetylides which have recently appeared[70, 113–115] allow the present discussion to be restricted to only a brief statement of the main stages in the development of this branch of synthesis.

Perhaps the most important changes introduced into the method since the time of the discovery of the reactions was its conversion from heterogeneous to homogeneous. The choice of the conditions under which all the components of the reaction mixture are present in the dissolved state allowed the yields to be greatly increased, the temperature to be decreased, the reaction time to be curtailed and the range of acetylenes employed in the condensation to be greatly extended. Various macrocyclic compounds with diacetylene groupings were obtained from bisacetylenes in extremely dilute solutions for the first time. Methods of oxidative condensation in a homogeneous medium proposed by Hay[116] and Eglinton[117,118] were used most extensively. In Hay's method the reaction is carried out in pyridine with a catalytic amount of copper(I) chloride, using oxygen as the oxidant. In Eglinton's method the solvent is a mixture of pyridine and methanol, and the oxidant copper(II) acetate.

Another significant contribution in the study of the oxidation reactions was Zal'kind and Fundyler's discovery[119,120] of the possibility of carrying out oxidative condensation of acetylenes in an acid medium.

The development of the ideas about the mechanism of the oxidative condensation of acetylenes received detailed discussion in reviews[70,115], which allows the consideration in the present review to be restricted to only the most interesting studies of the principal aspects of these concepts.

The first ideas about the mechanism of oxidative condensation were purely hypothetical. Thus Zal'kind and Fundyler[119,120] suggested that the process starts with the decomposition of acetylenic compound into radicals, which recombine to form a diacetylene derivative:

$$R{-}C{\equiv}CH \rightarrow R{-}C{\equiv}C^{\cdot} + H^{\cdot}\,,$$
$$2\,R{-}C{\equiv}C^{\cdot} \rightarrow R{-}C{\equiv}C{-}C{\equiv}C{-}R\,.$$

The authors advanced the hypothesis that the formation of derivatives of diacetylene is facilitated by an increase in the positive induction effect of the group or atom situated close to the triple bond. The hydrogen liberated is either used up in the hydrogenation of part of the acetylene or is oxidised by atmospheric oxygen to water. The part played by the copper salts and oxygen remains unexplained in Zal'kind's scheme.

Westcott and Baxendale[121] showed that Cu^{2+} ions are oxidants. Thus with a stoichiometric amount of $CuSO_4$ in

an aqueous buffer solution (pH 6) dimethylethynylcarbinol rapidly forms a diyne in 50% yield. The other half of the ethynyl compound is precipitated as copper(I) acetylide:

$$4\,RC{\equiv}CH + Cu^{2+} \rightarrow R[C{\equiv}C]_2R + 2\,RC{\equiv}CCu + 4H^+ .$$

Klebanskii and coworkers[122] proposed a three-stage mechanism for the formation of the diyne in aqueous solution:

$$\text{(I)}\ RC{\equiv}CH \rightleftarrows RC{\equiv}C^- + H^+ \ \text{(slow)},$$
$$\text{(II)}\ RC{\equiv}C^- + Cu^{2+} \rightarrow RC{\equiv}C^{\cdot} + Cu^+ \ \text{(rapid)},$$
$$\text{(III)}\ 2\,RC{\equiv}C^{\cdot} \rightarrow RC{\equiv}C{-}C{\equiv}CR \ \text{(rapid)}.$$

The authors consider that in an alkaline medium the acetylene slowly dissociates with formation of the acetylide ion, which is then oxidised by the Cu^{2+} ion into a radical. The Cu^+ ions do not affect the process. An analogous mechanism is also proposed for condensation in an acid medium but it is suggested that ionisation (1) takes place through the formation of an intermediate complex of type

$$RC{\equiv}C\cdot CuCl\cdot NH_4Cl,$$

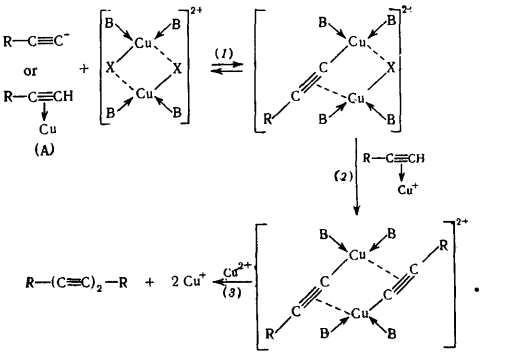
since on introducing an acetylenic compound into weakly acid (pH 4) solution of $CuCl_2$ and NH_4Cl the pH of the medium rapidly drops to pH 1.

Bohlmann and coworkers[123] found that the Klebanskii scheme does not correspond with the experimental results. Were the dissociation determining the rate of reaction to take place by Eqn. (1) the reaction rate would be first order. However, the reaction was always second order. To investigate the kinetics of the reaction, Bohlmann used a solution of the complex of copper(I) chloride with ethanolammonium chloride in 80% aqueous methanol. All the acetylenic compounds and copper(II) chloride are sufficiently soluble in this medium. The Cu^+ and Cu^{2+} are used in large excess. It was shown, by more than ten examples, that the reaction is second order. At pH 3 the reaction rate decreases with increase in the number of conjugated triple bonds. Thus the dimersiation time for half the initial quantity of phenylacetylene is 260 min, for phenyldiacetylene 6900 min, and for phenyltriacetylene 30 000 min. It is remarkable that in alkaline medium the reverse relation is observed (phenylacetylene 35 000 min, phenyldiacetylene 65 min). In pyridine solution the reaction rate increases with increase in the mobility of the acetylenic hydrogen; in acid medium the reverse is observed. In alkaline media the accelerating effect of Cu^+ ions is strongly expressed. The dependence of the reaction rate on the Cu^+ ion concentration is especially evident in the reactions of alkynes with increased mobility of the hydrogen. Thus on varying the concentration of Cu^+ ions from 0 to 100 the rate of dimerisation of the phenylacetylene increases 700 times and that of methyldiacetylene by about twice. The only probable explanation for the action of Cu^+ ions is the formation of π-complexes of the copper with the triple bond. This reaction can be regarded as a quasi-electrophilic addition. In this instance it is clear that with increase in the number of conjugated triple bonds the ability to form π-complexes should fall. The precise structure of these complexes is unknown but it can be assumed that the formation of a π-complex will be facilitated by an increase in the mobility of the acetylenic hydrogen to such an extent that even in acid media the dissociation:

$$R{-}C{\equiv}C{-}H \rightleftarrows R{-}C{\equiv}C^- + H^+$$
$$\quad\downarrow \qquad\qquad\quad \downarrow$$
$$\quad Cu \qquad\qquad Cu^+$$

can proceed.

Cu^{2+} ions take part in Bohlmann's scheme as an oxidant. Since a second-order reaction is observed at a large excess of Cu^{2+} ions the author suggests that the complex is formed from two molecules of the acetylenic compound. The general scheme of reaction can then be expressed in the following way:



In an acid medium copper(I) acetylide can be formed only as a π-complex (A), which then reacts according to (*1*). Thanks to the increase in the acidity of complex (A) and also the increase in the Cu^{2+} concentration, the reaction will be shifted to the right, to the side of the formation of a diacetylenic derivative.

If the reaction is carried out with compounds which contain two terminal acetylenic groups separated by a flexible chain, sufficiently long for ring closure, then the reaction is first order, since stage (*1*) is then an intramolecular reaction. Subsequent confirmation of Bohlmann's scheme was provided by the formation of products of mixed oxidative dimerisation. On assuming the radical nature of the process, the acetylenic radical formed initially should react with the second acetylenic radical selectively. However, it appeared that in the reaction of phenylacetylene with pentenynol in pyridine solution only 0.3% of the mixed dimerisation product is formed, which corresponds with a significantly greater reactivity of the phenylacetylene by the proposed mechanism. The yield of unsymmetrical products of the dimerisation is greater from acetylenic compounds with comparable reactivity.

The oxidative dimerisation mechanism proposed by Bohlmann reflects most completely the reaction process. However, much remains uncertain in this scheme. Thus, no explanation has been found for the reaction rate in alkaline media depending considerably on the amine concentration. The problem of the necessity for the reaction of a Cu^{2+} complex with an amine of definite composition remains open, since the complex is formed only when there is a large excess of amine. The nature of the amine plays a large part in the formation of the complex. Hay[116] showed that a high rate of reaction could be secured by using a total of 5–10 parts tetramethylenediamine per part of Cu^{2+} instead of a large excess of pyridine (as medium). The rate of dimerisation of phenylacetylene under strictly equal conditions varied in the ratio 40 : 7 : 1 on going from pyridine to 2-picoline to 2,6-lutidine.

Interesting results are given in a review[70] with reference to the private communication of Brandt, who found that the reaction of copper ions with acetylene can take place according to the scheme:

$$RC{\equiv}CH + Cu^+ \rightarrow RC{\equiv}CCu + H^+ \ \text{(fast)},$$
$$RC{\equiv}CCu + Cu^{2+} \rightarrow RC{\equiv}CCu^+ + Cu^+ \ \text{(slow)},$$
$$RC{\equiv}CCu^+ \rightarrow RC{\equiv}C^{\cdot} + Cu^+ \ \text{(fast)}.$$

An analysis of the results on the oxidative condensation of acetylenic compounds creates an impression of the possible existence of three different mechanisms for dimerisation in an alkaline medium, leading to a similar result: the oxidation of the acetylide ion, the oxidation of copper(I) acetylide, and finally the formation of an unstable acetylide derivative of copper(II), which decomposes into the acetylene radical and a copper(I) salt.

An example of the realisation of the first mechanism in a pure form is the oxidation of sodium phenylacetylide by permanganate in liquid ammonia[70]; diphenylbutadiene was obtained in 67% yield.

The possibility of the second path scarcely needs proof, since the lengthy time of the Glaser reaction carried out both oxidation of the copper acetylides previously liberated. Copper(II) can also be used as a strong oxidant:

$$R{-}C{\equiv}C{-}Cu + Cu^{2+} \rightarrow R{-}C{\equiv}C{-}C{\equiv}C{-}R + Cu^{+}.$$

Evidently the part of copper(II) here differs significantly from its role in the scheme proposed by Bohlmann, who suggests the formation of an intermediate acetylene complex of Cu^{2+} directly from a copper(II) compound. In the last stage (*3*) of the Bohlmann scheme copper(II) is introduced as an oxidant but this is evidently not necessary since the complex which is formed decomposes spontaneously with homolytic breaking of the transition metal (Cu^{2+})–carbon bond, owing to the instability of this bond.

The work of Coates and coworkers[30-33] also suggests that the copper(I) acetylides themselves already have a structure convenient for dimerisation. It is not difficult to see, for example, that the oxidation of the metal in the phosphinic complex of the acetylide (see p. 1759) leads to a compound analogous to the complex (B) in Bohlmann's scheme.

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On comparing the available information on the stability of the organic compounds of copper and silver with the acetylides of these metals, the following series can be compiled:

$$R{-}M \ll Ar{-}M < Ar{-}\overset{\displaystyle R}{\overset{|}{C}}{=}CH{-}M < R{-}C{\equiv}C{-}M < Ar{-}C{\equiv}C{-}M,$$

where R = alkyl, Ar = aryl, M = Cu or Ag.

Evidently the increase in the stability of the C–M bond in this series is explained, on the one hand, by the stability of the organic radical connected to the metal, and on the other, with the possibility of the formation of polymeric π-complexes. It is well known[124], for example, that phenylcopper is an insoluble polymeric substance. It can be suggested that the relative stabilisation of the C–Cu bond is attained here owing to the formation of Cu–Ph acceptor–donor bonds. In styryl (vinyl) compounds of Cu and Ag the possibility of complex formation is increased owing to the presence of mobile π-electrons of the double bond. Naturally the maximal stability is observed in acetylides.

On comparing the chemical reactivity of aryl derivatives and copper acetylides, clearly the Ar–Cu bond is considerably more active. Thus phenylcopper reacts with benzaldehyde[125], and acetophenone was obtained (54% yield) with acetyl chloride[125]. Information about such reactions with copper acetylides is not available. It should be noted that in addition to ketones a considerable amount of biphenyl is always formed in this reaction. Biphenyl was obtained exclusively in an attempt to condense carbon monoxide with phenylcopper[126].

Phenylcopper reacts with allyl bromide[125], forming allylbenzene in 31% yield. Copper acetylides undergo similar reactions but the yields are then usually higher.

The similarity of the copper acetylides to the organic compounds of copper also appears in the ability of the latter to form complexes with phosphines[127]. Thus, σ-cyclopentadienylcopper forms a stable complex with triethylphosphine $C_5H_5Cu.P(C_2H_5)_3$.

From the above examples it is evidently sufficiently clear that the acetylides of the metals of Group 1b, although exhibiting specific properties, also are closely connected with the organic compounds of these elements.

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U.D.C. 541.572.52

Dipole Moments and the Structure of π-Complexes of Metals

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Information on the dipole moments of π-complexes of metals is surveyed and systematised in this article: cyclopentadienyl, arene, alkene, carbonyl, and polymetallic complexes. The possibility of using the dipole moments method for finding the geometric structure of the π-complex molecules, the spatial position of the ligands, and the nature and polarity of the bonds which arise in complex formation has been shown. The results obtained in measurements of dipole moments are compared with data from infrared and NMR spectra, X-ray diffraction, and the chemical properties of the π-complexes. There is a bibliography of 298 references.

CONTENTS

I.	Introduction	763
II.	Cyclopentadienyl, arene, and cycloalkene complexes of the transition metals	764
III.	Carbonyls and nitrosyls of metals	766
IV.	Complexes of metal salts with unsaturated hydrocarbons	773
V.	Complexes of the halides of the elements of Groups III–V with aromatic hydrocarbons	774
VI.	Polymetallic $\pi\sigma$-complexes	775

I. INTRODUCTION

There is now an ever-increasing interest in the study of the structure of coordination compounds, in which the bond of the metal with the ligand is delocalised and brought about by interaction of the molecular π-orbitals of the ligand with the corresponding orbitals of the metal.

A series of monographs[1-4] and reviews[5-12] have generalised and systematised the information on the properties and structure of the π-complexes; these publications consider the results obtained by the methods of vibrational and NMR spectra, magnetochemistry, X-ray diffraction, and electron diffraction.

However, in none of these, nor in any of the other monographs[13-15] of a more general nature, is sufficient attention paid to the results of investigations of the polar properties of the π-complex molecules. Nevertheless a considerable number of papers has now been published[16-17] on the study of the structure and properties of coordination compounds by the dipole moment method, which gives valuable information on the geometrical structure of the molecules of the complexes, the spatial position of the ligands, the nature and polarity of the bonds arising in complex formation.

Interpretation of the values of the dipole moments does not require complicated mathematical equipment needed for dealing with the results from several other methods. However, it should be noted that the dipole moments method and vector calculations cannot always give an unambiguous characterisation of the structure of a complex molecule containing several polar groups. Because of this a knowledge of the value of the dipole moment is especially convenient when it is necessary to find which of several probable structures (*cis*- or *trans*-, centrosymmetric or otherwise) truly corresponds with the physical and chemical properties of the complex. The results obtainable on measuring the dipole moments are of special interest and cannot be replaced by X-ray structural investigations, since unlike the latter they characterise the structure of individual molecules in solution and not in a condensed phase.

The present review surveys material (up to 1968) on the study of polar properties and the structure of coordination compounds of the transition metals and the halides of the elements of Groups III–V with unsaturated and aromatic and nitrosyl complexes. We usually compare the conclusions nitrosyl complexes. We usually compare the conclusions drawn from the values of the dipole moments with the results of other methods of investigation (infrared and NMR spectroscopy, X-ray diffraction, etc.) and also from certain data on the chemistry of the π-complexes.

The methods of determining dipole moments and the problem of estimating and calculating atomic polarisation are not examined in this review as these problems were discussed earlier[16,18-24].