Translated from *Uspekhi Khimii*, 48, 1625-1683 (1979) U.D.C. 547.412

Reactions of Copper and Silver Organoacetylides

A.M.Sladkov and I.R.Gol'ding

The methods of synthesis of Group IB metal organoacetylides in weakly alkaline and neutral electron-donating media are examined and a systematic account is given of extensive experimental data concerning the reactions of copper and silver organoacetylides. Their chemical properties are compared with those of other classes of organic and organoelemental derivatives of the same metals. Much attention is devoted to the mechanisms of the reactions of copper and silver acetylides and their practical use in organic synthesis.
The bibliography includes 270 references.

CONTENTS

I.	Introduction	868
II.	Reactions involving the formation of Group IB metal organoacetylides	868
III.	Reactions of copper and silver organoacetylides with halogeno-derivatives	869
IV.	Copper and silver organoacetylides in addition reactions	886
V.	Oxidative condensation of Group IB metal organoacetylides	890
VI.	Reactions of silver organoacetylides with arenediazonium halides	890
VII.	Other reactions of copper and silver organoacetylides	891

I. INTRODUCTION

Since the publication of the first review[1] devoted to the chemistry of copper (COA) and silver (SOA) organoacetylides, this field of organometallic chemistry has greatly expanded and has been investigated in much greater depth. Copper and silver organoacetylides have been used successfully for the introduction of ethynyl groups into a wide variety of organic compounds. The heterocyclisation reaction via COA has developed greatly and heterocyclic compounds of new types have been synthesised. The ethynylation of organoelemental compounds by copper and silver organoacetylides is being used to an increasing extent. A new field of the chemistry of COA and SOA has arisen—the synthesis on their basis of ethynyl polynuclear clusters and complexes containing copper or silver together with transition metals. The synthetic scope of COA has greatly expanded with the latter used as homo- and hetero-cuprates—complexes with salts and organic derivatives of lithium, sodium, and magnesium. The COA and ethynyl cuprates have come to be used particularly frequently in the syntheses of natural products, their analogues and fragments, and physiologically active substances.

During the last ten years approximately 200 papers containing data on the structures and chemical properties of COA and SOA have been published, some of these studies having been reviewed[2-7], but the majority of the reviews are purely factual without due attention being devoted to COA and SOA from the standpoint of the characteristics of their structure and the mechanisms of their reactions.

The aim of the present review is a systematic examination and survey of extensive experimental data on COA and SOA and a discussion of the mechanisms of their reactions.

II. REACTIONS INVOLVING THE FORMATION OF GROUP IB METAL ORGANOACETYLIDES

The traditional methods for the synthesis of copper[8], silver[9], and gold[10] organoacetylides in strongly alkaline media have now been supplemented by a number of milder methods involving the use of new metallating agents, organoelemental derivatives of the acetylene series, and aprotic electron-donating solvents to which weak bases are added. These methods proved to be particularly suitable for sterically hindered or hydrolytically unstable acetylenes and acetylides as well as diacetylene compounds.

The transmetallation reaction can also be of preparative importance; copper(I) and silver(I) t-butoxides[11-13], copper(I) phenylmercaptide[14], copper(I) [15] and gold(I) [16] ketenides, as well as dry silver(I) acetate[17] have been used as metallating agents:

$$RC\equiv CH + m_i\text{-t-BuOM} \rightarrow RC\equiv CM \quad ,$$

$$M=Cu,\ R=Ph,\ SiMe_3;\ M=Ag,\ R=Ph \quad ,$$

$$PhC\equiv CH + Ph\,SCu\cdot(PPh_3)_3 \rightarrow PhC\equiv CCu\cdot PPh_3 \quad ,$$

$$PhC\equiv CH + \begin{matrix} M \\ M \end{matrix}\!\!>\!C=C=O + PhNH_2 \xrightarrow{L} PhC\equiv CM + PhNHCOMe \quad ,$$

where M = Cu and L = acetone or M = Au and L = pyridine.

The silver derivative of diazomethane also exhibits a metallating activity[18]:

$$PhC\equiv CH + \begin{matrix} Ag \\ Ag \end{matrix}\!\!>\!C=N=N \xrightarrow{\text{pyridine}} PhC\equiv CAg \quad .$$

The phosphine complexes of gold(I) organoacetylides are formed when the phosphine complexes of methylgold are acted upon by acetylenes[19,20]:

$$[AuMe(PPhR_2)] + R'C\equiv CH \xrightarrow{L} [(AuC\equiv CR')(PPhR_2)] + CH_4$$

$$R=Ph,\ R'=Ph,\ L=\text{benzene};\ R=Me,\ R'=CF_3,\ L=\text{ether}.$$

The principle of the synthesis of organocopper(I) and organosilver(I) compounds of the alkyl, vinyl, and aryl series, by treating the corresponding organoelemental derivatives with copper(I) and silver(I) salts[6], has been successfully transferred to acetylenes. Thus COA are formed almost quantitatively when tetra(arylethynyl)-borammonium is decomposed by copper(I) chloride[21,22]:

$$NH_4B(C\equiv CAr)_4 + CuCl \xrightarrow{\text{alcohol } NH_4OH} ArC\equiv CCu \quad ;$$

$$Ar=Ph;\ 2,4\text{-}Me_2C_6H_3 \quad .$$

The sterically hindered copper 2,4,6-tri-(t-butyl)-phenylacetylide was obtained in a mixture of hexane, ether,

and benzene via the mechanism[23]

$$2,4,6\text{-(t-Bu)}_3C_6H_2C\equiv CH \xrightarrow[2.\ CuI]{1.\ BuLi} 2,4,6\text{-(t-Bu)}_3C_6H_2C\equiv CCu \ .$$

This procedure is widely used nowadays for the synthesis of ethynyl organocuprates.

The synthesis of a new type of ethynyl derivatives of hexanuclear copper(I) clusters (I) is a novel application of this method[24-26]:

$$Ar_4Cu_6Cl_2 + 2LiC\equiv CR \xrightarrow[70-90\%]{\text{ether/benzene}} \underset{(I)}{Ar_4Cu_6(C\equiv CR)_2} \ ;$$

Ar=2-$Me_2NC_6H_4$; R=Ph; 4-MeC_6H_4, 2,4-$Me_2C_6H_3$, 2, 4, 6-$Me_3C_6H_2$, or $SiMe_3$.

The clusters (I) are also the products of a more complex reaction involving a transmetallation stage[25]:

$$6ArCu + 2RC\equiv CCu \xrightarrow[60\%]{\text{benzene}} (I) \ .$$

SOA can be obtained by treating Iotsich reagents with silver halides[27]:

$$BuC\equiv CMgBr + AgBr \xrightarrow[60\%]{\text{ether}} BuC\equiv CAg \ .$$

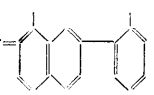
Certain representatives of organoelemental copper acetylides [compounds (II)] have been synthesised by the decomposition of ethynyl complexes of copper(I) halides in dimethyl sulphoxide (DMSO) using weak alkaline agents[28], together with dicopper(I) derivatives of diacetylene [compounds (III)][29,30], which cannot be obtained by other methods:

$$RC\equiv CH \xrightarrow[2.\ NH_4OH\ (dil.)]{1.\ CuCl,\ DMSO} \underset{(II)}{RC\equiv CCu} \ :$$

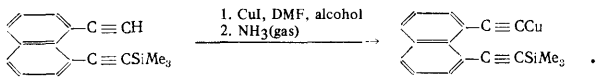
R=Bu_3P or Ph_2As

$$HC\equiv CArC\equiv CH \xrightarrow[2.\ NaHCO_3]{1.\ CuI,\ DMSO} \underset{(III)}{CuC\equiv CArC\equiv CCu} \ :$$

(a) Ar=2,2'-$C_6H_4ZC_6H_4$ (where Z=CH_2CH_2, *trans*-CH=CH, or C≡C), ;

(b) Ar=  .

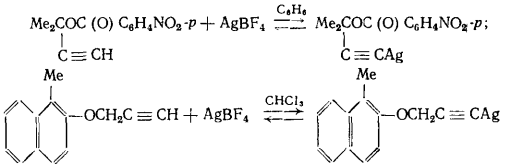
Mitchell and Sondheimer[31] obtained copper(I) arylacetylides by passing dry NH_3 for a short time through a suspension of arylacetylene and CuI in an ethanol–dimethylformamide (DMF) mixture; under these conditions, the trimethylsilyl protecting group attached to the second ethynyl group was preserved:



It has been shown[32] that copper arylacetylides are formed on heating terminal arylacetylenes and CuI in pyridine in the presence of K_2CO_3. Silver perchloroarylacetylides have been obtained by treating the corresponding acetylenes [$C_6Cl_5C\equiv CH$ and 4,4'-$(HC\equiv CC_6Cl_4)_2$] with $AgNO_3$ in a water–tetrahydrofuran (THF) mixture[33]. The oxidative disproportionation of acetylenes under the influence of copper(II) leads to COA:[11]

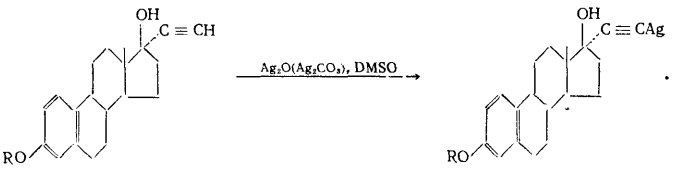
$$4PhC\equiv CH + 2Cu(OBu\text{-}t)_2 \rightarrow 2PhC\equiv CCu + (PhC\equiv C)_2 + 4\text{-t-BuOH}.$$

It has been established[34,35] that equilibrium in the system



is displaced significantly towards SOA when Ag_2CO_3 is introduced.

SOA unstable under the conditions of the synthesis are formed when 17α-ethynyl-17β-hydroxysteroids are acted upon by Ag_2O or Ag_2CO_3 in DMSO:[36]



SOA derived from disubstituted acetylenes (IV) have been obtained by the reaction of the latter with $AgNO_3$ in an aqueous or alcoholic medium[37-39]:

$$\underset{(IV)}{R_3M(C\equiv C)_nMR_3} + 2AgNO_3 \rightarrow Ag(C\equiv C)_nAg + 2R_3MNO_3 \ ;$$

n=1; M=Sn or Pb; R=Et or Ph; M=Si, R=Me or OMe; n=2 or 3; M=Pb; R=Et, C_6H_{13} or Ph .

The complex AgC≡CAg.AgCl was isolated in the decomposition of stereochemically pure *cis*- and *trans*-β-chlorovinylboronic acid with an aqueous solution of $AgNO_3$.[40]

It has been shown[41] that the complex PhC≡CH.CuCl is converted into copper phenylacetylide on treatment with solvents containing traces of water.

III. REACTIONS OF COPPER AND SILVER ORGANOACETYLIDES WITH HALOGENO-DERIVATIVES

1. Aryl and Heteroaryl Halides

A general reaction of all types of organic and heteroorganic copper(I) compounds is their condensation with aryl and heteroaryl halides in an inert atmosphere:

$$RCu + HalAr \rightarrow R\text{—}Ar + CuHal \ .$$

The compounds RCu of the first group, in which R is a powerful nucleophile [RCu = AlkCu.PR'_3, (π-C_5H_5) Cu.PR'_3, Ar_fCu, or ArC(O)OCu] [3] react in a non-ionising aprotic medium with a moderate electron-donating capacity (ether, THF, diglyme; Table 1). COA belong to the second group of the compounds RCu [where R = Alk,[43] Ar,[3] $SAlk_f$,[44,45] RS,[46] $(Me_3Si)_2N$, $(Me_3Si)_2NN(SiMe_3)$,[47] halogen[48], or CN [49]], in which the nucleophilicity of the residue R (and the amount of ionic character of the R–Cu bond) is reduced owing to coordination and possibly dative interactions of R with the copper atom. In this case the reaction medium consists of powerful electron-donating solvents (for example, DMSO, DMF, quinoline, or pyridine; see Table). 2-Methylpropenylcopper,[50] which occupies an intermediate position, approaches compounds of the first group as regards reactivity, while AlkOCu and ArOCu [51] approach compounds of the second group in this respect. The only example of the above reaction for silver(I) compounds is the condensation of perfluorophenylsilver with iodobenzene in DMF.[52]

The ethynylation of aromatic and heteroaromatic compounds with the aid of COA, first described in 1963, [53,54] is at present one of the most frequently used preparative methods in organic synthesis.

A procedure has been recently proposed for the introduction of the ethynyl group into an aromatic ring via COA, in accordance with a mechanism which does not involve their preliminary isolation[32]:

$$RC\equiv CH + IAr \xrightarrow{PyH,\ CuI,\ K_2CO_3} ArC\equiv CR \quad .$$

Table 1. The electron-donating properties and dielectric constants (ϵ) of certain aprotic solvents[42].

Solvent (D)	*Donor number* ($-\Delta H_{D,SbCl_5}$), kcal mole^{-1}	ϵ
Ether	19.2	4.3
Tetrahydrofuran	20.0	7.6
Acetone	17.0	20.7
Acetonitrile	14.1	38.0
Dimethylformamide	26.6	36.1
Dimethylacetamide	27.8	38.9
Pyridine	33.1	12.3
Hexamethylphosphoramide	38.8	30.0
Dimethyl sulphoxide	29.8	45.0
Benzonitrile	11.9	25.2
Nitrobenzene	4.4	34.8
Acetyl chloride	0.7	15.8
Benzoyl chloride	2.3	23.0

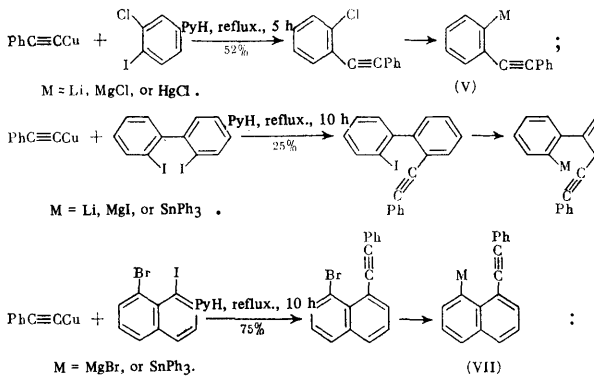
Apart from some simplification of the process, this method makes it possible to employ the complex, COA-forming terminal acetylenes which are unstable and difficult to isolate. However, one should note that successful condensation as a rule requires a large excess of CuI and of the corresponding acetylene.

In another modification of this method, used only in the synthesis of terminal arylacetylenes, a double molar excess of the acetylene compound relative to a ArI is necessary[55]:

$$(EtO)_2CHC\equiv CH \xrightarrow[2.\ CuI]{1.\ BuLi;\ hexane} \xrightarrow{PyH,\ ArI,\ 48\ h} ArC\equiv CCH(OEt)_2 \rightarrow ArC\equiv CH.$$

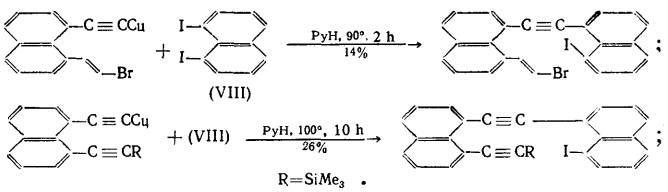
The reaction does not occur for Ar = 4-$O_2NC_6A_4$ and is facilitated in the presence of electron-donating substituents in the Ar group.

A wide variety of ethynyl derivatives of benzene, biphenyl, and naphthalene, which are the starting materials in the study of specific intramolecular electronic interactions of C≡C bonds, have been obtained by treating aryl iodides with COA. Kandil and Dessy[56] synthesised compounds (V)–(VII) with different geometrical dispositions of M and the C≡C bond:

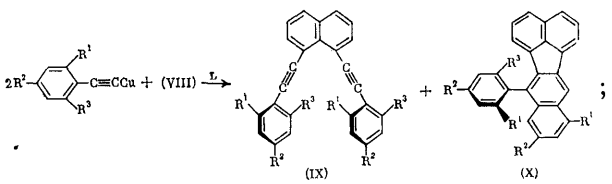


According to spectroscopic data, the metal M is not coordinated to the C≡C bond in these systems.

Interesting possibilities arise when 1,5- and particularly 1,8-di-iodonaphthalenes are used[57]. The products of the monosubstitution of 1,8-di-iodonaphthalene (VIII) have been obtained[31]:

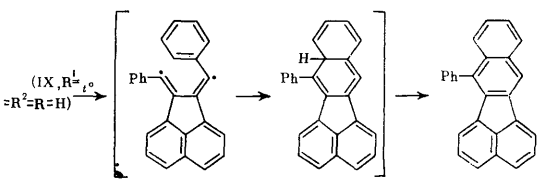


The interaction of COA with 1,8-di-iodonaphthalene has been studied in detail[58,59] and it has been shown that an increase of reaction time does not affect the overall yield of compounds (IX) and (X) (~80%), but alters sharply the (IX) : (X) ratio in favour of the latter compound if Ar = Ph and does not affect the composition of the products if Ar = mesityl [yield of (X) up to 10%] or *p*-anisyl [compound (IX) is not formed]:

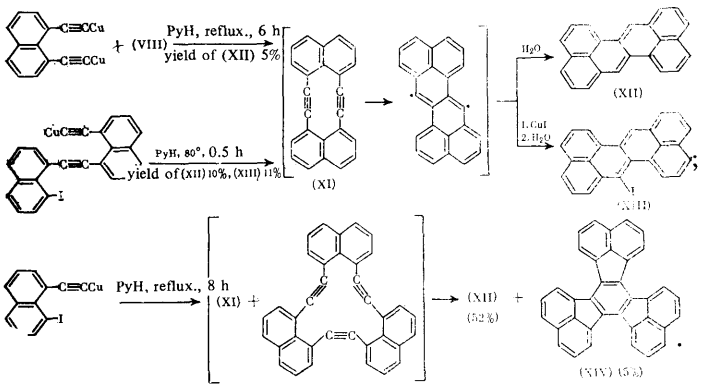


L = boiling pyridine, R^1, R^3 = H or Me; R^2 = H, Me, or OMe.

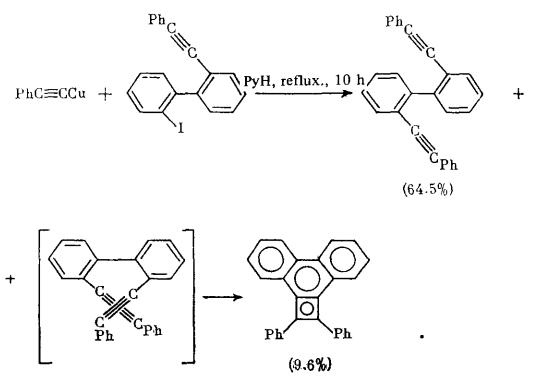
Although the system of C≡C bonds in 1,8-diethynyl derivatives of naphthalene has the non-linear *trans*-conformation[60], it is extremely reactive in intramolecular cyclisation processes, which apparently proceed via a radical mechanism. Thus it has been suggested[57] that 1,8-di(phenylethynyl)naphthalene undergoes thermal cyclisation to 7-phenylbenzo[*k*]fluoranthene via the mechanism



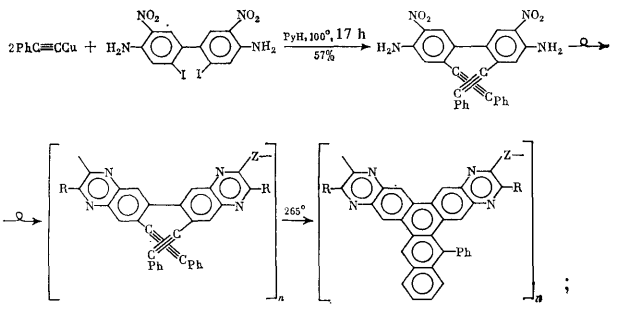
The formation of zethrene (XII), 7-iodozethrene (XIII), and decacyclene (XIV) instead to the expected dinaphthyl-1,6-bisdehydro[10]annulene (XI) [31,61] can also be readily accounted for by a radical mechanism:



It has been suggested that, when copper phenylacetylide reacts with 2-iodo-2'-phenylethynylbiphenyl, a system of crossing C≡C bonds can arise owing to rotational isomerism, in which intramolecular cyclisation takes place readily[56]

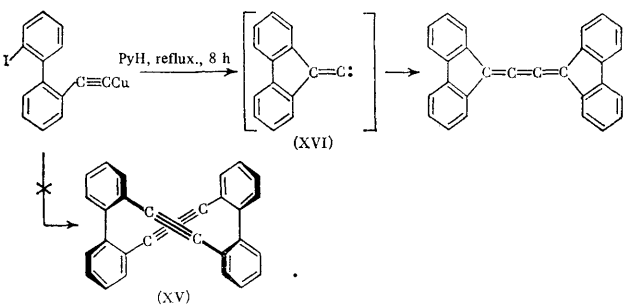


However, later it was shown[62] that the product of the cyclisation of 2,2'-di(phenylethynyl)biphenyl is 9-phenyldibenzo[*a*,*c*]anthracene, which is apparently formed by a radical mechanism analogous to that described by Bossambrock and Strechter[57]. The inclusion of such units in the polymer chain made it possible to increase significantly the thermal stability and to improve the workability of thermostable polymers. Thus the interaction of copper phenylacetylide with polyketoesters and polyesterketosulphones[63] based on 2,2'-di-iodobiphenyl-4,4'-di-carboxylic acid yielded thermally reactive binders for glass plastics [fibre glass?]. A method has been developed for the synthesis of heat-resistant polyphenylquinoxalines using 5,5'-diamino-2,2'-di(phenylethynyl)-benzidine as the tetra-amino-component[64]:

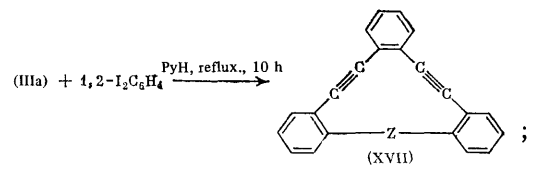


(a) R = Ph, Z = 4,4'-$C_6H_4OC_6H_4$; (b) R = 4-C_6H_4OPh, Z = 1,3-C_6H_4

At high dilutions (in pyridine) copper 2-iodo-2'-biphenylylacetylide does not form the expected homocondensation product (XV), but is converted, according to the authors[65], into di[fluorenylidene(9)]ethylene via a carbene (XVI) stage [intramolecular elimination of copper(I)]. When anaerobic conditions are not sufficiently carefully maintained, part of the initial acetylide undergoes oxidative dimerisation:

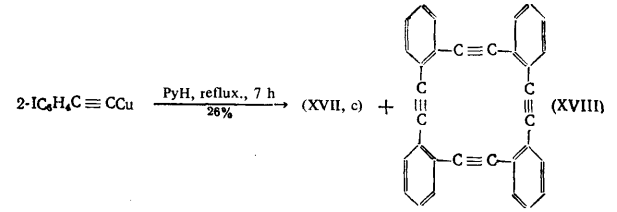


Staab and Rader[29] synthesised stable benzo[12]annulenes (XVII) by the interaction of copper(I) derivatives of diacetylenes (XIIa) with *o*-di-iodobenzene:

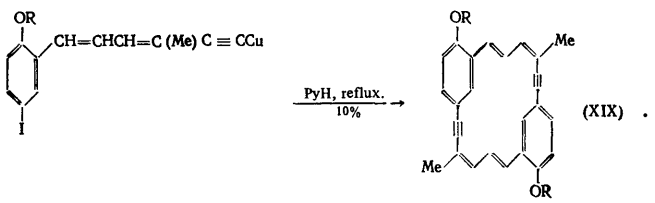


(a) Z = CH_2CH_2 (22%); (b) Z = *trans*-HC=CH (21%); (c) Z = C≡C (8%)

Previously compound (XVIIc) and the tetramer (XVIII) had been obtained by the homocondensation of copper *o*-iodophenylacetylide in pyridine[66]; structure (XVIIc) has been revised[67]:

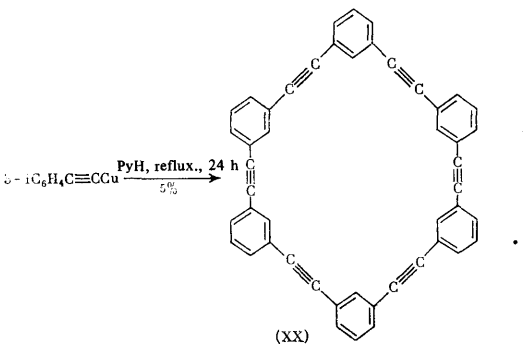


The same principle was used in the synthesis of the dehydro[18]annulenes (XIX, R = H, Me, or CH_2OMe) condensed with benzene[68]:



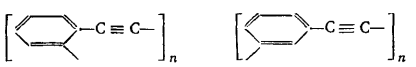
(XIX) .

We may note that, according to ultraviolet spectroscopic[67] and X-ray diffraction[69] data, there is no extended π-conjugation system in compounds (XVII, b and c). The same conclusion was also reached in relation to a 30-unit macrocyclic compound (XX) produced by the condensation of copper *m*-iodophenylacetylide[70]:



(XX)

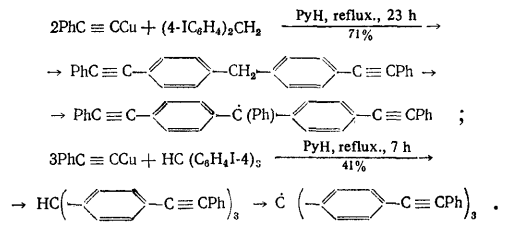
However, the main pathway in the homocondensation of copper *o*- and *m*-iodophenylacetylides in pyridine or DMF involves the formation of the open-chain polymeric systems (XXI) and (XXII) [poly(phenylene carbides)], the elementary unit of which retains the structure of the initial acetylene[71]:



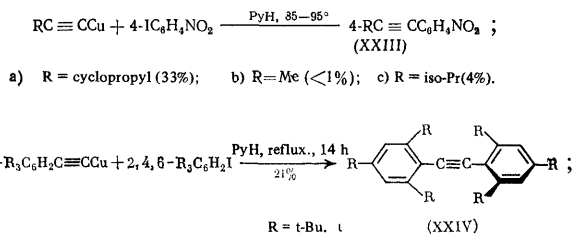
(XXI) (XXII) .

The polymers (XXI) and (XXII) (M_n = 2000–10000) are distinguished by a high content of carbon (approximately 95%), are readily soluble (up to 50 wt.%) in chloroform and benzene, soften at 170°C, and are readily worked into pressed articles, fibres, and films, which, after brief heat treatment at 500°C, withstand prolonged heating without loss of weight or shape (in an inert atmosphere and even in air) at 900–1000°C. Poly(phenylene carbides) can be actively combined with many transition metal compounds via π-complex formation. Heat treatment of such compositions yields carbon-containing materials with homogeneously distributed metal particles (approximately 100 Å), which ensure protection from radiation. It has been reported[71] that the interaction of copper acetylide with di-iodobenzene isomers in pyridine or DMF also leads to poly(phenylene carbides)[71].

Diarylacetylenes have proved to be convenient for the investigation of the ability of the C≡C bond to transmit electrons. Kotlyarevskii and coworkers[72,73] used copper phenylacetylide in the synthesis of triphenylmethyl free radicals containing phenylethynyl groups:

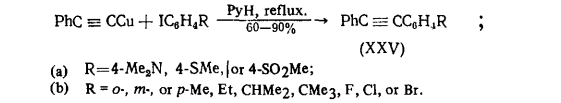


The transfer of electron density via a C≡C bond in the radical-anions (XXIII) [74] and (XXIV) [23] has also been investigated by EPR:

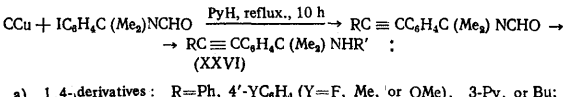


In contrast to tolanes, which do not contain bulky substituents and in which there is unhindered internal rotation of the benzene rings about the C≡C bond which leads to their preferential mutual coplanar disposition[75], di-(2,4,6-tri-t-butylphenyl)-acetylene (XXIV) constitutes a combination of two orthogonal π-systems[23].

Monosubstituted tolanes (XXVa) have been synthesised for the investigation of polar and stereochemical effects in the introduction of organoaluminium groups into C≡C bonds[76]; compounds (XXVb) served as models of the products of the reaction of the phenylethynyl radical with benzene derivatives[77]:



Ethynyl-substituted *N*-benzylamines, which can be readily obtained from the corresponding *N*-formyl derivatives (XXVI), proved to be effective agents for the prevention of cardiac arrhythmia[78]:



Examples of the use of COA in the synthesis of diarylacetylenes, including derivatives with functional groups, are presented in Table 2.

Functional groups can be introduced into tolanes, which are readily available via a reaction involving COA, also in the course of subsequent treatment (see, for example, Table 3).

Table 2. The applications of COA in the synthesis of diarylacetylenes by the reaction $ArC{\equiv}CCu + IAr' \rightleftharpoons ArC{\equiv}CAr'$.

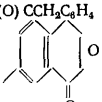
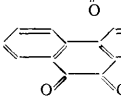
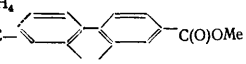
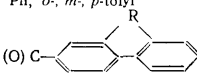
Ar	Ar'	Refs.	Ar	Ar'	Refs.
Ph	2-$C_6H_4C_6H_5$	56	Ph, 4-$O_2NC_6H_4$	4-HO (O) $CCH_2C_6H_4$	81
Ph	1-naphthyl	59			
Ph	2-$H_2NC_6H_4$	8	Ph		82
3-$MeOC_6H_4$	2-$AcNC_6H_4$	79			
Ph	2-PhC (O) NHC_6H_4	8			
Ph	2-H_2N-5-MeC_6H_3	8			
Ph	4-$AcNHC_6H_4$	79			
Ph	2-$OHCH_2C_6H_4$	8			
4-MeC_6H_4	2-$Me_2NC_6H_4$	26	Ph		83
Ph	MeO (O) C——C(O)OMe	63			
Ph	2-MeO (O) CC_6H_4	80	4-$MeOC_6H_4$	2-O_2N-4-$MeOC_6H_3$	84
			2,4-$Me_2C_6H_3$	2, 4, 6-$Me_3C_6H_2$	22
			PhC (O)	Ph; *o*-, *m*-, *p*-tolyl	85
			Ph	 RO (O) C—C (O) OR	63
				R=4,4', 4''-$C_6H_4OC_6H_4$-$SO_2C_6H_4OC_6H_5$	

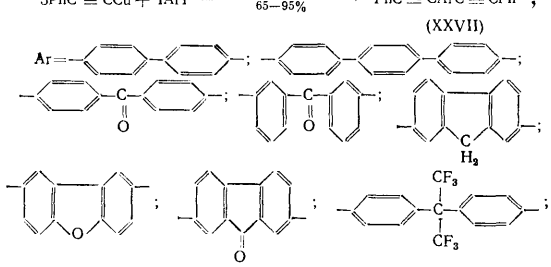
Table 3.

$$XC_6H_3C{\equiv}CC_6H_3Y \xrightarrow{L} X'C_6H_4C{\equiv}CC_6H_3Y'$$

X	Y	L	X'	Y'	Refs.
H	H	Anodic cyanation	H	4'-CN	86
H	H	$[PhC(O)O]_2 + I_2$, CCl_4	4-OC(O)Ph	4'-OC(O)Ph	87
2-CH_3	2'-CH_3	Bromosuccinimide, $[PhC(O)O]_2$, CCl_4	2-CH_2Br	2'-CH_2Br	67
2-Br	4'-F, Me, OMe, H	1. CuCN; 2. $LiAlH_4$	2-CH_2NH_2	4'-F, Me, OMe, H	78

The condensation of copper phenylacetylide with aromatic di-iodo-derivatives, previously described[8,53] in relation to di-iodobenzenes, yielded the diacetylene derivatives (XXVII), which are intermediates in the synthesis of heat-resistant and thermostable polyarylquinoxalines[64,83,88]:

$$3PhC{\equiv}CCu + IArI \xrightarrow[65-95\%]{PyH\ (DMF),\ reflux.} PhC{\equiv}CArC{\equiv}CPh \quad (XXVII)$$

Ar = 

Ethynylation in the *trans*-stilbene[29,89] and tolane[90] series has been carried out similarly:

$$2RC{\equiv}CCu + (2\text{-}IC_6H_4)_2Z \xrightarrow[60-70\%]{PyH,\ reflux.,\ 10\ h} (2\text{-}RC{\equiv}CC_6H_4)_2Z \ ;^{\dagger}$$

(a) R = *o*-tolyl, Z = *trans*-CH = CH;
(b) R = THP* -OCH_2, Z = *trans*-(Me)C = CH;
(c) R = Ph, Z = C≡C.

The initial configuration is largely retained in the reactions of copper vinylacetylides with aryl iodides[91-93]:

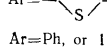
$$\underset{cis}{ROCH{=}CHC{\equiv}CCu} + IAr \xrightarrow{PyH,\ reflux.} \underset{cis}{ROCH{=}CHC{\equiv}CAr}$$

a) R=Me, Ar=2,4-$Y^1Y^2C_6H_3$ (60—90%), (Y^1=H, Y^2=H, Me, Cl, or NO_2; Y^1=NO_2, Y^2=H, or OMe); b) R=Et, or Bu, Ar=Ph (15%)

$$\underset{trans}{THPOCH_2CH{=}CHC{\equiv}CCu} + I\text{—}\langle S \rangle \xrightarrow[58\%]{PyH,\ reflux.,\ 6\ h} \underset{trans}{THPOCH_2CH{=}CHC{\equiv}C}\text{—}\langle S \rangle$$

The formation of a mixture of *cis*- and *trans*-products by condensation in these systems[94,95]

$$\underset{trans}{MeCH{=}CH\ (C{\equiv}C)_nCu} + IAr \xrightarrow{PyH,reflux} \underset{cis,\ trans}{MeCH{=}CH\ (C{\equiv}C)_nAr} \quad (XXVIII)$$

a) n=1, Ar=—$C{\equiv}CCH_2OTHP$;

(b) n=2, Ar=Ph, or 1-[^{3}H] Ph

is apparently associated merely with the instability of the *trans*-forms of compounds (XXVIII) under the reaction conditions.

The ethynylation of aromatic compounds with the aid of COA of the propargyl series is of great preparative value. Derivatives of aryl (heteroaryl) propargyl alcohols, aldehydes, and acids, which are intermediates in the synthesis of terminal aryl(heteroaryl)acetylenes, have been obtained by this method[23,96-102] (Table 4).

Arylpropargyl alcohols have been used for the chemical modification of penicillins[93] and in the synthesis of natural products of the coumarin series[102].

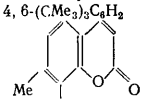
† Here and henceforth THP denotes 2-tetrahydropyranyl.

In contrast to the usual aryl iodides, the condensation of polyhalogenophenyl iodides (C_6Cl_5I, C_6Br_5I,[103] C_6F_5I,[103-104] and 4-XC_6F_4I, where X = H, F, Me, OMe, CF_3,[99] or 1,2-$I_2C_6F_4$[106,205]) with COA is complicated by transmetallation and reductive deiodination processes leading to a complex mixture of products, for example[106]:

$$2PhC\equiv CCu + 1,2\text{-}I_2C_6F_4 \xrightarrow{PyH,\ 120^\circ,\ 10\ h} 2\text{=}PhC\equiv CC_6HF_4\ (40\%) + 1,2\text{-}(PhC\equiv C)_2C_6F_4\ (25\%) + (PhC\equiv C)_2\ (20\%) + (2\text{-}C_6HF_4)_2\ (2\%)$$

Table 4.

$$RC\equiv CCu + IAr \xrightarrow{PyH} ArC\equiv CR$$

R	Ar	Refs.	R	Ar	Refs.
CH_2OH	2-thienyl	96	$CH(OMe)_2$	5-iodo-2-thienyl	101
CH_2OTHP	Ph, 1-naphthyl	97	$CH(OEt)_2$	Ph, 1-naphthyl	97
CH_2OTHP	4-$O_2NC_6H_4$, 3-Py, 4-MeO(O)CC_6H_4	98	$CH(OEt)_2$	5-X-2-thienyl (X=H, I, Me)	96, 97
CH_2OTHP	4-X-C_6F_4(X=H, F, Me, OMe, CF_3)	99	C(O)OEt	5-iodo-2-thienyl	97
CH_2OTHP	5-X-2-thienyl (X=H, I, Me)	96, 97	C(O)OEt	2, 4, 6-$(CMe_3)_3C_6H_2$	23
CH_2OTHP	3-$CF_3C_6H_4$	100	$C(Me)_2OTHP$		102

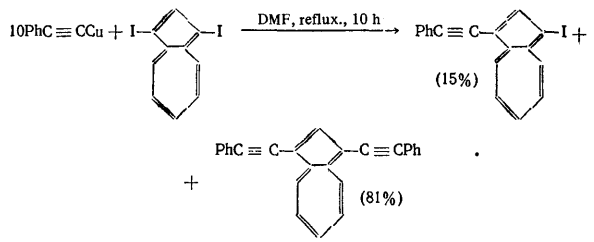
The yield of the corresponding biphenyls and 1,4-disubstituted butadiynes increases with increasing ionising capacity of the solvents (pyridine < DMF, hexamethylphosphoramide (HMP), DMSO),[99] with increase of temperature[99], and with increase of the O_2 content in the reaction mixture[103]. These factors apparently promote the exchange $RC\equiv CCu + IAr \rightleftharpoons RC\equiv CI + ArCu$, which leads to the appearance of new agents capable of condensation with the initial $RC\equiv CCu$ and ArI. In addition biphenyls and butadiynes can be formed as a result of the thermal or oxidative dimerisation of $RC\equiv CCu$ and CuAr.

Exchange processes play a major role also in the following reaction[99]:

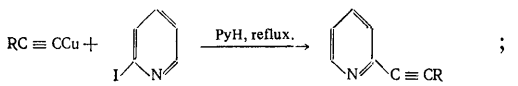
$$THPOCH_2C\equiv CCu + 4\text{-}IC_6HF_4 \xrightarrow[2.\ H^+]{1.\ PyH,\ reflux.} 4\text{-}HC_6F_4C\equiv CCH_2OH + 1,4\text{-}(OHCH_2C\equiv C)_2C_6F_4 + (4,4'\text{-}C_6HF_4)_2 + (HOCH_2C\equiv C)_2$$

COA are of great interest as agents for the ethynylation of heteroaromatic and non-benzenoid aromatic compounds. The iodo-derivatives of both electron-enriched (azulene, thiophen, and furan) and electron-deficient (compared with benzene) systems (pyridine) interact with COA much more vigorously than aryl iodides. The causes of this will be discussed when the mechanisms of the reactions of COA are considered.

Even in the presence of a large excess of copper phenylacetylide, 1,3-di-iodoazulene forms an appreciable amount of the monosubstituted product together with the disubstituted product[107]:

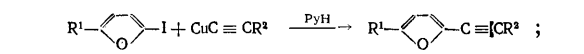


The condensation of COA with 2- and 3-iodopyridines is 5–10 times faster than the condensation with iodobenzene[8,108] and leads to high yields of pyridylacetylenes for the optimum reaction time (2 h):[108]

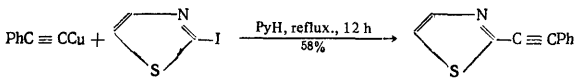


R=Ph (86%), 4-$MeOC_6H_4$ (68%), 4-$O_2NC_6H_4$ (52%), 4-PhC_6H_4 (54%), or Bu (95%)

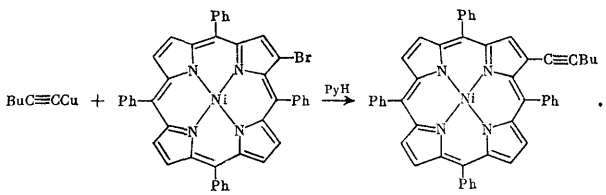
2-Iodo-derivatives of furan[96,109,110] and thiazole[110] as well as derivatives of 4-iodopyrazole[139] readily enter into a similar reaction:



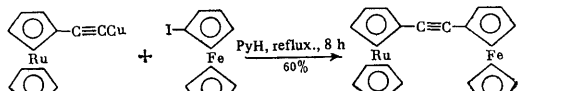
(a) R^1=H, R^2=CH_2OH, CH_2Ph, or Ph; (b) R^1=Me, R^2=CH_2OH; (c) R^1=C(O)OEt, R^2=Me; (d) R^1=CHO, or C(O)Me, R^2=Ph, or $C\equiv CPh$;



The condensation of COA with iodo-derivatives of the thiophen series has been frequently used by Bohlmann and by Atkinson, Curtis, and Taylor in the syntheses of the analogues of natural acetylenic products and their fragments (Table 5). This method provides unique possibilities for the introduction of asymmetric ethynyl groups in the 2,5-positions of the thiophen ring and the synthesis of disubstituted acetylenes containing 2-bithienyl groups. Examples of the interaction of COA with iodothiophens (the bromo-derivatives do not react) are presented below. The bromo-derivative of the Ni-tetraphenylporphyrin system is fairly reactive in relation to COA:[118]



Iodoferrocenes condense smoothly with COA, forming substituted ferrocenylacetylenes[111,119,120]:



As in the case of the mono iodo-derivative, copper ferrocenylacetylide reacts much more vigorously with 1,1-diiodoferrocene than does copper phenylacetylide[120]. The homocondensation of copper 1-ferrocenyl-1-iodoacetylide

yielded 2,2-ferrocenophane-1,3-diyne[121]:

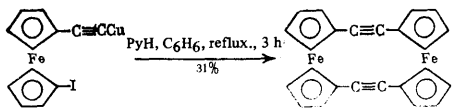
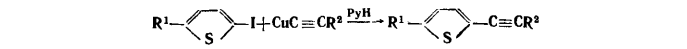
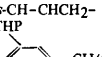
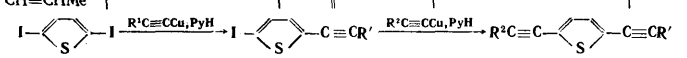


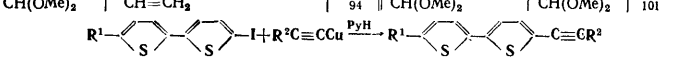
Table 5. The applications of COA in the synthesis of thienylacetylenes.



R^1	R^2	Refs.	R^1	R^2	Refs.
H	Ph, 1-ferrocenyl	111	CH_2OAc	*trans*-CH-CHCH$_2$-OTHP -AcO	114
H	CH-CHCH$_2$OTHP	112	C≡CMe	 , $CH(OMe)_2$	115
Ph	Me	96			
C(O)Et, CH(OEt) 2, I, CH=CHMe	Me	113	CHO	Me	96



R^1	R^2	Refs.	R^1	R^2	Refs.
Me	C≡CCH=CH$_2$	94	CH_2CH_2OH	C≡CMe	94
			C≡CMe	CH=CH$_2$	94
CH_2OTHP	C≡CCH=CH$_2$, CH=CHMe	94	CH(OTHP)CH_2OAc	C≡CMe	94
$CH(OMe)_2$	CH=CH$_2$	94	$CH(OMe)_2$	$CH(OMe)_2$	101

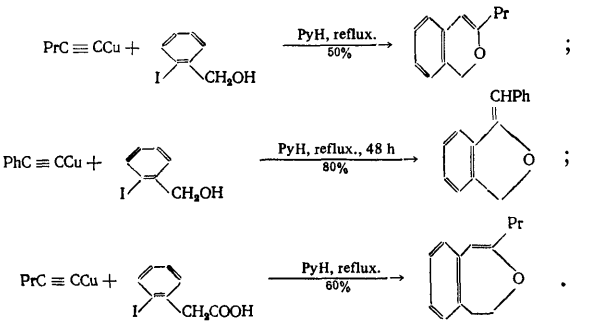


R^1	R^2	Refs.	R^1	R^2	Refs.
H	Me, CH_2OH, CH=CH$_2$, CH_2CH_2OH, C(O)Me, $CH(OE)_2$	117	Me, C(O)OMe	CH=CH$_2$	116
			I, C≡CCH(OMe)$_2$	$CH(OMe)_2$	117
H	CH_2OTHP	97			

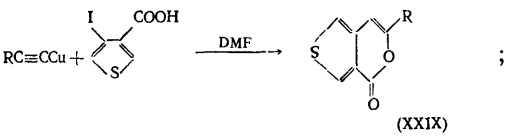
COA containing heteroaromatic substituents have been little investigated. Apart from the reactions discussed above, the condensation of copper 1-ferrocenylacetylide with 2-iodothiophen[111], 1-iodonaphthalene, and 2-iodophenol[119], of copper 2,5-dideutero-1-ferrocenylacetylide with iodobenzene[122], of copper 2-thienylacetylide with 2-iodothiophen[110], 5-formyl-2-iodothiophen, and 5-acetyl-2-iodothiophen[101], and of copper 2-pyridylacetylide with 2-iodoaniline[8] have been described.

Castro and coworkers established in early investigations[8,123] that the interaction of COA in DMF or pyridine with aryl halides containing nucleophiles Y = NH_2, SH, OH, or COOH in the *o*-position leads to heterocyclic products of the intramolecular nucleophilic addition of Y to the newly formed disubstituted C≡C bond π-linked to CuHal. In subsequent studies the range of *o*-substituted aryl halides and COA used was greatly extended, which made it possible to synthesise many heterocyclic systems which had been difficult to obtain hitherto or were completely new.

COA readily condense with *o*-iodobenzyl alcohol and *o*-iodophenylacetic acid, while the alkyl homologues of the latter form only homocyclisation products under these conditions[124]:



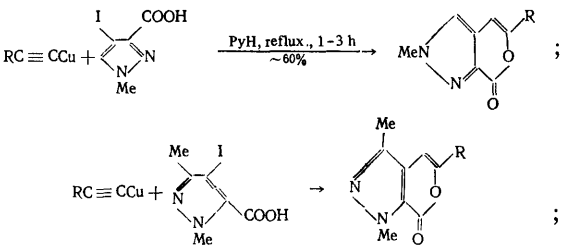
The first examples of a new class of heterocyclic compounds—substituted 1*H*-thieno[3,4-*b*]-2-alkyl(aryl)-1-pyranones (XXIX)—have been described[125]:



(XXIX)

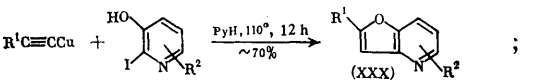
R=Pr, Bu, C_6H_{13} or Ph.

Similarly 4-iodo-*N*-methylpyrazolecarboxylic acids react with COA to form exclusively δ-lactones derived from 6-methyl-1-oxopyrano[3,4-*c*]pyrazole and 5,7-dimethyl-1-oxopyrano[3,4-d]pyrazole[126]:



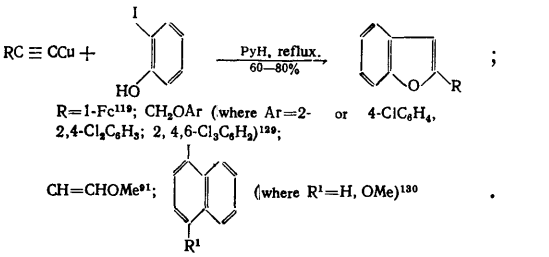
R=Ph, Pr, CH_3, or OMe.

The syntheses of condensed furan systems from *o*-iodoxyarene derivatives and COA have acquired considerable practical importance. Furo[3,2-*b*]pyridines (XXX a and b) have been obtained by this procedure for the first time[125, 127, 129]:



(a) R^1 = Pr, Bu, C_6H_{13}, CH_2CH_2OH, or Ph; R^2 = H;
(b) R^1 = Pr or Bu; R^2 = 2- or 4-Me.

Complex substituents have also been introduced into the 2-position of benzofuran with the aid of COA:



R=1-Fc[119]; CH_2OAr (where Ar=2- or 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$; 2, 4,6-$Cl_3C_6H_2$)[129];

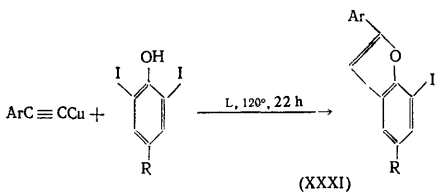
CH=CHOMe[91]; (where R^1=H, OMe)[130]

A wide variety of derivatives of this series—natural products and their analogues—have been synthesised similarly.

Table 6.

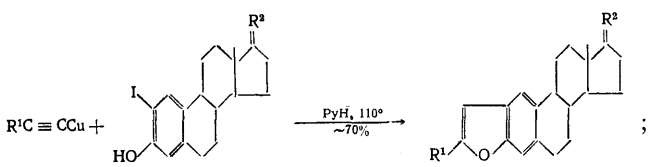
L	Ar	R	Yield of (XXXI), %
PyH	Ph	CHO	26
		$CH_2C(O)OMe$	44
		$CH_2CH(NHAc)C(O)OMe$	32
DMF	$4\text{-}MeOC_6H_4$	$CH_2C(O)OMe$	16
		$CH_2CH(NHAc)C(O)Me$	18
DMF	$4\text{-}MeO\text{-}3\text{-}iso\text{-}PrC_6H_3$	$CH_2C(O)OMe$	63
		$CH_2CH(NHAc)C(O)OMe$	40

4-Substituted 2,6-di-iodophenols react with copper phenylacetylide in pyridine and with COA whose benzene ring contains electron-donating substituents in DMF to form iodobenzofurans (XXXI), which are potential analogues of thyroxine (Table 6)[131]:



(XXXI)

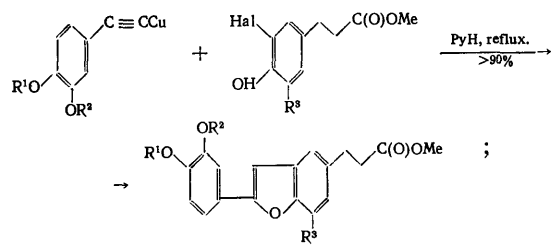
The use of COA opens a new pathway to the synthesis of heterocyclic steroids[132]:



(a) R^1=Pr, Bu, C_6H_{13}, or CH_2OH, Ph; R^2=O;
(b) R^1=Pr; R^2=



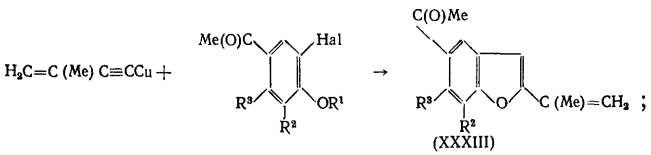
The natural "lignanes" (XXXII) are the only products of the reaction when the halogen is iodine; with bromine as the halogen, appreciable amounts of diarylbutadiynes were isolated[133]:



(XXXII)

(a) R^1 R^2=$-CH_2-$; R^3=H or OMe;
(b) R^1=R^2=Me; R^3=H or OMe.

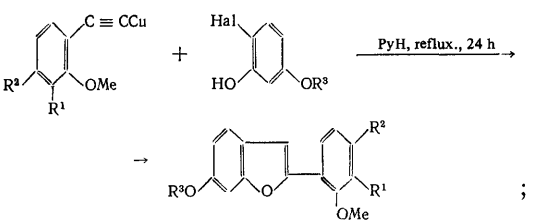
Natural products of the 5-acetyl-2-isopropenylbenzofuran series ("norlignanes") have been obtained by the condensation of copper isopropenylacetylide with 3-halogeno-4-hydroxyacetophenones in quinoline (XXXIIIa)[134] and pyridine (XXXIII, b–g).[135] Compound (XXXIIIa) is not formed if the initial phenol reacts in the free rather than acylated form[134]:



(XXXIII)

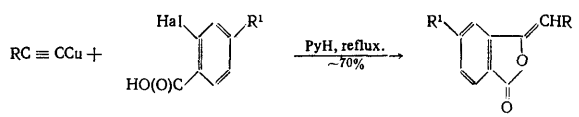
(a) Hal=Br, R^1=Ac, R^2=R^3=OAc; (b) Hal=Br, R^1=R^2=H, R^3=OH; (c) Hal=I, R^1=R^2=R^3=H;
(d) Hal=I, R^1=H, R^2=OMe, R^3=OH.

The synthesis of two natural products of the 2-arylbenzofuran series was described recently[136]:



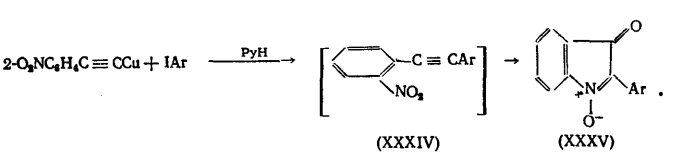
(a) R^1=OAc, R^2=OMe, R^3=CH_2Ph, Hal=I (78%);
(b) R^1=H, R^2=OCH_2Ph, R^3=Me, Hal=Br (34%)

The cyclisation reactions examined above take place unambiguously at the β-carbon atom (relative to copper), whereupon a hydrogen atom migrates from the functional group in the ring to the α-carbon atom of the ethynyl fragment of the COA. The mode of cyclisation of *o*-halogenobenzoic acids is reversed[8]: with R = n-Pr, R′ = H, and Hal = I, a mixture of 3-n-propylisocoumarin and 3-n-butylidenephthalide is formed, i.e. both cyclisation pathways operate[8]:



R=Ph; R^1=H, Cl; Hal=Cl

The key factor in the cyclocondensation of COA involving NO_2 and $C(O)NH_2$ groups is the migration of the O atom to the α-carbon atom. Thus heating of copper *o*-nitrophenylacetylide with aryl iodides in pyridine leads to 2-aryl-substituted isatogens[84] (Table 7):

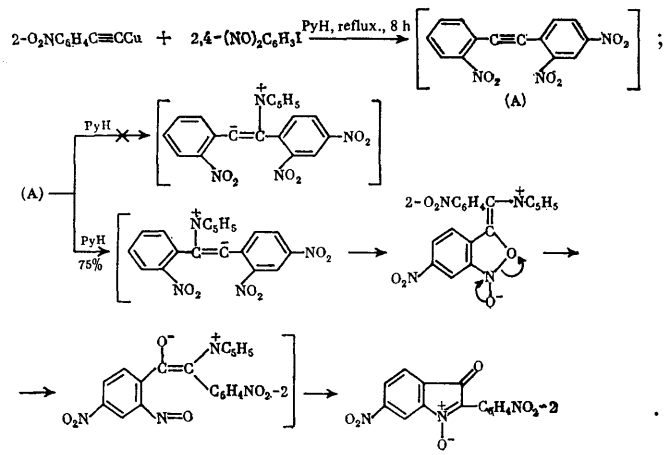


(XXXIV) (XXXV)

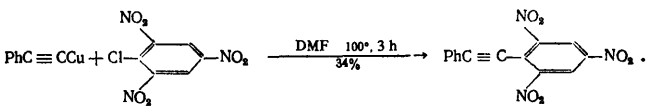
Table 7.

Ar	Yield of (XXXV), %	Ar	Yield of (XXXV), %
4-$MeOC_6H_4$	37	2-O_2N-4-$MeOC_6H_3$	66
4-$O_2NC_6H_4$	71	2-$C_6H_4C_6H_5$	73
2-O_2N-3-$MeOC_6H_3$	70	3-Py	22
		2-Thienyl	69

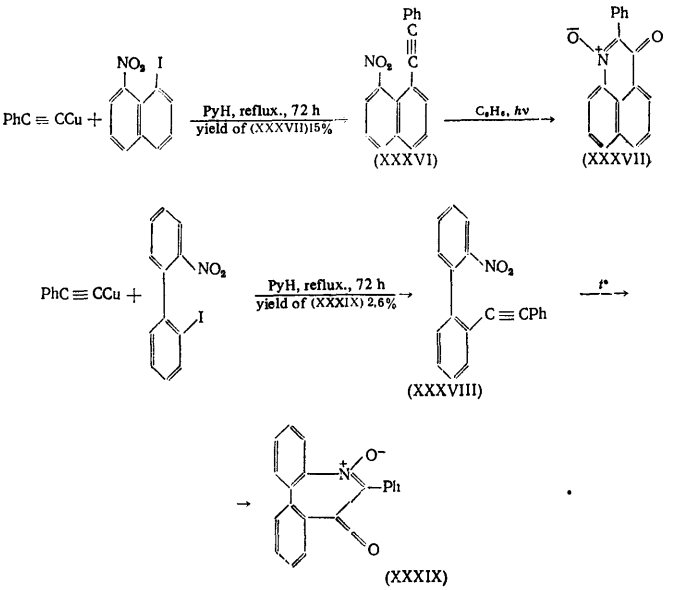
In conformity with the proposed mechanism, the cyclisation proceeds in the direction of the aromatic ring with the most pronounced electron-accepting properties:



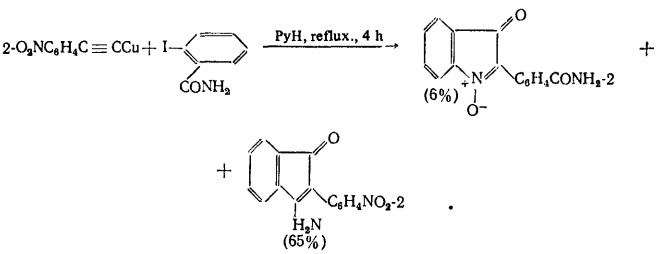
Steric factors (for example, *o*-substituents in the aryl group have a strong influence on the cyclisation. Thus the yield of (XXXIV) with Ar = 2-MeC_6H_4, 2-$MeOC_6H_4$, 2-$NO_2C_6H_4$, 2-alkOCOC_6H_4, or 1-naphthyl amounted to 70–90%; after prolonged heating in pyridine, the yields remained unchanged. Isatogen is apparently not formed in DMF:[8]



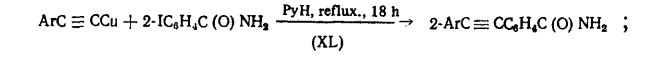
In the reactions of copper phenylacetylide with 1-iodo-8-nitronaphthalene and 2-iodo-2′-nitrobiphenyl only the products of the intramolecular cyclisation of the tolanes (XXXVI) and (XXXVIII) were isolated in a pure form—3-oxo-2-phenylbenzo[*d*,*e*]quinoline *N*-oxide (XXXVII) and 7-oxo-6-phenyldibenzo[*b*,*d*]azepine *N*-oxide (XXXIX):[137]



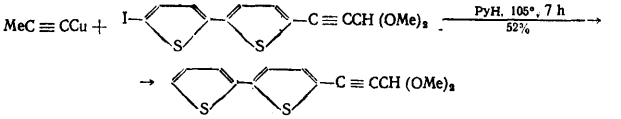
When copper phenylacetylide reacts with *o*-iodocarbamoylbenzene in pyridine, the product is 3-amino-2-phenylindenone; this reaction pathway predominates also in the case of copper *o*-nitrophenylacetylide[84]:



Electron-donating and bulky substituents Ar hinder the cyclisation of the tolanes (XL):[84]

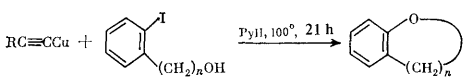


The reaction of COA with aryl halides also suffers from certain limitations. Thus COA having a discrete structure with bulky substituents at the C≡C bond, possessing a strong +*I* effect, do not condense with aryl halides (for example, copper t-butylacetylide does not react with C_6F_5I in pyridine[138]). On the other hand, electron-accepting substituents at the C≡C bond promote the reaction [for example, in the case of ($EtO_2CHC{\equiv}CCu$) [55]]. In the reaction

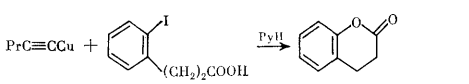


copper methylacetylide apparently behaves as a *C*-metallating agent. It can be assumed that COA exhibit an *O*-metallating activity in the intramolecular cyclisation

reactions[124]



$n = 2$, R = Pr (90%), Ph (100%); $n = 3$, R = Pr (54%), or Ph (85%) ;



We may note that HMP, which is a powerful electron-donating and ionising solvent (Table 1), has not found extensive applications in the synthesis of disubstituted arylacetylenes from COA and aryl halides[140]. It has been shown[141] that the Hal^- and CN^- ions inhibit the main reaction in this instance.

2. 1-Halogeno-olefins and 1-Halogenoacetylenes

The condensation of COA with 1-halogeno-olefins in pyridine or DMF has many features in common with the condensation of the series of compounds RCu, where R = Hal, CN, aryl, alkyl, R'C(O)O (see Refs. 142–144 and the literature quoted therein), Alk_f,[143,145] or SR'.[145] This type of reaction has not been described for silver(I) derivatives.

The interaction of copper(I) derivatives with 1-halogeno-olefins takes place stereospecifically with retention of the initial configuration of both the olefin[142–146] and the COA.[91] As for aryl halides, the reactivity of the halogen then decreased in the sequence I > Br ≫ Cl (F does not react), which is the reverse of that for the direct nucleophilic substitution at an sp^2-hybridised carbon atom[1].

The use of *trans*-chloro(iodo)vinylacetylenes (XLI), which are readily formed when the corresponding vinyl iodides interact with COA in pyridine[145,146], can greatly simplify the synthesis of monosubstituted diacetylenes:



(a) X=Cl, R=Ph, or $PhOCH_2$; (b) X=I, R=Bu, Ph, 4-ClC_6H_4, or 4-IC_6H_4.

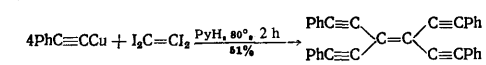
2-*C*-Ethynyl-1-*C*-phenyl-*o*-carbaborane(12) was obtained for the first time from 4-iodo-1-phenyl-*trans*-buten-1-yne.[147]

Electron-accepting substituents at the carbon atoms of the C≡C bond lower the reactivity of 1-iodo-olefins in reactions with COA. Thus the duration of the reaction involving *trans*-1-iodoalk-2-enyl sulphones (XLII) is greater by a factor of 5–10 compared with ICH=CHX (X = Cl or I),[144,148] and sulphones of the propene series (XLII, R' = Me) are more reactive than those of the styrene series (XLII, R' = Ph):[144]

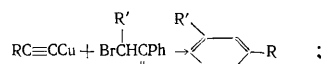


(a) R=4-MeC_6H_4, R'=H, Me, n-Bu, n-C_6H_{13}, or Ph; (b) R=Ph, R'=H, Me, or Ph; (c) R=Me; R'=Me, or Ph; (d) R=Et, R'=Me, or Ph .

Tetra(phenylethynyl)ethylene has been obtained via the mechanism[145]



It has been shown[150] that α-bromoketones react with COA under the same conditions (brief heating to a high temperature without a solvent or in nitrobenzene) as S_N1 halides(benzyl and allyl bromides). Since it has been suggested that the reaction proceeds via a stage involving an α-bromoenol coordinated to copper(I), it is useful to quote examples of such reactions in the present section of the review:



(XLIV)

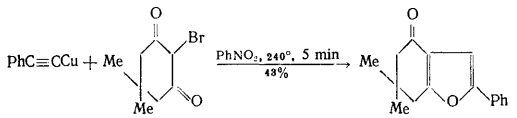
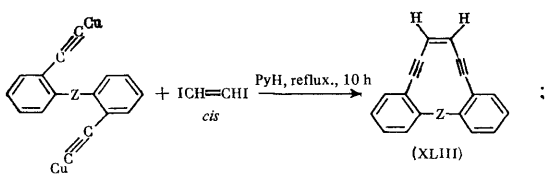


Table 8.

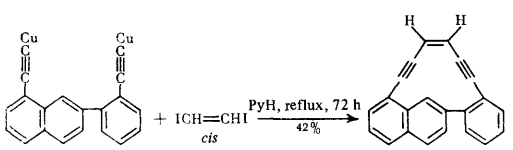
Reaction conditions	R	R'	Yield of (XLIV), %
Without solvent, 140°, 5 min	n-Pr	H	29
Nitrobenzene, 240°, 5 min	Ph	H	54
Nitrobenzene, 240°, 5 min	Ph	C (O) Ph	24

Staab and coworkers used *cis*-di-iodoethylene successfully in the synthesis of benzo[12]annulenes (XLIII)[29,30] and benzonaphtho[12]annulenes[149]:

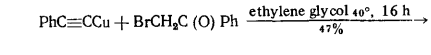


(XLIII)

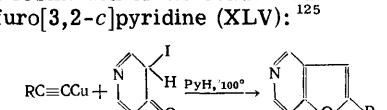
(a) Z = *trans*-HC=CH (17.5%); (b) Z = C≡C (10%); (c) Z = CH_2CH_2 (23%)



In a protic medium copper phenylacetylide promotes the reduction of ω-bromoacetophenone[150]:



The interaction of 3,5-di-iodo-4-pyridone with COA leads to the formation of the condensed heteroaromatic system of furo[3,2-*c*]pyridine (XLV):[125]



(XLV)

R=Ph, α-Py, n-Pr, n-C_6H_{13}, or CH_2CH_2OH

C-Derivatives of copper(I) (the compounds RCu) can be divided into definite groups in relation to 1-halogeno-acetylenes, as in the case of aryl halides. Thus, for

R = Ar, Ar_f,[151-153] and *o*-, *m*-, or *p*-*C*-carboranyl(12),[154] the ethynylation reaction takes place in ether and THF, for R = Alk_f it takes place in DMSO,[155] and for R = CN, it takes place in pyridine[156] and DMF.[157] COA belong to the last group[158].

The interaction of the cuprates $RCu.MgBr_2$ (R = Ar[159] or vinyl[160]) with 1-iodo(bromo)acetylenes is facilitated in the presence of DMF or $(Me_2N)_2C_2H_4$.

Curtis and Taylor[161] used bromopropargyl alcohol to obtain monosubstituted di- and tri-acetylene derivatives:

$$RC{\equiv}CCu + BrC{\equiv}CCH_2OH \xrightarrow{PyH,\ 35-50^\circ} R(C{\equiv}C)_2CH_2OH \rightarrow RC{\equiv}CC{\equiv}CH\ ;$$

R = Me, Ph, Me(OH)CH, $THPOCH_2$, $(EtO)_2CH$, MeC≡C, or 2-(2'-bithienyl).

A new direct ethynylating agent has been described—monobromoacetylene in DMF:[162]

$$Ar(C{\equiv}C)_nCu + BrC{\equiv}CH \xrightarrow{DMF,\ 0^\circ,\ 24\ h} Ar(C{\equiv}C)_nC{\equiv}CH\ :$$

a) *n* = 1, Ar = Ph, 1- or 2-naphthyl

b) *n* = 2, Ar = 1-naphthyl .

3. The Mechanisms of Reactions of COA with Aryl Halides, 1-Halogeno-olefins, and 1-Halogenoacetylenes

In the first studies Castro and coworkers[8,54] already considered the condensation of COA with aryl halides in pyridine within the framework of a general reaction involving nucleophilic substitution in an aromatic ring under the influence of copper(I) compounds, which had been investigated in detail previously[49] in relation to the CuX + ArAl → ArX + CuHal (X = Br, Cl, or CN) exchange. The findings obtained in this study were subsequently confirmed in an investigation of the exchange reactions of CuX with C_6F_5Hal (X = Cl, CN, or OAc),[163] FcHal (X = Cl, Br, or CN),[164,165] and IAr (X = C≡CPh,[124] Ph,[166] 2-furyl, or 2-thienyl[167]) in DMF, pyridine, and quinoline. It was established in all cases that the reactivity of Hal in ArHal decreases in the sequence I > Br ≫ Cl (F does not react), which is the reverse of that for direct nucleophilic substitutions; substituents in Ar have a consistent but weak influence on the rate of reaction, which is of second order overall and of first order with respect to each reactant.

Kinetic and thermodynamic parameters (Table 9) determined for the reaction

$$PhC{\equiv}CCu + IC_6H_4Y \xrightarrow{PyH,\ 100^\circ} PhC{\equiv}CC_6H_4Y + CuI$$

led to certain qualitative conclusions concerning the mechanism[124]: (a) copper phenylacetylide reacts in the dissociated, "monomeric" form (the rate of reaction is described by a second order equation):

$$-\frac{d[IC_6H_4Y]}{dt} = \frac{d[CuI]}{dt} = k_2[PhC{\equiv}CCu][IC_6H_4Y];$$

(b) the ring substitution under the influence of COA is indirectly nucleophilic (although the reactivity of IC_6H_4Y does decrease on passing from Y = NO_2 to Y = OMe or NH_2, the dependence of k_2 on the nature of Y is quantitatively weak); (c) the transition state is distinguished by a high degree of order (high negative activation entropy). According to the authors[124], these data confirm the four-centre concerted mechanism of the reaction of aryl halides with COA, proposed previously[8] (by analogy with the mechanism of Bacon and Hill[49]), which can be represented schematically in the following way in the presence of nucleophilic *o*-substituents in the ring (Y = QR'):[124]

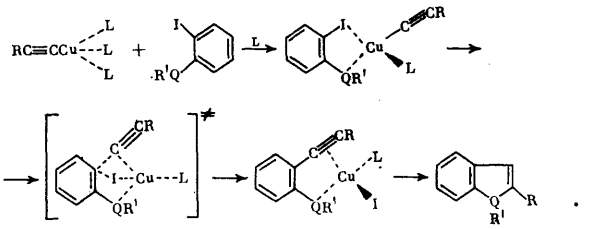


Table 9. Kinetic and thermodynamic parameters (calculated for 25°C) of the reaction

$$PhC{\equiv}CCu + IC_6H_4Y \xrightarrow{PyH,\ 100^\circ} PhC{\equiv}CC_6H_4Y + CuI$$

Y	k_2, litre mole^{-1} s^{-1}			Y	$\Delta F^{\neq}$, kcal	$\Delta H^{\neq}$, kcal	$\Delta S^{\neq}$, e.u.
	o-	*m*-	*p*-				
COOH	$7.0\cdot10^{-2}$	$2.9\cdot10^{-5}$	$4.6\cdot10^{-5}$	H	26	7,2	−63
OH	$8.6\cdot10^{-3}$	$1.3\cdot10^{-5}$	$2.0\cdot10^{-5}$	*o*-NO_2	26	16	−29
NO_2	$2.0\cdot10^{-3}$	$9.1\cdot10^{-5}$	$1.4\cdot10^{-4}$	*m*-NO_2	27	15	−36
OMe	$1.7\cdot10^{-5}$	$1.4\cdot10^{-5}$	$0.85\cdot10^{-5}$	*p*-NO_2	26	13	−41
NH_2	$3.4\cdot10^{-5}$	$1.0\cdot10^{-5}$	$1.4\cdot10^{-5}$				
H	$0.8\cdot10^{-5}$						

A significant factor in this mechanism is the initial I... Cu coordination, the copper atom retaining the tetrahedral configuration.

A similar mechanism has also been postulated by Burdon et al.[105], where the reactive form of COA is regarded as an ion pair, which can be involved in the equilibrium

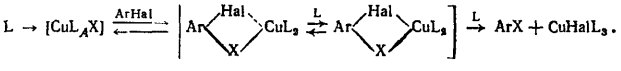
$$[CuL_AX] \rightleftarrows [CuL_B]^+X^-$$

contact ion pair — separated ion pair

(*A* = 1 − 3; *B* = 1 − 4; X = SBu, SPh, C≡CPh) ,

depending on the nature of the solvent ligand L.

The reaction is regarded as a competitive process involving the substitution of ligands at the central copper(I) atom:



It is assumed that only the contact ion pair, in which X is bound strongly to Cu(I) and cannot react independently of the latter, is reactive in the condensation. In the first stage ligands (solvent molecules) are displaced by the substrate ArHal (neutral process); this is followed by the nucleophilic substitution of Hal by X (via a four-centre mechanism), Hal being coordinated to copper(I), which leads to an indirect exchange of Hal for X in the second stage.

The weak dependence of the rate of condensation of COA with Y–ArHal on the nature of Y can be accounted for, within the framework of the four-centre mechanism (by analogy with the mechanism of Sato et al.[168]), by the opposite influence of Y on the rate of attack Hal → Cu and X → C (in Ar), the relative contributions of which determine the overall rate of reaction.

The formation of biaryls, disubstituted butadiynes, and reductive deiodination products from poly(halogenophenyl iodides)[90,106] can be accounted for by the electrophilic

exchange occurring in the intermediate four-centre complex in competition with the nucleophilic exchange and leading to the appearance of the additional condensation agents $ArHalCu$ and $IC{\equiv}CR$.

In order to describe the mechanism of this reaction, one may resort to the radical scheme considered by Atkinson et al.[96] [oxidative addition of a halogen to copper(I) and transfer of the ethynyl ligand from copper(II) to the aryl radical]. In the general case the interaction

$$ArC{\equiv}CCu + Ar_1Hal \rightarrow Ar_1^{\cdot} + Hal{-}Cu{-}C{\equiv}CAr \rightarrow ArC{\equiv}CAr_1 + CuHal$$

should occur in a "cage", although a free-radical reaction pathway can be postulated also for poly(halogenophenyl iodides).

The observation[96] that the reaction is accelerated when the reaction mixture is irradiated by infrared light, unconfirmed by experimental data, has been quoted in support of a radical mechanism. The concept of a radical mechanism has been developed by van Koten and Noltes, who proposed a mechanism with one-electron transfer in an oligomeric copper(I) complex for processes of this kind[169]:

$$(CuX)_n\,(DMF)_m + ArHal \rightarrow ArHal\,(CuX)_n\,(DMF)_m \rightarrow$$
$$\rightarrow Ar^{\cdot}\,(Cu^{II}XHal)\,(CuX)_{n-1}\,(DMF)_m \rightarrow ArX + CuHal\,(CuX)_{n-1}\,(DMF)_m \quad .$$

In a study of stable arylcopper compounds the same workers isolated and characterised hexanuclear copper clusters having the formula $Ar_4Cu_6X_2$.[25,26,170] The thermolysis of these clusters in DMF leads to biaryls[170] for X = Br or I and to tolanes[26] $ArC{\equiv}CAr_1$ for X = $C{\equiv}CAr$. In principle, such clusters can be formed and can play a definite role in those instances of the condensation of COA with aryl halides where the structure of the initial compounds (for example, for Ar = C_6X_5, where X = Cl, Br,[103] or F [99,104,106]) favours the exchange $RC{\equiv}CCu + HalAr = RC{\equiv}CHal + CuAr$. The subsequent course of the reaction (in addition to the condensation steps with liberation of CuHal) is then described by the scheme[26]

$$2RC{\equiv}CCu + 4CuAr \rightarrow Ar_4Cu_6(C{\equiv}CR)_2 \xrightarrow{t^\circ} ArC{\equiv}CR \quad ;$$
$$6ArCu + 2HalAr \rightarrow 2ArAr + Ar_4Cu_6Hal_2 \rightarrow ArAr + 2ArH + 2CuHal + 4Cu^\circ \quad ;$$
$$ArCu \xrightarrow{t^\circ} ArAr + ArH + Cu^\circ \quad .$$

On the other hand, in the general case the "cluster" mechanism is inconsistent with the kinetic data of Castro et al.[124], involves the formation of appreciable amounts of zero-valent copper together with CuHal, and cannot be regarded as a secondary mechanism accompaning the main mechanism of the condensation of COA with aryl halides.

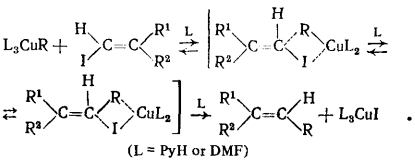
The condensation of COA with ArHal via an intermediate copper(III) compound, in accordance with the mechanism whose prototype is that of the exchange interaction of CuCl with aryl and vinyl iodides (R = Ar or vinyl)

$$CuCl + RI \rightarrow RCu(I)Cl \xrightarrow[-CuI]{+CuCl} RCu + 2CuCl_2 \rightarrow 2CuCl + RCuCl_2 \rightarrow RCl + CuCl \quad ,$$

put forward by Cohen et al.[171], is unlikely if only because the "soft" ligand ArHal cannot stabilise the "hard" Lewis acid copper(III).[172] However, this possibility cannot be ruled out for poly(halogenophenyl iodides).

It has been mentioned, incidentally[173], that copper(II) has a catalytic effect (in the form of a complex of $CuCl_2$ with NH_4Cl) in the reaction of COA with heteroaryl iodides, but the mechanism of the action of copper(II) is obscure.

The condensation of COA with 1-halogeno-olefins is regarded, by an analogy with aryl halides, as a competitive process involving the displacement of the ligand-solvent from the copper(I) coordination sphere by the substrate (1-halogeno-olefin) and the subsequent indirect nucleophilic exchange in the four-centre complex[142,145]:



(L = PyH or DMF)

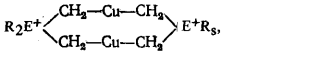
Since such condensation takes place unambiguously with retention of the initial configuration of the olefin and does not lead to dimerisation and reductive deiodination side products, the free-radical reaction mechanism is ruled out, as well as the intermediate formation of the copper(II) compound[142]. The addition of COA to the double bond of the olefin with subsequent elimination of CuHal should also lead to a more complex mixture of reaction products[145].

No information is available in the literature about the mechanism of the condensation of COA with 1-halogeno-acetylenes.

Thus, despite the unambiguous nature of the approach to the mechanism of the direct transfer of the ethynyl residue from copper(I) to the organic substrate (aryl, vinyl), the initial coordination of the halogen atom of the substrate to the copper(I) atom of the "depolymerised" (under the influence of the nitrogen-containing ligand-solvent) form of COA is generally assumed in all the schemes.

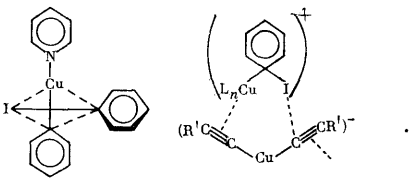
We believe that a common disadvantage of all the schemes discussed above is that they do not reflect the specific features of the COA both as coordination polymers[174] and as copper(I) compounds.

It is known that the polymeric (3c–2e) structure of the σ-aryl derivatives of copper(I) [and apparently silver(I)] is disturbed (as a result of complex formation) by nitrogen-containing electron-donating ligands (pyridine, DMF)[166,167,170]. Subsequent interaction of such complexes, for example, with ArI, can proceed in accordance with a four-centre mechanism via a tetrahedral transition state of type (XLVI).[166] On the other hand, the COA are inert in relation to the action of DMF, pyridine[124], and 2,2- and 4,4-bipyridyls[175] and form discrete (in most instances polynuclear) complexes with strong n-donor ligands—tertiary phosphines[174–176], arsines, stibines[174], cyclic amines[177], *o*-phenanthroline[175], and NH_3,[178] in which the π-interaction of copper(I) atoms with the C≡C bond persists. Evidently the "depolymerisation" of the COA in the L–RHal system (L is an electron-donating nitrogen-containing ligand-solvent, in most cases pyridine or DMF, R = Ar, vinyl, or ethynyl, and the halogen is usually iodine) should occur under the joint influence of both components and should lead immediately to the reaction complex. In view of the wide occurrence and stability of the $Cu^IX_2^-$ bridging anions in the form of discrete species[179] as well as part of the complexes $Y^+CuX_2^-$, where Y = R_4N or Ph_4As for X = Cl, Y = R_4N or Ph_4P for X = Br,[180] and Y = $Cu(PMe_3)_2$ for X = C≡CPh,[181] and the ylids



where E = P or As,[182] we suggest that this complex should have the zwitter-ionic structure (XLVII, R = Ar, Hal = I) incorporating the principal features of the structure of the

complex $[PMe_3.CuC{\equiv}CPh]_4$ [181]



(XLVI) (XLVII)

Since the reactivity of RI in condensation reactions with COA decreases in the series of substituents R ethynyl > vinyl ≫ aryl (alkyl substituents do not react)[1], in which the electronegativity of R and its capacity for the formation of bridge bonds (see below[215]) also diminish, we assume that there is no simple Cu–I coordination in the complex (XLVII). The cationoid component of (XLVII) is a system with a C_{Ar} bridge atom involved in a 3c–2e bond with copper and iodine atoms. The ease of formation of compound (XLVII) and the stability of its cationoid component should evidently increase when n-donor heteroatoms in the aromatic ring are in geometrical proximity to the copper atom (by analogy with stable Cu- and Ag-aryl compounds[170]). Indeed aryl iodides with the NH_2, OH, or COOH substituents in the *ortho*-position as well as 2-iododerivatives of furan, thiophen, and pyridine are much more reactive in reactions with COA than iodobenzene.

The ease of electron transfer from the anionoid component of (XLVII) to the cationoid component is determined by the electron-accepting properties of the ring; this results in the formation (on homolytic dissociation of the ≡C–Cu bond) of the ethynyl radical R'C≡C'. In the cationoid component the 3c–2e bond (Cu–C_{Ar}–I) is converted into a 2c–2e bond (Cu–I) with formation of an aryl radical when the aryl is a weak acceptor, or into a Cu–C_{Ar} bond with formation of the I' radical species when the aryl is a strong acceptor. Recombination of the radicals in the "cage" should lead to the final products.

Within the framework of the proposed mechanism, the influence of the substituents in Ar on the rate of reaction of ArI with COA is to a large extent cancelled out by their opposed influence on the ease of formation of a complex of type (XLVII) and subsequent one-electron transfer as well as the radical mechanism of the last reaction stage. In this interpretation the condensation of COA with RI (R = Ar, vinyl, or ethynyl) is related to the nucleophilic substitution in diaryliodonium salts catalysed by copper(I) salts, for which the following mechanism has been proposed[183]:

$$Ar_2I^+Cl^- + CuCl \rightleftharpoons Ar_2I^+ + CuCl_2^- \xrightarrow{e} \underset{\text{(ion pair)}}{Ar_2I^+CuCl_2^-} \longrightarrow$$
$$\longrightarrow ArI + ArCl + CuCl \quad .$$

The electron-donating ligand-solvent, which stabilises the cationoid component of the complex (XLVII), should not exhibit a high ionising capacity which would hinder significantly the interaction within the ion pair (XLVII); otherwise (HMP, ϵ = 30, Table 1) the yield of the ethynylation products is sharply reduced[140,141].

Furthermore, the formation of a complex by the ligand-solvent with the copper atom in the cationoid component should influence the oxidation-reduction potential and the strength of the C–Hal bond.

Finally, copper t-butylacetylide[138] as well as silver and gold organoacetylides[174], in which the coordination of the metal atom to the C≡C bond is weak, apparently form under the conditions of reactions of the given type complexes with a nitrogen-containing ligand-solvent, inert with respect to RI (R = Ar, vinyl, or ethynyl), and not structures of type (XLVII); furthermore, one must assume that oxidation of the anionoid component of silver(I) and gold(I) complexes proceeds with greater difficulty than in the case of COA.

4. Compounds with an Element–Halogen Bond

Many inorganic and organoelemental compounds, containing readily polarisable E–Hal bonds, where E is as a rule a nucleophilic heteroatom, react vigorously with COA and SOA in solvents with moderate electron-donating capacities, forming MHal and σ-E-ethynyl derivatives. The simplest examples of reactions of this kind are provided by those of COA with Cl_2, Br_2, I_2, and IBr,[1] for example[147,184]:

$$HCB_{10}H_{10}CC{\equiv}CCu + I_2 \xrightarrow[68\%]{\text{heptane}} HCB_{10}H_{10}CC{\equiv}CI + CuI \quad ;$$
$$Cl_2C{=}CClC{\equiv}CCu + Br_2 \xrightarrow{CCl_4} Cl_2C{=}CClC{\equiv}CBr \quad .$$

Halogens react analogously with SOA:[33,185,186]

$$Me_2CHC{\equiv}CAg + I_2 \rightarrow Me_2CHC{\equiv}CI + AgI \quad :$$
$$C_6Cl_5C{\equiv}CAg + Cl_2 \xrightarrow[90\%]{CCl_4} C_6Cl_5CC{\equiv}CCl \quad :$$
$$4,4'\text{-}(AgC{\equiv}CC_6Cl_4)_2 + Cl_2 \xrightarrow[85\%]{CCl_4} 4,4'\text{-}(ClC{\equiv}CC_6Cl_4)_2 \, .$$

A method has been developed recently for the synthesis of 1-bromo- and 1-iodoacetylenes via SOA without the preliminary isolation of the latter[187]:

$$RC{\equiv}CSiAlk_3 \xrightarrow[2.\ Hal_2]{1.\ AgNO_3} RC{\equiv}CHal \quad ;$$
(a) Hal=I, R=C (Me)=CHCO (O) Me;
(b) Hal=Br, R=C (Me)=CHCO (O) Me,
CH=CHCO (O) Me, Ph (Et) C (OH), or Ph_2C (OH) .

In contrast to the synthesis via COA, the synthesis of 1-chloro- and 1-bromo-acetylenes via SOA is not complicated by the formation of oxidative dimerisation products.

Trisphenylethynyl derivatives of phosphorus, arsenic, and antimony have been obtained by the reaction of silver(I) phenylacetylide with ECl_3 (E = P, As, or Sb) in a benzene–THF mixture[188]:

$$3PhC{\equiv}CAg + ECl_3 \xrightarrow[50\text{–}70\%]{} E(C{\equiv}CPh)_3 \, .$$

Copper(I) phenylacetylide reacts only with PCl_3, forming (even in the presence of a large excess of PCl_3) tris-(phenylethynyl)phosphine[1].

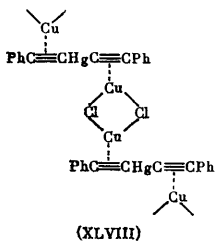
The interaction of silver(I) arylacetylides with $HgHal_2$ leads to bisarylethynyl derivatives of mercury[188]:

$$2RC{\equiv}CAg + HgHal_2 \xrightarrow[\sim 90\%]{THF} Hg(C{\equiv}CR)_2 + 2AgHal \quad :$$
Hal=Cl, Br, or I; R=Ph, C≡CPh .

An analogous reaction has also been described for C_6F_5Ag [52] and for ethoxy-(*p*-tolylimino)methylsilver, i.e. $[p\text{-}MeC_6H_4N{=}C(OEt)Ag]_3$, which is unusually stable in air[189].

In solvents with a moderate electron-donating capacity (THF, alcohol, ether, and acetone) COA react with $HgHal_2$ (Hal = Cl or Br), regardless of the ionising capacity of the solvents, to form complexes having the formal composition $(RC{\equiv}C)_2HgCu_2Cl_2$, to which the structure of

the coordination polymers (XLVIII) was attributed on the basis of Raman spectroscopic data and chemical properties[190]:



(XLVIII)

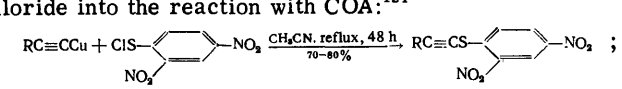
The polymeric complex (XLVIII) has also been obtained by the interaction of copper(I) phenylacetylide with *trans*-β-chlorovinylmercury in CH_3CN and THF and as a result of the oxidative disproportionation of bis(phenylethynyl)-mercury under the influence of copper(II) chloride in the same solvents[190]. On treatment with pyridine, the complex (XLVIII) is converted into bis(phenylethynyl)mercury, while treatment with aqueous ammonia yields copper phenylacetylide (apparently as a result of the selective interaction of the nitrogen-containing ligands with the metal atoms)[191].

Organoelemental halides are beginning to play an increasingly notable role in the chemistry of organic derivatives of copper(I) and silver(I). So far only a few examples of such reactions have been described, for example, the reaction of RM with Me_3SiCl (M = Cu, R = Me_3SiCH_2;[192] M = Ag, R = C_6F_5 [52]), the reaction of ArCu with R_2SnBr_2 [R = Me, Ar = YC_6H_4, where Y = 2-Me_2NCH_2, 2-Me_2N, 4-Me_2N, 2-MeO, 2,6-$(MeO)_2$, or 2,4,6-$(MeO)_3$; R = Ph, Ar = 2-Me_2NCH_2],[193] which take place in weakly polar solvents with a moderate electron-donating capacity. Similar reactions involving COA and SOA take place in more polar media.

In the search for systems with optical manifestations of conjugation via a phosphorus(III) atom, arylbis-(4-nitrophenylethynyl)phosphines were synthesised (with a low yield owing to side reactions)[194]:

$$4\text{-}O_2NC_6H_4C{\equiv}CCu + Cl_2PAr \xrightarrow{THF} (4\text{-}O_2NC_6H_4C{\equiv}C)_2PAr \ ;$$
Ar=4-YC_6H_4, where Y=H, Cl, OMe, or NMe_2 .

Castro et al. introduced 2,4-dinitrophenylsulphenyl chloride into the reaction with COA:[124]



R = n-Pr or Ph.

Organotin compounds are readily ethynylated with the aid of silver alkylacetylides having functional groups[195]:

$$(EtO)_2CHC{\equiv}CAg + BrSnPh_3 \xrightarrow[80\%]{\text{acetone, } 80^\circ} Ph_3SnC{\equiv}CCH(OEt)_2 \ .$$

It has been noted that copper(I) arylacetylides are extremely inert in relation to organotin halides[193]:

$$4\text{-}MeC_6H_4C{\equiv}CCu + Br_2SnMe_2 \xrightarrow[28\%]{17 \text{ days}} 4\text{-}MeC_6H_4C{\equiv}CSn(Br)Me_2 \ .$$

When copper acetylide and 1-*C*-ethynyl-*o*-carbaborane were heated with MeHgBr in a heptane–THF mixture, (*o*-carbaboranyl-1-*C*-ethynyl)methylmercury was obtained[147].

The reactions of covalent transition metal halide complexes with organic derivatives RM, where M = Cu(I) or Ag(I) and R is a powerful inductive acceptor, are of great interest. Thus the halogen atom in the complexes $ClIr(CO)(PPh_3)_2$, $ClRh(CO)(PPh_3)_2$, $ClRh(C_8H_{12})(PPh_3)$, and $Fe(CO)_4I_2$ is substituted by the C_6F_5 group on treatment with C_6F_5Ag in ether[196]; *cis*-$(PPh_3)_2PtCl_2$ reacts with [*p*-$MeC_6H_4N{=}C(OEt)Ag]_3$ in $CHCl_3$, forming a monosubstituted product[189]. In the synthesis of σ-aryl- and σ-carbaboranyl-π-cyclopentadienyldicarbonyliron via the reaction

$$RCu + BrFe(CO)_2(\pi\text{-}C_5H_5) \xrightarrow{\text{ether, THF}} R\text{—}Fe(CO)_2(\pi\text{-}C_5H_5) \ ;$$
R=Ph, 3- and 4-FC_6H_4; *o*- and *m*-$HCB_{10}H_{10}C$—; or *o*- and *m*-—$CB_{10}H_{10}C$— ,

use was made of aryl and carbaboranyl derivatives of copper(I), apparently in the form of cuprates[197].

Table 10.

$$CuI \xrightarrow{HNEt_2} (HNEt_2)_nCuI \xrightarrow[HNEt_2]{HC{\equiv}CR} (HNEt_2)_nCuC{\equiv}CR + HI{\cdot}HNEt_2 \xrightarrow{MCl} MC{\equiv}CR + (HNEt_2)_nCuCl \ .$$

MCl	R	MCl	R
CpNi(PPh$_3$)Cl *trans*-$(PEt_3)_2PdCl_2$ *trans*-$(PMe_2)_2PtCl_2$	H, Me H, Me, CH_2OH H	*cis*- and *trans*-$(PR'_3)_2PtCl_2$, R' = Et, Bu *cis*- and *trans*-$(PBu_3)_2PtCl_2$	H, Ph C≡CH, 4-HC≡CC_6H_4

The catalytic effect of copper(I) salts in condensation reactions of nickel, palladium, and platinum halide complexes with acetylenes in Et_2NH is attributed to the possibility of the formation under these conditions of amine complexes of COA [198,199] (Table 10). The catalytic reaction proceeds with retention of the initial configuration of the metal atom, which made it possible, in particular, to simplify significantly the synthesis of the *cis*-isomers of platinum(II) complexes which are difficult to obtain:

Under the same conditions, high-molecular-weight polyconjugated polymers, which are stable in air and contain both homogeneous and alternating metal atoms in the chain, were obtained[200,201] via the reaction

$$trans\text{-}(HC{\equiv}CC{\equiv}C)_2M(PBu_3)_2 + trans\text{-}Cl_2M'(PBu_3)_2 \xrightarrow[85\text{–}95\%]{CuI/Et_2NH,\ 20^\circ,\ 20\text{–}50\ h} \rightarrow trans\text{-}[-(PBu_3)_2M(C{\equiv}C)_2(M'(PBu_3)_2(C{\equiv}C)_2-]_n \ ;$$
(a) M=M'=Pt (M_w 20 000); (b) M=M'=Pd; (c) M=Pt, M'=Pd; (d) M=Pd, M'=Pt (M_w 26 000)

In the reaction involving the bisdiacetyleneplatinum(II) complex products resulting from the monosubstitution of the Cl atoms in *trans*-$(PBu_3)_2M'Cl_2$ (M' = Pt or Pd) were isolated[201].

The mechanism proposed[202] for the catalytic action of the Q = $PdCl_2(PPh_3)_2/CuI/NEt_2X$ system, where X = H or Et, which is highly effective in single-stage syntheses of aryl- and vinyl-acetylenes[202] as well as α-ethynyl ketones[203],

$$RHal + HC{\equiv}CR' \xrightarrow[70\text{–}90\%]{Q} RC{\equiv}CR'$$
R=Ar, Vin or C(O)R"

always includes stages involving the formation of σ-ethynyl derivatives of palladium(II) in accordance with the scheme discussed above:

$$(PPh_3)_2PdCl_2 \xrightarrow{R'C{\equiv}CH,\ CuI,\ NHEt_2} (PPh_3)_2Pd(C{\equiv}CR')_2 \rightarrow$$
$$\rightarrow (R'C{\equiv}C)_2 + (PPh_3)_2Pd(0) \xrightarrow{RHal} (PPh_3)_2Pd\begin{matrix}R\\Hal\end{matrix} \rightarrow$$
$$\xrightarrow{R'C{\equiv}CH,\ CuI,\ HNEt_2} (Ph_3P)_2Pd\begin{matrix}R\\C{\equiv}CR'\end{matrix} \rightarrow RC{\equiv}CR' + (Ph_3P)_2Pd(O) \ .$$

The ethynyl derivatives of benzene, pyridine[202], pyrimidene[204], and pyridazine[205] were obtained by this method; in contrast to COA, the $(PPh_3)_2PdCl_2/CuI$ catalytic system makes it possible to introduce aryl bromides into reactions with terminal acetylenes[202].

The reaction of COA, isolated beforehand, with the complexes $Cl_2Pt(PR'_3)_2$ proceeds similarly to the catalytic process[199,206] (Table 11).

Table 11.

$$RC\equiv CCu + Cl_2Pt(PR'_3)_2 \xrightarrow[60-80\%]{L} (PR'_3)Pt(C\equiv CR)_2$$

R	R'	Isomer	L
Ph	Et	*cis*	Acetone + $Me_2NCH_2CH_2NMe_2$; 20°
Ph	Et	*trans*	ditto
C_6F_5	Ph	*cis*	Boiling benzene
$CH=CH_2$	Et	*cis*	Acetone + $Me_2NCH_2CH_2NMe_2$; 20°
$CH=CH_2$	Et	*trans*	ditto

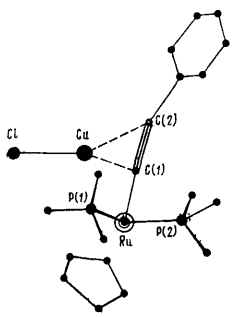


Figure 1. The molecular structure of $(\pi\text{-}C_5H_5)Ru(PPh_3)_2.(C\equiv CPh)CuCl$ (XLIXb); the benzene rings at the phosphorus atoms are not shown.

New types of discrete heteronuclear copper(I) and silver(I) compounds, in which the C≡C groups play an important structure-forming role, have been synthesised by the interaction of COA and SOA with iron, ruthenium, rhenium, iridium, and rhodium halide complexes. These compounds have been partly considered in two reviews[7,207].

The 1 : 1 COA adducts, which have the simplest structures, can be formed as a result of direct exchange and subsequent π-binding of CuHal to the C≡C group[208-211]:

$$RC\equiv CCu + [HalML_n] \rightarrow [L_nM(C\equiv CR)CuHal] .$$

Monomeric ethynyl complexes of ruthenium (XLIX), containing linearly coordinated copper(I) atoms according to X-ray diffraction data (R = Ph) (Fig. 1)[208], have been obtained by the reaction[209]

$$RC\equiv CCu + ClRu(\pi\text{-}C_5H_5)(PPh_3)_2 \xrightarrow{C_6H_6\ \text{reflux.,}\ 20\ h} \underset{(XLIX)}{(\pi\text{-}C_5H_5)Ru(PPh_3)_2(C\equiv CR)CuCl} ;$$

(a) R=Me (55%); (b) R=Ph; (c) R=4-MeC_6H_4 (7%) .

In complexes (XLIX) the π-bond between the copper atom and the C≡C group is resistant to the action of PPh_3 in benzene and is decomposed only by a powerful agent such as the tridentate chelating ligand $MeC(CH_2PPh_2)_3$.[209]

In contrast to (XLIX), in complexes (L)—the dimeric products of the interaction of copper(I) arylacetylides with $(\pi\text{-}C_5H_5)Fe(CO)_2Hal$ (Hal = Cl or Br), a Cu–Cl–Cu bridge bond is formed and the copper atoms have a trigonal coordination environment (Fig. 2)[210-212]:

$$ArC\equiv CCu + HalFe(CO)_2(\pi\text{-}C_5H_5) \xrightarrow{Q,\ \text{relufx.}} [(\pi\text{-}C_5H_5)Fe(CO)_2(C\equiv CAr)CuHal]_2 .$$

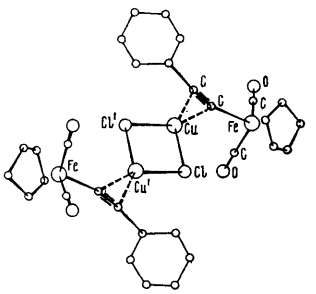


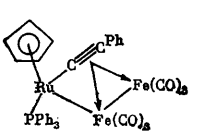
Figure 2. The molecular structure of $[(\pi\text{-}C_5H_5)Fe(CO)_2.(C\equiv CPh)CuCl]_2$ (L, Ar = Ph, Hal = Cl).

Table 12.

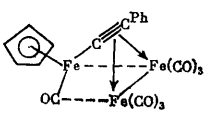
Hal	Q	Ar	Yield of (L), %	Hal	Q	Ar	Yield of (L), %
Cl	Acetone	Ph	42	Cl	THF	C_6F_5	20
Cl	THF	4-MeC_6H_4	27	Br	THF	Ph	10
Cl	THF	4-FC_6H_4	16				

The complexes (L) have been obtained also by specific synthesis from $(\pi\text{-}C_5H_5)Fe(CO)_2(C\equiv CPh)$ and CuHal (the yield is 55% for Hal = Cl and 20% for Hal = Br) in acetone[211]. The use of bromo-derivatives in the direct and specific syntheses lowers the yield of (L) significantly (Table 12).

The thermal decomposition of (L) *in vacuo* results in the formation of ferrocene and diarylbutadiyne[210]. Treatment of (XLIX) and (L) with the carbonyl $Fe_2(CO)_9$ in benzene led to trinuclear clusters with the tentative structures (LI) [210] and (LII):[211]



(LI)

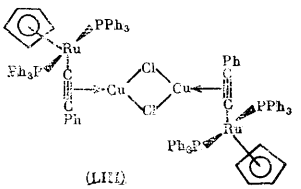


(LII)

In compounds (L) there is no direct interaction between the metal atoms; X-ray diffraction data indicate the presence of a strongly delocalised electron system incorporating the acetylenic fragment, Fe and Cu atoms, and possibly the benzene ring[212].

The structure (LIII), which is analogous to (L), has been attributed to the 1 : 1 dimeric adduct, isolated together with (XLIXb) in the reaction of PhC≡CCu with

$ClRu(PPh_3)_2(\pi\text{-}C_5H_5)$:[209]



(LII)

The discrete ethynylrhenium complex (LIV) apparently also belongs to the above type of compounds[209]:

$$PhC{\equiv}CCu + cis\text{-}ClRe(CO)_3(PPh_3)_2 \xrightarrow[65\%]{C_6H_6,\ reflux.,\ 6\ h} [(PPh_3)_2Re(CO)_3(C{\equiv}CPh)CuCl]_n \quad (LIV)$$

One may expect that, when $n = 1$, (LIV) will have a structure similar to that of (XLIX) and, when $n = 2$, its structure will resemble that of (L).

Thus it has been established for both (XLIX) [208] and (L) [212] and it has been postulated for (XLVIII), (LIII), and (LIV) that each copper atom is linked centrosymmetrically to one C≡C fragment. It is postulated that the complexes (L) are stabilised as a result of the large contribution of the dative component ($d \rightarrow \pi^*$) to the π-bond between the copper atom and the C≡C group[212].

The 1 : 1 adduct of copper(I) 4-tolylacetylide with $ClRu(\pi\text{-}C_5H_5)(PPh_3)_2$ (XLIXc) as well as the monoethynyl products of the condensation of copper(I) fluorophenylacetylides with $ClRu(\pi\text{-}C_5H_5)(PPh_3)_2$ (LV) and $ClRe(CO_3).(PPh_3)_2$ (LVI), which contain no π-linked copper(I) atoms, react with an excess of the corresponding COA, the process being accompanied by a redistribution of the PPh_3 ligand and the formation of diacetylenecopper(I) complexes of a new type[204], for the prototype of the structure of which the zwitter-ionic structure of tertiary phosphine complexes of COA was chosen[181]:

According to X-ray diffraction data[213] (Fig. 3), the complex (LVII) includes a cationoid group, comprising a copper(I) atom asymmetrically π-linked to two C≡C fragments and located in a planar trigonal configuration, and an anionoid group with a central octahedral Re(I) atom; interaction between the metal atoms in (LVII) is unlikely. It is of interest that, among all known phosphine complexes of copper(I), the Cu–P bond length is smallest in (LVII):

$$C_6F_5C{\equiv}CCu + cis\text{-}[ClRe(CO)_3(PPh_3)_2] \xrightarrow{THF,\ reflux.,\ 24\ h} [Cu(PPh_3)]^+[Re(C{\equiv}CC_6F_5)_2(CO)_3(PPh_3)]^- + Re(C{\equiv}CC_6F_5)(CO)_3(PPh_3)_2$$
(LVII), 21% (LVI), 6%

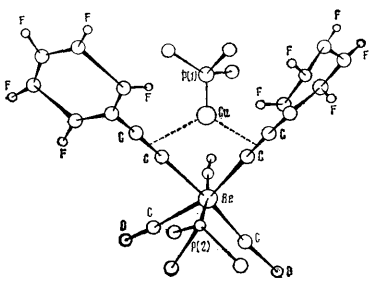
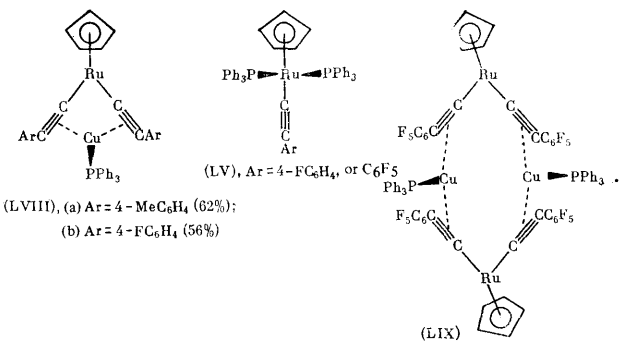


Figure 3. The molecular structure of $[Cu(PPh_3)]^+[Re(C{\equiv}CC_6F_5)_2(CO)_3(PPh_3)]^-$ (LVII); the benzene rings at the phosphorus atoms are not shown.

By analogy with (LVII), a zwitter-ionic structure has been attributed to the main products of reaction of $ArC{\equiv}CCu$ with $ClRu(\pi\text{-}C_5H_5)(PPh_3)_2$—the monomeric (in benzene) complexes (LVIII) and the dimeric complex (LIX):[209]



(LVIII), (a) Ar = 4-MeC_6H_4 (62%); (b) Ar = 4-FC_6H_4 (56%)

(LV), Ar = 4-FC_6H_4, or C_6F_5

(LIX)

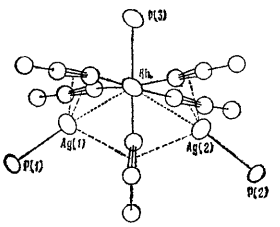
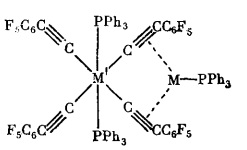


Figure 4. The molecular structure of $PhAg_2(C{\equiv}CC_6F_5)_5.(PPh_3)_3$ (LXI); the pentafluorobenzene rings as well as benzene rings at the phosphorus atoms are not shown.

Together with compound (LVIIIb), the complex (LVa) was isolated from the reaction mixture (yield 5%). The complex (LIX) was obtained after refluxing for 7 h a mixture of $C_6F_5C{\equiv}CCu$ with $ClRu(\pi\text{-}C_5H_5)(PPh_3)_2$ in benzene; an increase of reaction time (to 13 h) results in the formation of (LVb) only. It is suggested that the copper and ruthenium in compounds (LVIII) and (LIX) are univalent and bivalent and that there is no bond between them[209]. The zwitter-ionic complexes $[M'(C{\equiv}CC_6F_5)_4(PPh_3)_2]^-.[M(PPh_3)]^+$ (LX), which are isostructural with (LVIII), have been obtained in a low yield by the reaction of $C_6F_5C{\equiv}CM$ (M = Cu [214] or Ag [215]) with $ClIr(CO)(PPh_3)_2$ in toluene and of $C_6F_5C{\equiv}CAg$ with $ClRh(PPh_3)_3$ in THF and dimethoxyethane (DME).[215]



(LX), (a) M^I = Ir (III), M = Cu (I) or Ag (I); (b) M^I = Rh (III), M = Ag (I)

In the latter case the main product (yield 10%) is an unusual trinuclear complex $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ (LXI),[215,216] which has been investigated in detail[215,217].

It contains (Fig. 4) a central Rh atom in a regular octahedral coordination with a PPh_3 molecule and five σ-ethynyl ligands. Each silver atom has a tetrahedral coordination environment, which includes a PPh_3 molecule and three asymmetric π-ethynyl fragments, the *trans*-C≡C group being π-linked to both silver atoms. Data for the coordination environment of the silver and rhodium atoms as well as the absence of interaction between them make it possible to represent structure (LXI) as zwitter-ionic: $[Ag(PPh_3)]_2^{2+}[(PPh_3)Rh^{III}(C{\equiv}CC_6F_5)]^{2-}$. The shortened [compared with other phosphine complexes of copper(I) and silver(I) compounds] P → M bond [M = Cu(I) or Ag(I)] in (LVII) and (LXI) shows that there is a strong M–P d_π–d_π interaction, according to Churchill and DeBoer[217].

The mechanism of the interaction of SOA with $ClRh(PPh_3)_3$ is apparently of fundamentally the same type for all the reactions of COA and SOA with complex transition metal halides examined and is based on a key role of the intermediate $Rh(C{\equiv}CAr)_3(PPh_3)_3$, which is a product of the oxidative addition of two SOA molecules to the complex $Rh(C{\equiv}CAr)(PPh_3)_3$ formed in the first (exchange) stage. Subsequent substitution of the PPh_3 ligands by the ethynyl anion with simultaneous transfer of PPh_3 to the Ag atom should lead to the zwitter-ionic complexes (LXb) and (LXI) according to the mechanism of Abu Salah and Bruce[215].

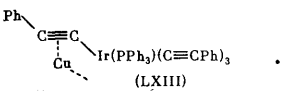
Bruce and coworkers obtained for the first time the ethynyl hexanuclear clusters (LXII) having the general formula $M_4M'_2(C{\equiv}CAr)_8(PPh_2R)_2$ (Table 13) by the reaction of COA [214,218] and SOA [215] with *trans*-$ClIr(CO)(PPh_2R)_2$ and *trans*-$ClRh(PPh_3)_3$ and of COA with *trans*-$ClRh(CO).(PPh_2R)_2$.[214]

Table 13.

M	M′	Ar	R	M	M′	As	R
Cu	Ir	Ph, C_6F_5	Ph, Me	Cu	Rh	Ph, C_6F_5, 4-MeC_6H_4, 4-FC_6H_5	Ph, Me
Cu	Ir	4-MeC_6H_4, 4-FC_6H_4	Ph				
Ag	Ir	Ph, C_6F_5	Ph	Ag	Rh	Ph, C_6F_5	Ph

COA react with *trans*-$ClM'(CO)(PPh_3)_2$ (M′ = Ir or Rh) and *trans*-$ClRh(PPh_3)_3$ on refluxing in benzene or toluene. Reactions of the complexes *trans*-$ClM'(CO)(PPh_2Me)_2$ are better differentiated—in benzene [M′ = Ir(PhC≡CCu) or $Rh(C_6F_5C{\equiv}CCu)$] or DME [M′ = Ir($C_6F_5C{\equiv}CCu$) or Rh(RhC≡CCu)].[214] The reactions of SOA with *trans*-$ClIr(CO)(PPh_3)_2$ take place in toluene and those with *trans*-$ClPh(PPh_3)_3$ proceed in a more polar medium (THF, DME).[215] We may note that the yields of (LXII) decrease on passing from Ir to Rh and from Cu to Ag. The rhodium clusters (LXII) are apparently less stable than the iridium clusters and the extensive formation of diarylbutadiynes in reactions of rhodium halide complexes with COA and SOA is specifically attributed to this fact[214,215]. The enhancement of the electron-accepting properties of the ring in ArC≡CCu and the replacement of PPh_3 by the stronger electron-donating ligand PPh_3Me stabilise the clusters (LXII, M = Cu).[214]

The reaction of the complex PhC≡CCu.PPh_2Me with *trans*-$ClIr(CO)(PPh_3)_2$ proceeds with exchange of the phosphine ligand at the Ir atom and leads to $Ir_2Cu_4.(C{\equiv}CPh)_8(PPh_2Me)_2$ with a low yield[214]. According to X-ray diffraction data[218,219], the "skeleton" of the cluster $Ir_2Cu_4(C{\equiv}CPh)_8(PPh_3)_2$ consists of a slightly distorted octahedron in which the equatorial positions are occupied by the Cu atoms and the apical positions are occupied by Ir atoms (Fig. 5). Each $(Ph_3P)Ir$ fragment is σ-linked to four ethynyl ligands and the Ir–C≡CPh system has the transoid configuration (LXIII), unusual for acetylene complexes, which ensures the possibility of the formation of a Cu–Ir bond and the π-interaction of the copper atom with two acetylene groups belonging to different iridium atoms:



(LXIII)

A distinctive feature of the structure of the cluster is a pronounced asymmetry of such interaction.

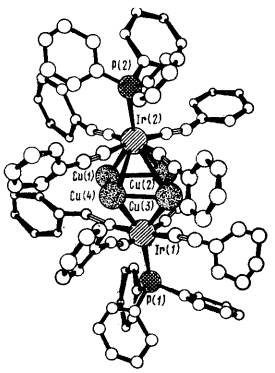


Figure 5. The molecular structure of $Cu_4Ir_2(PPh_3)_2.(C{\equiv}CPh)_8$ (LXII, M = Cu, M′ = Ir, Ar = R = Ph).

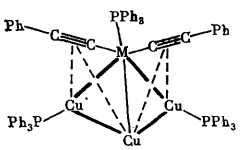


Figure 6. The proposed molecular structure of the cluster $IrCu_3(C{\equiv}CPh)_2(PPh_3)_2$.

It has been suggested[215,244] that all the clusters (LXII) have structures of the same type; the formal valence states of the metal atoms in them are identical: Ir(IV), Rh(IV), Cu(0), and Ag(0). The clusters (LXII) are electron-enriched systems; for M = Cu, it is assumed that the excess electrons are located in the antibonding M′–Cu and Cu–Cu orbitals and are responsible for a bond order of 3/4.[214] A structure (Fig. 6) intermediate between (LXa) and (LXII, M = Cu, M′ = Ir) has been attributed for the electron-deficient cluster $IrCu_3(C{\equiv}CPh)_2(PPh_3)_2$, which has been isolated together with $Ir_2Cu_4(C{\equiv}CPh)_8(PPh_3)_2$ in the reaction of PhC≡CCu with *trans*-$ClIr(CO)(PPh_3)_2$ in benzene[214].

The clusters (LXII, M = Cu, M′ = Ir, Ar = Ph or 4-MeC_6H_4, and R = Ph) react with $Fe_2(CO)_9$ in benzene, forming the octanuclear clusters $Ir_2CuFe_2(C{\equiv}CAr)_8(CO)_8 \cdot (PPh_3)_2$, which retain the Ir_2Cu_4 "skeleton" and do not contain CO bridge groups[214].

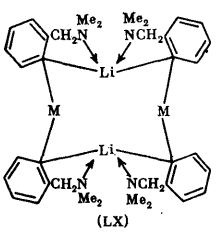
IV. COPPER AND SILVER ORGANOACETYLIDES IN ADDITION REACTIONS

Although the mechanisms of the numerous reactions of COA and SOA with nucleophilic, electrophilic, and 1,3-dipolar compounds considered in this section have not been investigated at all, it is possible to isolate in a purely formal manner the common stage in reactions of this kind where the reactant adds directly to the monomeric R≡C–M (M = Cu or Ag) fragment. In terms of topological features, these reactions can be subdivided into three groups: (1) addition of nucleophiles to copper and silver atoms in COA and SOA; (2) addition of electrophiles and nucleophiles to the ≡C–M (M = Cu or Ag) bond; (3) addition of 1,3-dipolar compounds to the C≡C bond in COA.

1. Addition of Nucleophiles to the Copper and Silver Atoms in COA and SOA

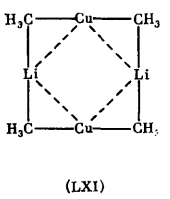
Like organocopper compounds RCu (R = alkyl, vinyl, or aryl), COA react with alkali metal salts in ether and THF to form reactive heterocuprates having the empirical formula $M^+[RC{\equiv}CCuX]^-$ (M = Na, X = CN; M = Li, X = Hal).[3] The reaction of alkali metal organoacetylides RC≡CM with COA (M = Li, Na, or K) and SOA (M = Na or K) in liquid ammonia yielded homoethynyl cuprates and argentates $M[M'(C{\equiv}CR)]_{n+1}$ (M = alkali metal; M′ = Cu(I) or Ag(I); n = 1 or 2), and the available information about them has been surveyed[1]. Mixed ethynyl homocuprates based on COA and various types of organolithium or organomagnesium compounds $M^+[RC{\equiv}CCuR']^-$ (M = Li or MgHal) [3,5] have no analogues in the SOA series.

It has been suggested[170,172] that all organocuprates are structurally similar and have the cluster structure with metal bridge atoms and an electron-deficient 2e–3c M–C–M bond characteristic of Group IB metal compounds. On the basis of experimental data, this type of structure has been proposed for the homocuprates (LX) [170,220] (and the corresponding homoargentates[221]) and the homocuprate (LXI) [172] {cf. with the structure $[CuCH_2SiMe_3]_4$ of a discrete centrosymmetric tetramer consisting of a planar square of Cu atoms, involved in the linear coordination C–Cu–C and the 3c–2e Cu–C–Cu bonds[207]}.



(LX)

M = Cu (I) or Ag (I)



(LXI)

It has been noted that the reactivity of organocuprates is determined by the strength of the M–C–M bridge bond and increases when the latter is weakened in the series N≡C– < C≡CR < aryl < alkyl.[220]

Van Koten and Noltes discovered a fundamentally new structural-chemical type of reactions of COA—the formation of mixed organocopper compounds with ArCu.[24-26] They had shown earlier[222] that, depending on the nature and position of the complex-forming substituent in the ring, arylcopper compounds ArCu react with the halides CuHal to form either 1 : 1 polymers (Ar = 2-$Me_2NCH_2C_6H_4$ or 4-$Me_2NC_6H_4$; Hal = Br) or discrete hexanuclear clusters $Ar_4Cu_6Hal_2$ (Ar = 2-$Me_2NC_6H_4$, Hal = Cl or Br), whose structure has been investigated in detail in relation to $(5\text{-Me-2-}Me_2NC_6H_3)_4Cu_6Br_3$.[170,223] Ethynyl clusters of the type $Ar_4Cu_6(C{\equiv}CR)_2$ (I), where Ar = 2-$Me_2NC_6H_4$, the methods of synthesis of which (including syntheses from COA and ArCu) were examined above, contain an octahedral skeleton of copper atoms, by analogy with the study of Guss et al.[223] (and on the basis of spectroscopic data), the equatorial copper atoms being involved in trigonal coordination with Ar (2e–3c Cu–C bond), the Me_2N group (2e–2c Cu–N bond), and the C≡CR fragment (4e–3c Cu–C bridge bond), while the apical copper atoms are involved in diagonal coordination with Ar (2e–3c Cu–C bridge bond) (Fig. 7)[25].

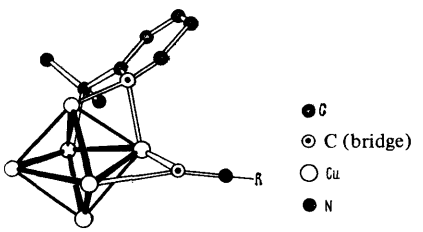


Figure 7. The proposed molecular structure (fragment) of $Ar_4Cu_6(C{\equiv}CR)_2$ clusters (I, Ar = 2-$Me_2NC_6H_4$, R = Ph or 4-MeC_5H_4).

Thermal decomposition of such clusters leads consistently to tolanes[24,26]:

$$Ar_4Cu_6(C{\equiv}CR)_2 \xrightarrow{t^\circ} ArC{\equiv}CR + Ar_3Cu^I_4Cu^0_2(C{\equiv}CR) \rightarrow$$
$$\rightarrow [ArCu^I_3Cu^0_3(C{\equiv}CR)] + 2\,ArCu \rightarrow ArC{\equiv}CR + 4Cu^0 \quad .$$

It has been shown[26] that clusters of type (I) (see Section II) play a key role in 1 : 1 reactions of COA with ArCu of the type

$$RC{\equiv}CCu + ArCu \xrightarrow{DMF,\ 135^\circ} RC{\equiv}CAr + Cu^0 \ ;$$
(a) Ar = 2-$Me_2NC_6H_4$, R = Ph, 2-MeC_6H_4, 2, 4-$Me_2C_6H_3$, 2, 4, 6-$Me_3C_6H_2$, 4-$MeOC_6H_4$, 4-ClC_6H_4, or 4-$O_2NC_6H_4$;
(b) Ar = 4-$Me_2NC_6H_4$, R = 4-YC_6H_4 (where Y = Me, OMe, Cl, or NO_2)

with Ar = 2-$Me_2NC_6H_4$; when Ar = 4-$Me_2NC_6H_4$, the reaction proceeds in all probability via mixed polymeric compounds in which copper atoms form regular bridge bonds with alternating Ar and C≡CR groups. Thus the reaction under consideration reduces to the thermal decomposition of intermediate mixed organocopper compounds, asymmetric dimerisation of the organic residues in the 2e–3c bond with the copper atom occurring more specifically in clusters[26]. It is noteworthy that the symmetrical dimerisation of the arylacetylene residue takes place similarly in the thermal decomposition of copper and silver arylacetylides[224].

The formation of mixed intermediates (of either polymeric or cluster type) can be postulated also in the reaction[225]

$$YC_6H_4C{\equiv}COOH + CH_3Cu \xrightarrow[55-70\%]{\text{ether, } 20^\circ} \left[YC_6H_4C{\equiv}CCOOCu\right] \xrightarrow[-CO_2]{} YC_6H_4C{\equiv}CCu \xrightarrow{2CH_3Cu} \rightarrow YC_6H_4C{\equiv}CCH_3 + Cu^0 \quad ;$$

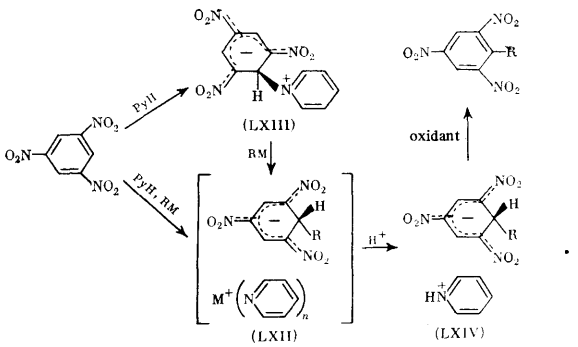
Y=H, 3-Cl, 3-F, 4-Me, or 4-Cl

In this case butylcopper is less reactive than methylcopper; the alkylcopper compounds do not contain lithium salts and were used in proportions of 3 : 1 in relation to arylpropiolic acids. The intermediate formation of COA was demonstrated by a model reaction of the COA obtained beforehand with CH_3Cu:

$$RC{\equiv}CLi \xrightarrow{CuI} RC{\equiv}CCu \xrightarrow[R=Ph\,(75\%),\ or\ C_{12}H_{25}\,(35\%)]{3CH_3Cu,\ ether,\ 20^\circ} RC{\equiv}CCH_3 \quad .$$

2. The Addition of Electrophiles and Nucleophiles to the ≡C–M (M = Cu or Ag) Bond

Nilsson, Wennerstrom, and coworkers investigated nucleophilic substitution in aromatic compounds by treatment with arylcopper compounds and showed that the compounds RM [M = Cu, R = 2,6-$(MeO)_2C_6H_3$,[226] 2-furyl, 2-thienyl[227], PhC≡C, n-BuC≡C;[228] M = Ag, R = 2,6-$(MeO)_2$. C_6H_3 [229] or PhC≡C [228,229]] react with 1,3,5-trinitrobenzene (TNB) in pyridine to form σ-anionic Meisenheimer complexes (LXII), which coexist with the pyridinium complex (LXIII).



For aryl derivatives of copper and silver, the formation of (LXII) was demonstrated by spectroscopic methods and by the isolation of the pyridinium salts (LXIV) in a pure form (with a yield of 20–40% for M = Cu and 80% for M = Ag). The evidence for the formation of the ethynyl complexes (LXII) is not so rigorous, because it is assumed that their absorption in the visible region is masked by the absorption due to the complexes (LXIII). Treatment of the reaction mixture with dilute H_2SO_4 does not lead in this case to (LXIV) and yield TNB for PhC≡CAg (80% relative to the initial amount), while a more complex set of products is obtained for PhC≡CCu (67% of TNB, 6% of diphenylbutadiyne, 5% of 2,4,6-trinitrotolane, and 6% of its intramolecular cyclisation product 4,6-dinitro-2-phenylisatogen).

The difference between the chemical behaviour of organoderivatives of copper(I) and silver(I) can be clearly traced in relation to the σ-anionic complexes (LXII): thus the complexes (LXII) with M = Ag are more stable and are formed in higher yields than those with M = Cu. The explanation is that the copper(I) complexes (LXII) can be oxidised by atmospheric oxygen or NO_2 groups to R-2,4,6-trinitrobenzenes and RR, while the silver(I) complexes (LXII) require a more powerful oxidant (CrO_3).[226-229]

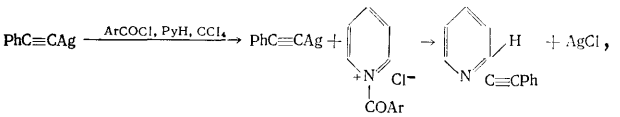
We believe that the acylation of COA and SOA by carboxylic acid halides is the commonest instance of the addition of electrophiles to the ≡C–M bond. This reaction has broad analogies in the chemistry of organocopper(I) and organosilver(I) compounds. Thus $(\pi\text{-}C_5H_5)Cu.P(n\text{-}Bu)_3$, ArCu, C_6F_5Cu,[3] ArOCu,[230] and C_6F_5Ag [52] react smoothly with RCOCl in ether or in the presence of an excess of the acid chloride.

In order to account for the characteristics of the interaction of SOA and COA with acid chlorides (XA), it is convenient to employ the reaction mechanism proposed by Nef for silver phenylacetylide as early as 1899,[231] which is apparently valid for both COA and SOA:

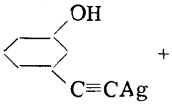
$$RC{\equiv}CM + ClCR' \rightarrow \left[R'{-}\overset{O^+M^+}{\overset{|}{C}}{-}Cl \quad C{\equiv}CR\right] \xrightarrow{-MCl} R'CC{\equiv}CR \quad .$$

Within the framework of this mechanism, the factors promoting an increase of the effective charge on the oxygen atom of XA will favour the reaction. Indeed, the data in Table 14 show that electron-donating substituents R′ and the formation of complexes of XA with $AlCl_3$ and Et_3N constitute in many instances the necessary conditions for the acylation of COA and SOA. It has been noted[232] that 3,5-dinitrobenzoyl chlorides does not react to silver alkylacetylides even in the presence of $AlCl_3$. The acylation of the isomeric *cis*- and *trans*-$C_6H_{13}CH{=}CHC{=}CAg$ proceeds with retention of configuration[233].

In a carbon tetrachloride–pyridine mixture the interaction of silver phenylacetylide with an acylpyridinium salt, and not with XA, becomes the dominant pathway for Ar = Ph and is apparently the only pathway for Ar = 4-$NO_2C_6H_4$ and 3-$NO_2C_6H_4$:[234]



It is of interest to note that this type of reaction does not occur in the systems PhC≡CAg + MeCOCl, n-BuC≡CAg + RCOCl (R = Me or 4-$O_2NC_6H_4$), and



+ RCOCl

(R = Me, Ph, or 4-$O_2NC_6H_4$).

The ethynyl derivative of 1,2-dihydroquinoline was obtained in the reaction of PhC≡CAg with PhCOCl in a carbon tetrachloride–quinoline mixture[234].

The reaction of the copper derivatives of aryl propargyl ethers with PhC(O)Cl under the conditions proposed by the authors of the review[235,236] (benzene, Et_3N, PyH) is accompanied by a prototropic rearrangement with the

resulting α-acetylenic ketones and leads to allenic ketoethers (Ar = Ph or 4-MeC_6H_4):[237]

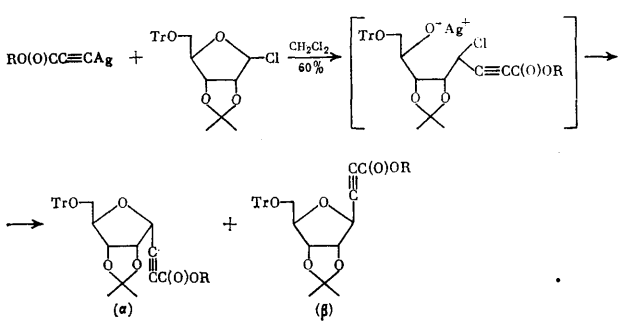
$$ArOCH_2C{\equiv}CCu + PhCOCl \xrightarrow[\sim 30\ \%]{C_6H_6,\ Et_3N,\ PyH} [ArOCH_2C{\equiv}CC(O)Ph] \rightarrow$$
$$\rightarrow ArOCH{=}C{=}CHC(O)Ph$$

Table 14. Acylation of COA and SOA by carboxylic acid halides:

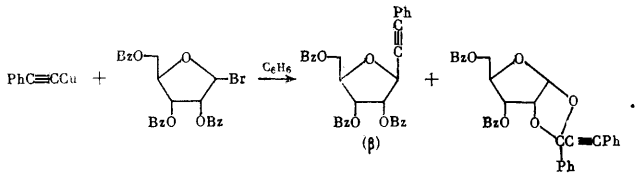
$$RC{\equiv}CM + R'COHal \xrightarrow{L} RC{\equiv}CC(O)R'$$

M	R	R'COHal	L	Yield, %	Refs.
Ag	Bu	MeCOCl	CCl_4	42	232
Ag	Bu	MeCOCl	CCl_4 + $AlCl_3$	44	232
Ag	Bu	$ClCH_2COCl$	CCl_4	57	232
Ag	Bu	PrCOCl	CCl_4	53	232
Ag	Bu	MeCOBr	CCl_4	60	232
Ag	Bu	$BrCH_2COBr$	CCl_4	36	232
Ag	Bu	PhCOCl	CCl_4	0	232
Ag	Bu	PhCOCl	CCl_4, $AlCl_3$	72	232
Ag	Bu	PhCOBr	CCl_4	26	232
Ag	Bu	PhCOBr	CCl_4, $AlCl_3$	67	232
Ag	C_6H_{13}	MeCOCl	CCl_4	61	232
Ag	C_6H_{13}	$ClCH_2COCl$	CCl_4	41	232
Ag	Bu	$EtO(O)C(CH_2)_4COCl$	CCl_4	36	232
Ag	*cis*-$C_6H_{13}CH{=}CH$	$MeO(O)C(CH_2)_6COCl$	CCl_4	—	233
Ag	*trans*-$C_6H_{13}CH{=}CH$	$MeO(O)C(CH_2)_6COCl$	CCl_4	—	233
Ag	Ph	PhCOCl	excess XA	—	231
Ag	Ph	PhCOCl	CCl_4, pyridine	15	234
Cu	Pr	MeCOCl	excess XA	75	124
Cu	Pr	$Ph(CH_2)_2COCl$	excess XA	81	124
Cu	C_8H_{11}	MeCOBr	excess XA	40	141
Cu	C_8H_{11}	PhCOCl	C_6H_5CN	58	141
Cu	Ph	PhCOCl	C_6H_6, NEt_3, PyH	42	235, 236
Cu	Ph	4-BrC_6H_4COCl	C_6H_6, NEt_3, PyH	58	236
Cu	Ph	4-$O_2NC_6H_4COCl$	C_6H_6, NEt_3, PyH	52	236
Cu	Ph	*trans*-PhCH=CHCOCl	C_6H_6, Et_3N, PyH	40	236
Cu	Ph	3-$O_2NC_6H_4COCl$	C_6H_6, Et_3N, PyH	53	236
Cu	Ph	1,4 = $(ClOC)_2C_6H_4$	C_6H_6, Et_3N, PyH	45	236
Cu	Ph	1,3 = $(ClOC)_2C_6H_4$	C_6H_6, E_3N, PyH	42	236
Cu	1, 3, 5-$Mn_3C_6H_2$	PhCOCl	C_6H_6, Et_3N, PyH	41	236

The reaction of SOA with 2,3-*O*-isopropylidene-5-*O*-trityl-β-D-ribofuranosyl chloride, leading to a 1 : 3 mixture of the α- and β-anomers[238] as in the case of XA, can be represented in terms of the following mechanism (R = Me or Et):



The analogous reaction of copper phenylacetylide with 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl bromide is complicated by a secondary process[239]:



Within the framework of the above mechanism of the acylation of COA and SOA by carboxylic acid halides, it is possible to describe the interaction of the complex Et_2PhP. PhC≡CCu with terephthaloyl chloride in THF [236] as well as the interaction of the complexes PhC≡CM (M = Cu or Ag) with CO_2:[12]

$$PhC{\equiv}CM \xrightarrow[2.\ CO_2,\ 60°,\ 50\ atm]{1.\ L,\ THF} [PhC{\equiv}CC(OM) \xrightarrow{3.\ CH_3I} PhC{\equiv}CC(O)OCH_3$$

a) L=PBu_3, M=Cu (50%), or Ag (70%); (b) L = t-BuNC, M = Cu (71%) or Ag (65%).

The reversible insertion of CO_2 in the ≡C–Cu bond has been observed in the system[240]

$$PhC{=}CC(O)OCu \cdot (PBu_3)_3 \underset{}{\overset{DMF}{\rightleftharpoons}} PhC{=}CCu \cdot (PBu_3)_3 + CO_2$$

at atmospheric pressure and a low temperature. The nature of the ligand determines the state of equilibrium: a ligand with a high σ-donor capacity accelerates the decarboxylation [$PBu_3 < PPh_3 < P(OMe)_3$]. Treatment of the reaction mixture with methyl iodide leads to two products: PhC≡CC(O)OMe and PhC≡CMe.

Table 15.

$$ArC{\equiv}CCu + Pt(C_2H_4)(PPh_3)_2 \xrightarrow{L} \left[Ph_3P,\ Pt(C{\equiv}CAr),\ Cu,\ PPh_3\right] \xrightarrow{ArC{\equiv}CCu} \rightarrow Pt(C{\equiv}CAr)_2(PPh_3)_2 + 2Cu^0$$

Ar	L	Yield, %	As	L	Yield, %
Ph	benzene	15	4-FC_6H_4	benzene	12
4-MeC_6H_4	THF	11	C_6F_5	benzene	25

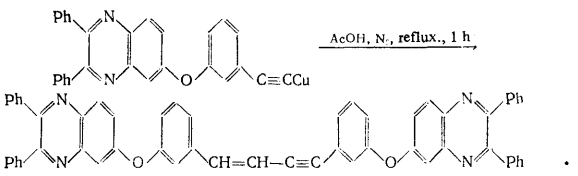
In terms of their formal features, certain reactions of COA, which have no analogy in the chemistry of SOA, can be included in the present section. It is assumed that the reaction of ArC≡CCu with $Pt(C_2H_4)(PPh_3)_2$ proceeds via the intermediate product of the oxidative addition of ArC≡CCu to a zerovalent platinum compound[206] (Table 15). The ethynyl derivative of platinum formed has the *cis*-configuration for Ar = C_6F_5 and the *trans*-configuration in all remaining cases.

The Straus condensation[241,242] or COA can be regarded as addition of the COA complex to a terminal acetylene:

$$2RC{\equiv}CCu \xrightarrow{AcOH,\ N^a} RC{\equiv}CCu \cdot CuOAc + HC{\equiv}CR \xrightarrow{AcOH,\ O_2} \underset{trans}{RC{\equiv}CCH{=}CHR};$$

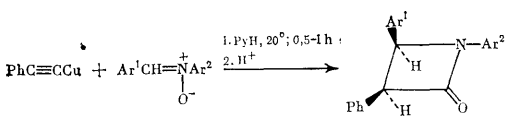
R=Ph, $PhCH{=}CH_2$, or $MeO(O)C(CH_2)_n$, where $n = 0, 1, 8$.

It has been shown recently that this reaction proceeds smoothly also in an oxygen-free medium[243]:



3. Addition of 1,3-Dipolar Compounds to the C≡C′ Bond in COA

It was shown in 1972 that *C,N*-diarylnitrones undergo a cycloaddition reaction with copper phenylacetylide, leading to *cis*-β-lactams, which are difficult to obtain by other methods[244]:



(a) Ar^2 = Ph, Ar^1 = Ph, or 2-YC_6H_4 (where Y = Me or Cl); (b) Ar^1 = Ph, Ar^2 = 4-ClC_6H_4.

A detailed study of this reaction established that it is accompanied by the base-catalysed isomerisation of the initial *cis*-form of the β-lactam into the *trans*-form[245] (Table 16):

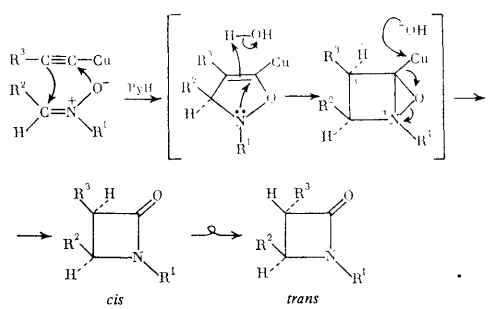
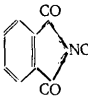
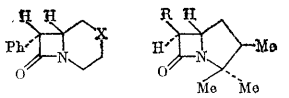


Table 16. β-Lactams derived from COA and nitrones.

R^1	R^2	R^3	Yield of lactam, %	*cis* : *trans*
Ph	Ph	Ph	32	5:3
Ph	Ph	4-MeC_6H_4	50	7:3
Ph	4-MeC_6H_4	Ph	40	4:1
Ph	3-MeC_6H_4	Ph	25	5:4
Ph	2-MeC_6H_4	Ph	25	10:11
Ph	4-$MeOC_6H_4$	Ph	28	*trans*-isomer
4-PhC_6H_4	4-ClC_6H_4	Ph	45	*trans*-isomer
4-MeC_6H_4	Ph	Ph	25	3:4
4-MeC_6H_4	4-ClC_6H_4	Ph	14	5:4
Ph	Ph	Bu	66	12:1
Ph	4-$MeOC_6H_4$	Bu	55	*cis*-isomer
4-MeC_6H_4	4-ClC_6H_4	Bu	9	*trans*-isomer
Ph	4-MeC_6H_4	EtO(O)C	42	*trans*-isomer
Ph	4-MeC_6H_4		31	9:1
Ph	4-ClC_6H_4	ditto	12	*cis*-isomer
Ph	4-ClC_6H_4	PhN(Me)CH_2	52	1:1
Ph	4-$MeOC_6H_4$	PhN(Et)CH_2	39	*trans*-isomer
Ph	4-ClC_6H_4	4-EtO(O)$CC_6H_4NHCH_2$	75	*cis*-isomer

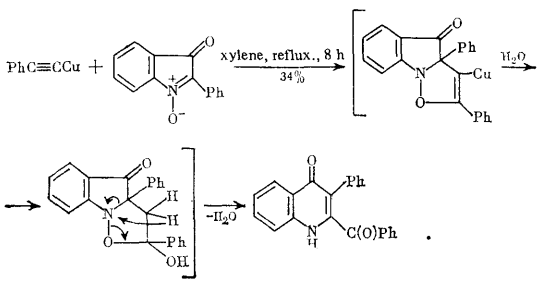
When D_2O was added to the reaction medium, lactams containing the D label in the 3-position were obtained, which demonstrated the incorporation of an H atom from the solvent in this position. The addition of $H_2{}^{18}O$ did not lead to the incorporation of ^{18}O atoms into the final product. Copper n-butylacetylide is less reactive than PhC≡CCu; the *cis*-isomer then predominates in the product. On the other hand, EtO(O)CC≡CCu is more reactive than PhC≡CCu and only the *trans*-isomer is formed in pyridine in this case. The replacement of pyridine by EtOH makes it possible to obtain a 3 : 1 mixture of the *cis*- and *trans*-isomers (R^1 = Ph, R^2 = 4-MeC_6H_4, R^3 = EtO(O)C).

COA based on aminoacetylenes were not isolated beforehand and were used *in situ*. Unstable cyclic nitrones were also introduced into the reaction, which made it possible to synthesise the bicyclic compounds (LXV) and (LXVI):

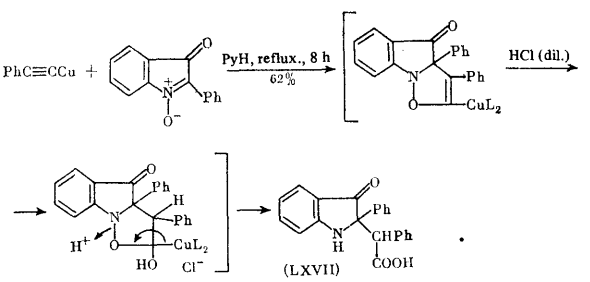


(LXV), X = O or CH_2 (LXVI), R = Ph, Bu, or EtO(O)C.

Aromatic bicyclic nitrones react with COA via two pathways, depending on the solvating (in relation to the C atom) capacity of the medium[74]. In xylene the reaction of copper phenylacetylide with 2-phenylisatogen leads to 2-benzoyl-3-phenyl-4-quinolone:

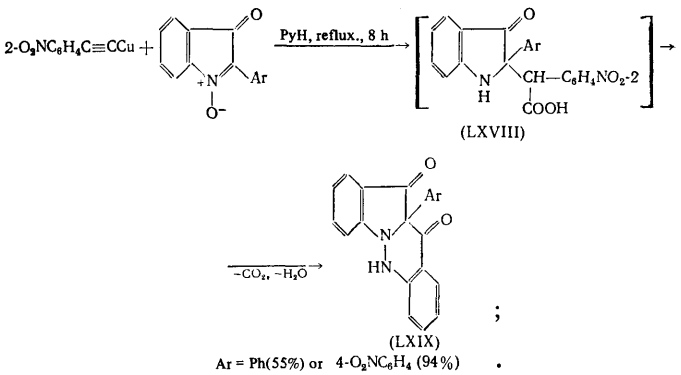


The copper atom is solvated in pyridine, so that the mode of its addition to isatogen is inverted for steric reasons:



The formation of cinnolines (LXIX) from copper 2-nitrophenylacetylide and 2-arylisatogens apparently proceeds via the indolinone (LXVIII), which is analogous

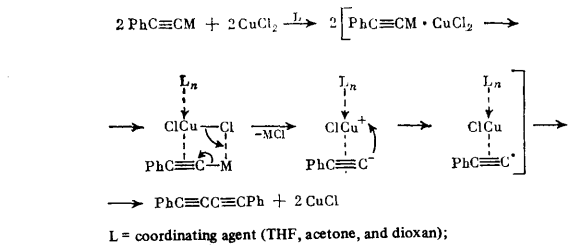
to compound (LXVII):[74]



V. OXIDATIVE CONDENSATION OF GROUP IB METAL ORGANOACETYLIDES

The oxidative condensation of COA under the influence of O_2 in the presence of coordinating agents of the amine type (strong donors), which stabilise the copper(II) valence state, has been examined in a review[1]. The formation of dicyanogen from CuCN is analogous to this reaction[246].

Extensive experimental data have now accumulated on the use of coordinating agents of moderate electron-donating capacity (Table 1), which destabilise the copper(II) state and stabilise the copper(I) state. Under these conditions, the oxidative condensation of aromatic organolithium and organomagnesium compounds, which lead to either open-chain or cyclic polyarylenes, takes place particularly effectively under the influence of $CuCl_2$.[246,247] The present authors were able to introduce for the first time silver(I) and gold(I) phenylacetylides into the oxidative condensation reaction in THF, acetone, and dioxan[248]:



L = coordinating agent (THF, acetone, and dioxan);
M = Cu(I), Ag(I), or Au(I).

According to this mechanism, the valence state of the metal in the organoacetylide does not change during the reaction and the specific role of copper reduces to a decrease of the oxidation potential of the ethynyl anion and the stabilisation of the ethynyl radical by the π-coordination of Cu...$\overset{C}{\underset{C}{|||}}$, which ensures a convenient geometrical disposition of these radicals for recombination in the "cage". It may be that the dative component Cu $\rightarrow \overset{C}{\underset{C}{|||}}$ predominates in this coordination, which imparts nucleophilic properties to the ethynyl radicals and facilitates their recombination. We may note that, according to Fedenck[249], the free-radical recombination of RC≡C· is thermodynamically unfavourable; it has also been shown that the free radicals PhC≡C· have electrophilic properties and form only tolanes in aromatic hydrocarbons[77]:

$$PhC{\equiv}Cl \xrightarrow{h\nu,\ ArH} PhC{\equiv}CAr \quad .$$

The oxidative dimerisation of COA under the influence of certain transition metal chlorides ($TlCl_3$, $FeCl_3$, $NiCl_2$, $CoCl_2$, $CrCl_3$ [248]) in a fairly wide variety of media (alcohols, nitriles, ether, ethyl acetate, and nitromethane) can also take place in the framework of the above mechanism. The copper(I) chloride formed in the initial stage then remains in the reaction complex as a result of the π-interaction with the C≡C bond.

In solvents with a moderate electron-donating capacity certain oxidants enter into additional interactions with COA. Thus the formation of phenylchloroacetylene in the reactions of copper phenylacetylide with transition metal chlorides[250] can be represented by the following mechanism by analogy[251] with the reaction $R^{\cdot} + CuX_2 \rightleftharpoons [RCuX_2 \rightarrow R^{+}CuX_2^{-}] \rightarrow RX + CuX$:

$$PhC{\equiv}\underset{\underset{Cu^{I}}{|}}{C}{\cdot} + MCl_n \rightarrow PhC{\equiv}CCl + MCl_{n-1} \quad .$$

Thus the composition of the products of the oxidative condensation of COA is determined by the contribution of both reaction pathways of the ethynyl radical. For example, when copper phenylacetylide is treated with bromine (in ether) and chlorine (in CCl_4), a large amount of diphenylbutadiyne is formed together with the corresponding phenylhalogenoacetylenes. On the other hand, the bromination of copper 4-nitrophenylacetylide takes place unambiguously—without the formation of a dimerisation product[1]. In the reaction of tetracyanoethylene (in THF) with 4-$YC_6H_4C{\equiv}CCu$ the main product is phenylethynyltricyanoethylene for Y = H and $(4\text{-}YC_6H_4C{\equiv}C)_2$ for Y = I. Tetracyanoquinodimethane oxidises PhC≡CCu smoothly (in CH_3CN) to diphenylbutadiyne[252].

We may point to the syntheses of dicyanodiacetylene by the reaction of NCC≡CCu with $K_3[Fe(CN)_6]$ in a water–benzene mixture[253] and of diphenyltetra-acetylene from PhC≡CC≡CCu under the influence of $CuCl_2$ in water[254] as practical examples of the oxidative condensation of COA in an amine-free medium. The oxidation of the acetylides $Cu(C{\equiv}C)_nR$ (R = H or Cu) (which are in their turn the products of the oxidative dehydropolycondensation of acetylene in an aqueous ammonia solution of $CuCl_2$) by an aqueous solution of $FeCl_3$ or $K_3[Fe(CN)_6]$ yielded a linear polymer (carbine)—a new allotropic form of carbon[255].

It has been shown[249] that the catalytic reaction

$$PhC{\equiv}CH \xrightarrow{PyH,\ CuCl,\ O_2} (PhC{\equiv}C)_2$$

can proceed via the intermediate copper phenylacetylide. Possibly the COA occur in the pathways of catalytic oxidative dimerisation reactions also in many other instances[1].

VI. REACTIONS OF SILVER ORGANOACETYLIDES WITH ARENEDIAZONIUM HALIDES

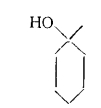
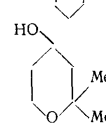
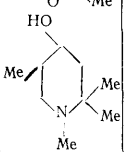
It was shown in 1964 [256] that in an aqueous medium (at pH ~3) arenediazonium chlorides react with SOA of the phenylacetylene series to form azoethynyl compounds (LXX), which are difficult to obtain by other methods:

$$RC{\equiv}CAg + ArN_2^{+}Cl^{-} \rightarrow \underset{(LXX)}{RC{\equiv}CN{=}NAr} \quad .$$

The study of this reaction began with benzenediazonium chlorides containing electron-accepting substituents in the 2- or 4-position in the ring[257,258]. Subsequently the arenediazonium chlorides $YC_6H_4N_2^+Cl^-$, where Y = H,[259] 2-Me, or 4-Me,[260] were introduced into the reaction under the same conditions but using this time SOA of the propargyl type. Thus benzene- and toluene-diazonium chlorides form compounds (LXX) in yields of 8–35% for R = 2-$YC_6H_4C(O)OCH_2$ (Y = H [259] or Cl [260]). Reactions of 4-$YC_6H_4N_2^+Cl^-$ (Y = H or Cl) with silver acetylides derived from 1-ethynyl-1-cyclohexanol, 2,2-dimethyl-4-ethynyltetrahydro-4-pyranol, and 4-ethynyl-1,2,5-trimethyl-4-piperidinol lead to (LXX) in yields of 70–90%.[261] When purified benzenediazonium chlorides and bromides were used and the reaction was carried out in an alcohol–chloroform mixture, the yields of (LXX) with R and Ar belonging to the benzene series were increased greatly and it was possible to isolate the unstable azoethynyl compounds with R = Ph and Ar = Ph and even 4-$MeOC_6H_4$.[262]

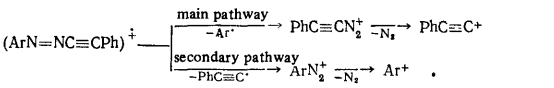
Compounds (LXX) known at the present time and obtained via SOA are listed in Table 17.

Table 17. The azoethynyl compounds $RC{\equiv}CN{=}NC_6H_4Y$ (LXX).

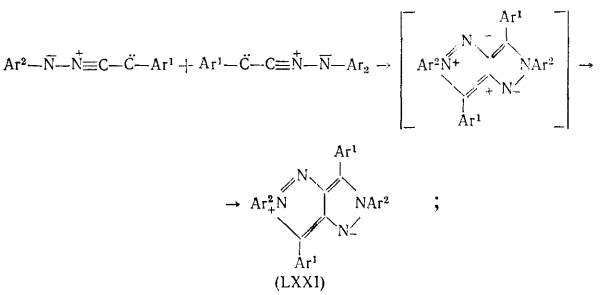
R	Y	Refs.	R	Y	Refs.
Ph	4-Cl, 4-Br, 4-NO_2	257, 258, 262		H, 4-Cl	261
4-$HC{\equiv}CC_6H_4$	4-Br	257			
Ph	2-Cl	258			
4-ClC_6H_4	4-NO_2	258			
4-$O_2NC_6H_4$	4-Cl	258, 262			
Ph	H, 4-I, 4-CN, 4-OMe	262		H, 4-Cl	261
	4-EtO(O)C, 2-PhC(O), 2MeO(O)C = 4-Cl				
4-BrC_6H_4	4-Cl, 4-NO_2	264			
4-MeC_6H_4	4-Cl, 4-NO_2	264			
$PhC(O)OCH_2$	H, 2-Me, 4-Me	259		H, 4-Cl	261
2-$ClC_6H_4C(O)OCH_2$	H	260			

The possible mechanisms of the interaction of SOA with arenediazonium chlorides have been discussed[1]; we may note that this reaction has no analogies in the chemistry of organic compounds of copper(I) and silver(I) and is apparently related to the reactions of diazonium salts with powerful nucleophiles—organomagnesium and organozinc compounds[1] and R_fCs [R_f = $C(CR_3)_3$, $(CR_3)_2CF$, or $CF_2CF_2CF_2CF_2$ [263]].

The structure of compounds (LXX) has been investigated by infrared and ultraviolet spectroscopy, NMR, and mass-spectrometry[258,262]. It has been shown that the inclusion of the C=C group in the azobenzene structure leads to a strong bathochromic shift in the ultraviolet spectrum[258]. According to mass-spectrometric data, the fragmentation of (LXX) of the benzene series takes place preferentially with elimination of aryl and not phenylethynyl groups[262]:



The thermal cyclodimerisation of (LXX), leading to derivatives of a new heteroaromatic mezoionic system—2,3,5,6-tetra-aryl-1,2,4,5-tetra-azapentalenes (LXXI)—leads to great synthetic possibilities for SOA:[262,264]



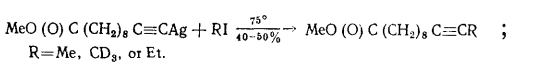
(LXXI)

Ar^1=4-XC_6H_4, Ar^2=4-YC_6H_4; (a) X=H, Y=Cl, Br, or NO_2; (b) X=NO_2, Y=Cl; (c) X=Br, Y=Cl, NO_2; (d) X=Me, Y=Cl, or NO_2 .

Compounds (LXXI) fuse at temperatures in excess of 320°C and are distinguished by high thermal and hydrolytic stabilities: they do not decompose *in vacuo* on heating to 500°C and withstand prolonged boiling in 65% H_2SO_4.[264] A dimer of type (LXXI) is not formed for Ar^1 = Ph and sterically hindered Ar^2 = 2-$PhC(O)C_6H_4$.[262]

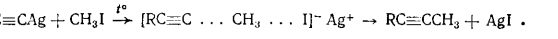
VII. OTHER REACTIONS OF COPPER AND SILVER ORGANOACETYLIDES

In contrast to COA, SOA react with alkyl iodides (on heating in a sealed tube) via the mechanism[265]

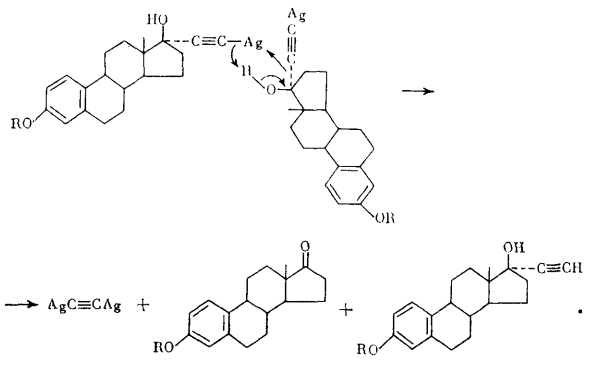


R=Me, CD_3, or Et.

When the reaction is carried out in ether or benzene, a terminal acetylene, corresponding to the initial SOA, is formed together with an alkylacetylene. Since RH and RR are absent from the reaction products, it is assumed that the alkylation of SOA proceeds via a "push-pull" mechanism rather than a free radical mechanism:

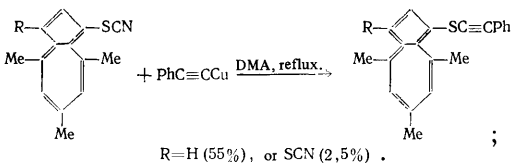


It has been observed that the silver derivative of 17α-ethynyl-17β-hydroxyoestratriene is stable in methanol but disproportionates in aprotic solvents (DMSO, benzene, THF) via the mechanism (R = cyclo-C_5H_9):[36]



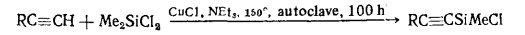
Coppy phenylacetylide reacts with bromocyanogen in an ether–acetonitrile mixture to form PhC≡CCN (yield 60%) and $(PhC{\equiv}C)_2$ (yield 28%); under these conditions, copper methylacetylide is converted into dimethyldiacetylene (yield 65%).[266]

Thiocyanoazulenes react with copper phenylacetylide in dimethylacetamide (DMA) to form thioethynyl derivatives[267]:



R=H (55%), or SCN (2,5%) .

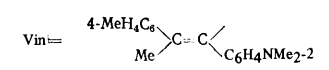
It has been suggested[193] that the catalytic reaction

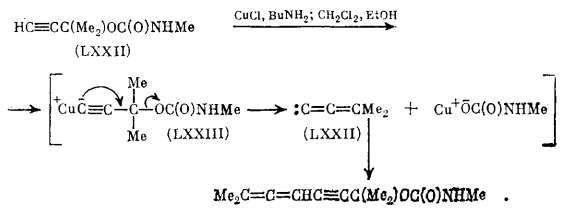


takes place with participation of the intermediate RC≡CCu.

The formation and decomposition of the COA (LXXIII) are adduced to account for the mechanism of another catalytic reaction[268].

By analogy with stable arylcopper compounds[170], the vinyl complex $Vin_2Cu_4Br_2$ has been recently obtained; by treatment with ArC≡CLi, it was converted into a copper(I) vinylethynyl complex $(VinCu_2C{\equiv}CAr)_n$,[269] where





The structure of this complex should differ from that of the arylethynyl clusters $Ar_4Cu_6(C{\equiv}CR)_2$, which has been proposed by ten Hoedt et al.[25] (Fig. 7) and confirmed by X-ray diffraction data[270].

---o0o---

The data presented in the review show that Group IB metal organoacetylides (in the first place COA) have been firmly incorporated in practical organic syntheses. At the same time the review does not consider numerous instances of the use of COA as homo- and hetero-cuprates, which are widely employed in the synthesis of physiologically active substances (for example, prostaglandins). The reactions of terminal acetylenes and their organoelemental and organometallic derivatives, which take place under the influence of catalytic amounts of copper(I) salts, apparently with participation of COA in a pure form or as cuprates, are of great interest.

It is to be expected that further development of this field of organometallic chemistry will involve a deeper investigation of the mechanisms of the reactions of Group IB metal organoacetylides and the discovery of their new synthetic possibilities.

REFERENCES

1. A. M. Sladkov and L. Yu. Ukhin, Uspekhi Khim., 27, 1750 (1968) [Russ. Chem. Rev., No. 10 (1968)].
2. A. M. Sladkov, "Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilina, Alma-Ata, 1972" (Reports at the IVth All-Union Conference on the Chemistry of Acetylene, Alma-Ata, 1972), Vol. 1, p. 29.
3. J. F. Norman, Uspekhi Khim., 42, 645 (1973) [Russ. Chem. Rev., No. 4 (1973)].
4. G. Bähr and P. Burda, in Houben-Weyl, "Methoden der Organische Chemie", Georg Thieme Verlag, Stuttgart, 1970, Vol. XIII/1, p. 727.
5. G. H. Posner, Organic Reactions, 22, 253 (1975).
6. A. N. Nesmeyanov, in "Metody Elementoorganicheskoi Khimii. Podgruppa Medi, Skandiya, Titana, Vanadiya, Khroma, Margantsa. Lantanoidy i Aktinoidy" (Methods of Organoelemental Chemistry. The Copper, Scandium, Titanium, Vanadium, Chromium, and Manganese Sub-group. Lanthanides and Actinides), Izd. Nauka, Moscow, 1974, pp. 49, 68.
7. L. P. Yur'eva, in "Metody Elementoorganicheskoi Khimii. π-Kompleksy Perekhodnykh Metallov s Arenami, Dienami; Soedineniya s σ-Svyaz'yu C–M" (Methods of Organoelemental Chemistry. Transition Metal π-complexes of Arenes and Dienes; Compounds with a C–M σ-Bond), Izd. Nauka, Moscow, 1976, p. 350.
8. C. E. Castro, E. J. Gaughan, and D. C. Owsley, J. Org. Chem., 31, 4071 (1966).
9. O. H. Johnson and J. R. Holum, J. Org. Chem., 23, 738 (1958).
10. G. E. Coates and C. Parkin, J. Chem. Soc., 3224 (1962).
11. T. Tsuda, T. Hashimoto, and T. Saegusa, J. Amer. Chem. Soc., 94, 658 (1972).
12. T. Tsuda, K. Ueda, and T. Saegusa, Chem. Comm., 380 (1974).
13. M. W. Logue and G. L. Moore, J. Org. Chem., 40, 131 (1975).
14. W. T. Reichle, Inorg. Nucl. Chem. Letters, 5, 981 (1969).
15. E. T. Blues, D. Bryce-Smith, B. Kettlewell, and M. Roy, Chem. Comm., 921 (1973).
16. E. T. Blues, D. Bryce-Smith, I. W. Lawston, and G. D. Wall, Chem. Comm., 513 (1974).
17. R. Vestin and E. Ralf, Acta Chem. Scand., 3, 101 (1949).
18. E. T. Blues, D. Bryce-Smith, J. G. Irwin, and I. W. Lawston, Chem. Comm., 466 (1974).
19. C. M. Mitchell and F. G. Stone, J. Chem. Soc., Dalton Trans., 102 (1972).
20. A. Johnson and R. G. Puddephatt, J. Chem. Soc., Dalton Trans., 1384 (1977).
21. V. A. Sazonova and N. Ya. Kronrod, Zhur. Obshch. Khim., 26, 1876 (1956).
22. S. Staicu, I. G. Dinulescu, F. Chiraleu, and M. Avran, J. Organometal. Chem., 117, 385 (1976).
23. H. E. Zimmerman and J. R. Dodd, J. Amer. Chem. Soc., 92, 6507 (1970).
24. G. van Koten and J. G. Noltes, Chem. Comm., 575 (1974).
25. R. W. M. ten Hoedt, G. van Koten, and J. G. Noltes, J. Organometal. Chem., 133, 113 (1977).
26. G. van Koten, R. W. M. ten Hoedt, and J. G. Noltes, J. Org. Chem., 42, 2705 (1977).
27. J. P. Danehy and J. A. Nieuwland, J. Amer. Chem. Soc., 58, 1609 (1936).

28. I. R. Gol'ding, A. M. Sladkov, and V. S. Myl'nikov, Izv. Akad. Nauk SSSR, Ser. Khim., 2062 (1969).
29. H. A. Staab and R. Rader, Chem. Ber., **103**, 1157 (1970).
30. H. A. Staab and P. Günthert, Chem. Ber., **110**, 619 (1977).
31. R. H. Mitchell and F. Sondheimer, Tetrahedron, **26**, 2141 (1970).
32. M. S. Shvartsberg, A. A. Moroz, and A. N. Kozhevnikova, Izv. Akad. Nauk SSSR, Ser. Khim., 875 (1978).
33. M. Ballester, J. Castaner, J. Riera, I. Tabernero, and C. Cornet, Tetrahedron Letters, 2353 (1977).
34. H. Schlossarczyk, W. Sieber, M. Hesse, H.-J. Hansen, and H. Schmid, Helv. Chim. Acta, **56**, 875 (1973).
35. U. Koch-Pomeranz, H.-J. Hansen, and H. Schmid, Helv. Chim. Acta, **56**, 2981 (1973).
36. R. Vitali, S. Gladiali, and R. Gardi, Gazzetta, **102**, 673 (1972).
37. C. Beerman and H. Hartmann, Z. anorg. allgem. Chem., **276**, 20 (1954).
38. R. Müller and H. Beyer, Chem. Ber., **92**, 1018 (1959).
39. H. Hartmann and K. Komorniczyk, Naturwiss., **51**, 214 (1964).
40. A. N. Nesmeyanov, A. K. Prokof'ev, and A. E. Borisov, Izv. Akad. Nauk SSSR, Ser. Khim., 1922 (1973).
41. W. Manchot, Annalen, **387**, 257 (1912).
42. V. Gutmann, "Coordination Chemistry in Non-aqueous Solutions" (Translated into Russian), Izd. Mir, Moscow, 1971, p. 30.
43. P. L. Coe and N. E. Milner, J. Fluor. Chem., **2**, 167 (1972/73).
44. L. M. Yagupolski, N. V. Kondratenko, and V. P. Sambur, Synthesis, 721 (1975).
45. T. Kitazume and N. Ishikawa, Bull. Chem. Soc. Japan, **48**, 361 (1975).
46. K. Adams and A. Feretti, J. Amer. Chem. Soc., **81**, 4927 (1959).
47. F. D. King and D. R. M. Walton, Chem. Comm., 256 (1974), Synthesis, 738 (1975).
48. R. G. R. Bacon and H. A. O. Hill, J. Chem. Soc., 1097 (1964).
49. R. G. R. Bacon and H. A. O. Hill, Quart. Rev., **19**, 121 (1965).
50. M. Nilsson and R. Wahren, J. Organomet. Chem., **16**, 515 (1969).
51. G. M. Whitesides, J. S. Sadowsky, and J. Lilburn, J. Amer. Chem. Soc., **96**, 2829 (1974).
52. K. K. Sun and W. T. Miller, J. Amer. Chem. Soc., **92**, 6985 (1970).
53. A. M. Sladkov, L. Yu. Ukhin, and V. V. Korshak, Izv. Akad. Nauk SSSR, Otd. Khim., 2213 (1963).
54. C. E. Castro and R. D. Stephens, J. Org. Chem., **28**, 2163, 3313 (1963).
55. J. S. Kiely, P. Boudjouk, and L. L. Nelson, J. Org. Chem., **42**, 2626 (1977).
56. S. A. Kandil and R. E. Dessy, J. Amer. Chem. Soc., **88**, 3027 (1966).
57. B. Bossenbrock and H. Strechter, J. Amer. Chem. Soc., **89**, 7111 (1967).
58. J. Ipaktschi and H. A. Staab, Tetrahedron Letters, 4403 (1967).
59. H. A. Staab and J. Ipaktschi, Chem. Ber., **104**, 1170 (1971).
60. A. E. Jungk and G. M. J. Schmidt, Chem. Ber., **104**, 3272 (1971).
61. H. A. Staab, J. Ipaktschi, and A. Nissen, Chem. Ber., **104**, 1182 (1971).
62. E. H. White and A. A. F. Sieber, Tetrahedron Letters, 2713 (1967).
63. A. Banihashemi and C. S. Marvel, J. Polymer Sci., Polymer Chem., Ed., **15**, 2653, 2667 (1977).
64. F. L. Hedberg and F. E. Arnold, J. Polymer Sci., Polymer Chem., Ed., **14**, 2607 (1976).
65. H. A. Staab, E. Wehinger, and W. Thorwart, Chem. Ber., **105**, 2290 (1972).
66. I. D. Campbell, G. Eglinton, W. Henderson, and R. A. Raphael, Chem. Comm., 87 (1966).
67. H. A. Staab and F. Graf, Chem. Ber., **103**, 1107 (1970).
68. Z. Tozuka, T. Otsubo, Y. Sekata, and S. Misimi, Mem. Inst. Sci. Ind. Res., Osaka Univ., **30**, 83 (1973); Chem. Abs., **79**, 66 092 (1973).
69. H. Irngartinger, L. Leiserowitz, and G. M. J. Schmidt, Chem. Ber., **103**, 1119 (1970).
70. H. A. Staab and K. Neuhoeffer, Synthesis, 424 (1974).
71. R. D. Stephens and W. C. Kray, US P. 3 749 700 (1970).
72. N. I. Myakina and I. L. Kotlyarevski, Izv. Akad. Nauk SSSR, Ser. Khim., 1405 (1973).
73. N. I. Popova, G. I. Skubnevskaya, Yu. N. Molin, and I. L. Kotlyarevskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2424 (1969).
74. C. E. Hudson and N. L. Bauld, J. Amer. Chem. Soc., **94**, 1158 (1972).
75. A. Liberles and B. Matlosz, J. Org. Chem., **36**, 2711 (1971).
76. J. J. Eisch and C. K. Hordis, J. Amer. Chem. Soc., **93**, 2974 (1971).
77. G. Martelli, P. Spagnolo, and M. Tiecco, J. Chem. Soc. (B), 1413 (1970).
78. D. C. Remy, W. A. van Saun, E. L. Engelhardt, M. L. Torchiana, and C. A. Stone, J. Medicin. Pharmaceut. Chem., 18, 142 (1975).
79. T. D. Roberts, L. Munchausen, and H. Schechter, J. Amer. Chem. Soc., 97, 3112 (1975).
80. C. E. Castro and R. D. Stephens, J. Amer. Chem. Soc., **86**, 4358 (1964).
81. M. P. Briede, USSR P. 424 856; Byul. Izobret, No. 15 83 (1974).
82. M. P. Briede and O. Ya. Neiland, Zhur. Org. Khim., **6**, 1701 (1970).
83. A. M. Berlin, N. M. Kofman, E. S. Krongauz, A. N. Novikov, and I. R. Gol'ding, Izv. Akad. Nauk SSSR, Ser. Khim., 441 (1975).
84. C. C. Bond and M. Hooper, J. Chem. Soc. (C), 2453 (1969).
85. M. S. Shvartsberg, A. N. Kozhevnikova, and I. L. Kotlyarevskii, Izv. Akad. Nauk SSSR, Ser. Khim., 466 (1967).
86. K. Yoshida and T. Fueno, J. Org. Chem., **38**, 1045 (1972).
87. M. O. Conzales Garcia, Rev. Fac. Cienc. Univ. Oviedo, **4**, 18 (1963).
88. V. V. Korshak, E. S. Krongauz, A. M. Berlin, B. R. Lifshits, and T. Kh. Dymshits, USSR P. 457 689; Byul. Izobret., No. 52, 56 (1975).
89. H. A. Staab and P. Günthert, Chem. Ber., **110**, 619 (1977).
90. B. J. Whitlock and H. D. Whitlock, J. Org. Chem., **37**, 3569 (1972).
91. G. A. Kraus and K. Frazier, Tetrahedron Letters, 3195 (1978).
92. A. N. Volkov, Yu. M. Skvortsov, I. I. Danda, and M. F. Shostakovakii, Zhur. Org. Khim., **6**, 897 (1970).

93. F. Bohlmann and C. Hühn, Chem. Ber., 110, 1183 (1977).
94. F. Bohlmann, P. Blaszkiewicz, and E. Bresinsky, Chem. Ber., 101, 4163 (1968).
95. E. R. H. Jones, S. Safe, and V. Thaller, J. Chem. Soc. (C), 1038 (1967).
96. R. E. Atkinson, R. F. Curtis, and J. A. Taylor, J. Chem. Soc. (C), 578 (1967).
97. R. E. Atkinson, R. F. Curtis, D. M. Jones, and J. A. Taylor, J. Chem. Soc. (C), 2173 (1969).
98. M. A. Harris, I. McMillan, J. H. C. Nayler, N. F. Osborne, M. J. Pearson, and R. Southgate, J. Chem. Soc., Perkin Trans. I, 1613 (1976).
99. I. Barrow and A. E. Pedler, Tetrahedron, 32, 1829 (1976).
100. M. M. Kwatra, D. Z. Simon, R. L. Salvador, and P. D. Cooper, J. Medicin. Pharmaceut. Chem., 21, 253 (1978).
101. F. Bohlmann and J. Kocur, Chem. Ber., 107, 2115 (1974).
102. R. D. H. Murray and I. T. Forbes, Tetrahedron Letters, 3077 (1977).
103. M. D. Rausch, A. Siegel, and L. P. Klemann, J. Org. Chem., 34, 468 (1969).
104. R. Filler and E. W. Heffern, J. Org. Chem., 32, 3249 (1967).
105. J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, J. Chem. Soc., Perkin Trans. I, 763 (1972).
106. R. S. Dickson and L. J. Michel, Austral. J. Chem., 28, 1943 (1975).
107. V. A. Nefedov and L. K. Tarygina, Zhur. Org. Khim., 12, 1763 (1976).
108. I. L. Kotlyarevskii, V. N. Andrievskii, and M. S. Shvartsberg, Khim. Geterotsikl. Soed., 308 (1967).
109. R. I. Katkevich, S. P. Korshunov, and L. I. Vereshchagin, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 11, 705 (1966).
110. T. Teitei, P. J. Collin, and W. H. F. Sasse, Austral. J. Chem., 25, 171 (1972).
111. M. D. Rausch, A. Siegel, and L. P. Klemann, J. Org. Chem., 31, 2703 (1966).
112. F. Bohlmann, K.-M. Kleine, and C. Arndt, Chem. Ber., 99, 1642 (1966).
113. R. F. Curtis and J. A. Taylor, J. Chem. Soc. (C), 1813 (1969).
114. F. Bohlmann and P.-D. Hopf, Chem. Ber., 106, 3621 (1973).
115. F. Bohlmann and W. Skuballa, Chem. Ber., 106, 497 (1973).
116. R. E. Atkinson, R. F. Curtis, and G. T. Phillips, J. Chem. Soc. (C), 2011 (1967).
117. E. Bohlmann and J. Kocur, Chem. Ber., 108, 2149 (1975).
118. H. J. Callot, Tetrahedron Letters, 4987 (1973).
119. M. D. Rausch and A. Siegel, J. Org. Chem., 34, 1974 (1969).
120. M. Rosenblum, N. Brawn, J. Papenmeier, and M. Applebaum, J. Organomet. Chem., 6, 173 (1966).
121. M. Rosenblum, N. M. Brawn, D. Chiappenelii, and J. Tancrede, J. Organomet. Chem., 24, 469 (1970).
122. M. D. Rausch and A. Siegel, J. Organomet. Chem., 17, 117 (1969).
123. A. M. Malte and C. E. Castro, J. Amer. Chem. Soc., 89, 6770 (1967).
124. C. E. Castro, R. Halvin, V. K. Honwad, A. Malte, and S. Mojé, J. Amer. Chem. Soc., 91. 6464 (1969).
125. S. A. Mladenovic and C. E. Castro, J. Heterocycl. Chem., 5, 227 (1968).
126. S. F. Vasilevskii, E. L. Rubinshtein, and M. S. Shvartsberg, Izv. Akad. Nauk SSSR, Ser. Khim., 1175 (1978).
127. D. C. Owsley and C. E. Castro, Org. Synth., 52, 128 (1972).
128. P. I. Abramenko and V. G. Zhiryakov, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 17, 695 (1972).
129. O. V. Afanas'eva, A. G. Makhsumov, and Sh. U. Abdullaev, see Ref. 2, Vol. 1, p. 244.
130. M. Brenner and C. Brusch, Tetrahedron Letters, 419 (1977).
131. M. T. Cox and J. J. Holohan, Tetrahedron, 31, 633 (1975).
132. M. Stefanović, L. Krstić, and S. Mladenović, Tetrahedron Letters, 3311 (1971).
133. F. G. Schreiber and R. Stevenson, J. Chem. Soc., Perkin Trans. I, 1514 (1976).
134. F. Bohlmann and U. Bühmann, Chem. Ber., 105, 863 (1972).
135. F. G. Schreiber and R. Stevenson, J. Chem. Soc., Perkin Trans. I, 907 (1977).
136. R. P. Duffley and R. Stevenson, J. Chem. Soc., Perkin Trans. I, 802 (1977).
137. C. C. Leznoff and R. J. Hayward, Canad. J. Chem., 49, 3596 (1971).
138. E. T. Bogoradovskii, V. S. Zavgorodskii, K. S. Mingaleva, and A. A. Petrov, Zhur. Obshch. Khim., 44, 142 (1974).
139. A. N. Sinyakov and M. S. Shvartsberg, Izv. Akad. Nauk SSSR, Ser. Khim., 1126 (1979).
140. S. E. Wentworth, Polymer Preprints, 15, 697 (1974).
141. J. F. Normant, M. Bourgain, and A.-M. Rone, Compt. rend., 270, C, 354 (1970).
142. A. Commercon, J. Normant, and J. Villieras, J. Organomet. Chem., 93, 415 (1975).
143. P. L. Coe, N. E. Milner, and J. A. Smith, J. Chem. Soc., Perkin Trans. I, 654 (1975).
144. W. E. Truce, A. W. Borel, and P. J. Marek, J. Org. Chem., 41, 401 (1976).
145. J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, J. Chem. Soc., Perkin Trans. I, 639 (1972).
146. L. Yu. Ukhin, A. M. Sladkov, and V. N. Gorshkov, Zhur. Org. Khim., 4, 25 (1968).
147. L. I. Zakharkin, V. N. Kalinin, I. R. Gol'ding, A. M. Sladkov, and A. V. Grebennikov, Zhur. Obshch. Khim., 41, 823 (1971).
148. W. E. Truce and G. C. Wolf, J. Org. Chem., 36, 1727 (1971).
149. H. A. Staab and Hwa Ja Shin, Chem. Ber., 110, 631 (1977).
150. K. Gump, S. W. Woje, and C. E. Castro, J. Amer. Chem. Soc., 89, 6770 (1967).
151. F. Waugh and D. R. M. Walton, J. Organomet. Chem., 39, 275 (1972).
152. D. W. Knight and G. Pattenden, J. Chem. Soc., Perkin Trans. I, 641 (1975).
153. R. G. Gastinger, E. F. Tokas, and M. D. Rausch, J. Org. Chem., 43, 159 (1978).
154. L. I. Zakharkin and A. I. Kovredov, Izv. Akad. Nauk SSSR, Ser. Khim., 1676 (1976).
155. P. L. Coe and N. E. Milner, J. Organomet. Chem., 70, 147 (1974).
156. A. M. Sladkov and L. Yu. Ukhin, Izv. Akad. Nauk SSSR, Ser. Khim., 392 (1964).
157. S. R. Landor, B. Demetriow, R. Grzeskowiak, and D. F. Pavey, J. Organomet. Chem., 93, 129 (1975).

158. R. E. Atkinson and J. A. Taylor, Tetrahedron Letters, 2919 (1968).
159. W. Verboom, H. Westmijze, H. J. T. Bos, and P. Vermeer, Tetrahedron Letters, 1441 (1978).
160. J. F. Normant, A. Commercon, and J. Villieras, Tetrahedron Letters, 1465 (1975).
161. R. F. Curtis and J. A. Taylor, J. Chem. Soc. (C), 186 (1971).
162. Y. Okamoto, K. L. Chellapa, and S. K. Kundi, J. Org. Chem., 37, 3185 (1972).
163. L. J. Belle, M. W. Buxton, and G. Fuller, J. Chem. Soc., 3372 (1965).
164. M. Sato, T. Ito, I. Motoyama, K. Watanabe, and K. Hata, Bull. Chem. Soc. Japan, 42, 1976 (1969).
165. M. Sato, I. Motoyama, and K. Hala, Bull. Chem. Soc. Japan, 43, 1860 (1970).
166. M. Nilsson and O. Wennerström, Acta Chem. Scand., 24, 482 (1970).
167. M. Nilsson and C. Ullenius, Acta Chem. Scand., 24, 2379 (1970).
168. M. Sato, I. Motoyama, and K. Hata, Bull. Chem. Soc. Japan, 43, 2972 (1970).
169. G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, Tetrahedron Letters, 223 (1976).
170. G. van Koten, "Synthesis and Characterisation of Polynuclear Organocopper Compounds", Utrecht, 1974.
171. T. Cohen, J. Wood, and A. G. Dietz, Tetrahedron Letters, 3555 (1974).
172. R. G. Pearson and C. D. Gregory, J. Amer. Chem. Soc., 98, 4098 (1976).
173. R. E. Atkinson, R. F. Curtis, and G. T. Phillips, Chem. Ind. (London), 2101 (1964).
174. M. L. H. Green, "Organometallic Compounds", Methuen, London, Vol. 2, p. 274.
175. A. Camus and N. Marsich, J. Organomet. Chem., 21, 249 (1970).
176. I. A. Garbuzova, I. R. Gol'ding, Ya. V. Genin, A. M. Sladkov, D. Ya. Tsvankin, and V. T. Aleksanyan, Izv. Akad. Nauk SSSR, Ser. Khim., 1328 (1978).
177. I. R. Gol'ding, I. A. Garbuzova, A. M. Sladkov, and V. T. Aleksanyan, "V Vsesoyuznaya Konferentsiya po Khimii Atsetilena, Tezisy Dokladov" (The Vth All-Union Conference on the Chemistry of Acetylene. Abstracts of Reports), Izd. Metsniereba, Tbilisi, 1975, p. 455.
178. R. Nast and W. Pjab, Chem. Ber., 89, 415 (1956).
179. G. Newton, H. Dan Caughman, and R. C. Taylor, J. Chem. Soc., Dalton Trans., 258 (1974).
180. G. A. Bowmaker, L. D. Blockliss, and R. Whiting, Austral. J. Chem., 26, 29 (1973).
181. P. W. Corfield and H. M. M. Shearer, Acta Cryst., 21, 957 (1966).
182. H. Schidbaur, Acc. Chem. Res., 8, 62 (1975).
183. H. E. Bachofner, F. M. Beringer, and L. Meites, J. Amer. Chem. Soc., 80, 4269 (1958).
184. A. Roedig, V. Kimmel, and W. Lippert, Tetrahedron Letters, 1219 (1971).
185. A. P. El'tekov, Zhur. Russ. Fiz. Khim. Obshch., 9, 226 (1977).
186. M. Ballester, J. Castaner, J. Riera, I. Tabernero, and C. Cornet, Tetrahedron Letters, 2353 (1977).
187. E. Gelencher, Candidate's Thesis, Moscow Technological Institute of the Food Industry, Moscow, 1978.
188. I. R. Gol'ding and A. M. Sladkov, Izv. Akad. Nauk SSSR, Ser. Khim., 529 (1972).
189. G. Minghetti, F. Bonati, and M. Massobrio, Inorg. Chem., 14, 1974 (1975).
190. I. A. Garbuzova, I. R. Gol'ding, N. N. Travkin, A. M. Sladkov, and V. T. Aleksanyan, Koord. Khim., 5, 345 (1979).
191. A. M. Sladkov, L. Yu. Ukhin, and Zh. I. Orlova, Izv. Akad. Nauk Beloruss. SSR, Ser. Khim., 2586 (1968).
192. M. F. Lapper and R. Pearce, Chem. Comm., 24 (1973).
193. G. van Koten, C. A. Shaap, and J. G. Noltes, J. Organomet. Chem., 99, 175 (1975).
194. B. I. Stepanov, L. I. Chekunina, and A. I. Bokanov, Zhur. Obshch. Khim., 43, 2648 (1973).
195. O. H. Johnson and J. R. Holum, J. Org. Chem., 23, 738 (1958).
196. R. L. Bennett, M. I. Bruce, and R. C. F. Gardner, J. Chem. Soc., Dalton Trans., 2653 (1973).
197. L. I. Zakharkin, A. I. Kovredov, M. G. Mairamov, and A. V. Kazantsev, Izv. Akad. Nauk SSSR, Ser. Khim., 1673 (1977).
198. K. Sonogashira, T. Yatake, Y. Tohda, S. Takahashi, and N. Hagihara, Chem. Comm., 291 (1977).
199. K. Sonogashira, S. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi, and N. Hagihara, J. Organomet. Chem., 145, 101 (1978).
200. K. Sonogashira, S. Takahashi, and N. Hagihara, Macromol., 10, 879 (1977).
201. K. Sonogashira, S. Kataoka, S. Takahashi, and N. Hagihara, J. Organomet. Chem., 160, 319 (1978).
202. K. Sonogashira, Y. Tohda, and N. Hagihara, Tetrahedron Letters, 4467 (1975).
203. Y. Tohda, K. Sonogashira, and N. Hagihara, Synthesis, 777 (1977).
204. K. Edo, H. Yamanaka, and T. Sakamoto, Chem. Pharm. Bull., 26, 3843 (1978).
205. Y. Abe, A. Ohsawa, H. Arai, and H. Igeta, Heterocycl., 9, 1397 (1978).
206. O. M. Abu Salah and M. J. Bruce, Austral. J. Chem., 29, 73 (1976).
207. A. Camus, N. Marisch, G. Nardin, and L. Randaccio, Inorg. Chem. Acta, 23, 131 (1977).
208. M. I. Bruce, O. M. Abu Salah, R. E. Davis, and N. V. Raghavan, J. Organomet. Chem., 64, C48 (1974).
209. O. M. Abu Salah and M. I. Bruce, J. Chem. Soc., Dalton Trans., 2311 (1975).
210. M. I. Bruce, R. Clark, J. Howard, and P. Woodward, J. Organomet. Chem., 42, C107 (1972).
211. O. M. Abu Salah and M. I. Bruce, J. Chem. Soc., Dalton Trans., 2302 (1974).
212. R. Clark, J. Howard, and P. Woodward, J. Chem. Soc., Dalton Trans., 2027 (1974).
213. O. M. Abu Salah, M. I. Bruce, and A. D. Redhouse, Chem. Comm., 855 (1974).
214. O. M. Abu Salah and M. I. Bruce, Austral. J. Chem., 29, 531 (1976).
215. O. M. Abu Salah and M. I. Bruce, Austral. J. Chem., 30, 2639 (1977).
216. O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and B. G. DeBoer, Chem. Comm., 688 (1974).
217. M. R. Churchill and B. G. DeBoer, Inorg. Chem., 14, 2630 (1975).
218. O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and S. A. Bezman, Chem. Comm., 858 (1972).
219. M. R. Churchill and S. A. Bezman, Inorg. Chem., 13, 1418 (1974).
220. G. van Koten and J. G. Noltes, Chem. Comm., 940 (1972).

221. A. J. Leusink, G. van Koten, J. W. Marsman, and J. G. Noltes, J. Organomet. Chem., **55**, 419 (1973).
222. G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, Inorg. Chem., **16**, 1782 (1977).
223. J. M. Guss, R. Mason, K. M. Thomas, G. van Koten, and J. G. Noltes, J. Organomet. Chem., **40**, C79 (1972).
224. N. N. Travkin, I. R. Gol'ding, T. A. Sladkova, B. G. Gribov, A. M. Sladkov, and N. F. Kononov, Zhur. Obshch. Khim., **46**, 1088 (1976).
225. R. Levene, J. Y. Becker, and J. Klein, J. Organomet. Chem., **67**, 467 (1974).
226. C. Björklund, M. Nilsson, and O. Wennerström, Acta Chem. Scand., **24**, 3599 (1970).
227. M. Nilsson, C. Ullenius, and O. Wennerström, Tetrahedron Letters, 2713 (1971).
228. O. Wennerström, Acta Chem. Scand., **25**, 789 (1971).
229. O. Wennerström, Acta Chem. Scand., **25**, 2341 (1971).
230. T. Kawaki and H. Hashimoto, Bull. Chem. Soc. Japan, **45**, 1499 (1972).
231. J. V. Nef, Annalen, **308**, 264 (1899).
232. R. B. Davis and D. H. Scheiber, J. Amer. Chem. Soc., 78, 1675 (1956).
233. L. Crombie and B. P. Griffin, J. Chem. Soc., 4435 (1958).
234. T. Agawa and S. I. Miller, J. Amer. Chem. Soc., 83, 449 (1961).
235. A. M. Sladkov and I. R. Gol'ding, Zhur. Org. Khim., **3**, 1338 (1967).
236. A. M. Sladkov and I. R. Gol'ding, "Khimiya Atsetilina, Trudy III Vsesoyuznoi Konferentsii" (The Chemistry of Acetylene. Proceedings of the IIIrd All-Union Conference), Izd. Nauka, Moscow, 1972, p. 45.
237. A. Kh. Filippova, G. S. Lyashenko, and N. S. Vyazankin, see Ref. 177, p. 104.
238. F. G. De Las Heras, S. Y.-K. Tam, R. S. Klein, and J. J. Fox, J. Org. Chem., **41**, 84 (1976).
239. N. Hamamichi, T. Miyasaka, and K. Arakawa, Chem. Pharm. Bull., **26**, 898 (1978).
240. T. Tsuda, Y. Chujo, T. Chujo, and T. Saegusa, Chem. Comm., 963 (1975).
241. F. Straus, Annalen, **342**, 226 (1905).
242. M. Akhtar and B. C. L. Weedon, Proc. Chem. Soc., 303 (1958).
243. R. F. Kovar, G. F. L. Ehlers, and F. E. Arnold, J. Polymer Sci., Polymer Chem., Ed., **15**, 1081 (1977).
244. M. Kinugasa and S. Hashimoto, Chem. Comm., 466 (1972).
245. L. K. Ding and W. J. Irwin, J. Chem. Soc., Perkin Trans. I, 2382 (1976).
246. T. Kauffmann, Angew. Chem., Int. Ed., **13**, 291 (1974).
247. T. Kauffmann, Angew. Chem., Int. Ed., **18**, 1 (1979).
248. A. M. Sladkov and I. R. Gol'ding, Dokl. Akad. Nauk SSSR, **200**, 132 (1971).
249. L. G. Fedenok, Candidate's Thesis, Institute of Catalysis, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1975.
250. A. M. Sladkov and I. R. Gol'ding, see Ref. 2, Vol. 1, p. 59.
251. C. L. Jenkins and J. K. Kochi, J. Amer. Chem. Soc., **94**, 856 (1972).
252. L. Yu. Ukhin, A. M. Sladkov, and Zh. I. Orlova, Izv. Akad. Nauk SSSR, Ser. Khim., 705 (1969).
253. F. J. Brockman, Canad. J. Chem., **33**, 507 (1955).
254. M. Nakagawa, J. Chem. Soc. Japan, Pure Chem. Sect., **72**, 561 (1951); Chem. Abs., **46**, 6602 (1951).
255. A. M. Sladkov, V. I. Kasatochkin, Yu. P. Kudryavtsev, and V. V. Korshak, Izv. Akad. Nauk SSSR, Ser. Khim., 2697 (1968).
256. A. M. Sladkov and L. Yu. Ukhin, Izv. Akad. Nauk SSSR, Ser. Khim., 1552 (1964).
257. A. M. Sladkov, Doctoral Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1967.
258. A. M. Sladkov, L. Yu. Ukhin, and G. N. Forshkova, Zhur. Org. Khim., **2**, 1456 (1966).
259. A. G. Makhsumov, K. S. Tillyaev, and A. Shukurov, Zhur. Vses. Khim. Obshch. im. Mendeleeva, **20**, 585 (1975).
260. A. Shukurov, A. G. Makhsumov, K. S. Tillyaev, and A. M. Sladkov, see Ref. 177, p. 152.
261. I. N. Azerbaev, R. Karazhigitova, T. A. Yagudeev, N. N. Nureshakova, and T. G. Sarbaev, see Ref. 2, Vol. 1, p. 319.
262. S. J. Huang, V. Paneccasio, F. DiBattista, D. Picker, and G. Wilson, J. Org. Chem., **40**, 124 (1975).
263. B. L. Dyatkin, L. G. Zhuravkova, B. I. Martynov, S. R. Sterlin, and I. L. Knunyants, Chem. Comm., 618 (1972).
264. A. Matsumoto, J. H. Lee, M. Yoshida, and O. Simamura, Bull. Chem. Soc. Japan, **47**, 946 (1974).
265. M. E. Isabelle and L. C. Leitch, Canad. J. Chem., **36**, 440 (1958).
266. P. L. Compagnon and B. Grosjean, Synthesis, 448 (1976).
267. Yu. N. Porshnev, T. N. Dvornikova, and V. B. Mochalin, Zhur. Org. Khim., **12**, 2019 (1976).
268. J. D. Renwick, Chem. Ind., 1637 (1966).
269. R. W. M. ten Hoedt, G. van Koten, and J. G. Noltes, J. Organomet. Chem., **161**, C13 (1978).
270. R. W. M. ten Hoedt, J. G. Noltes, G. van Koten, and A. L. Spek, J. Chem. Soc., Dalton Trans., 1800 (1978).

Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow