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η^2-Alkyne copper(I) and silver(I) compounds; from polymeric $[\text{M}^{\text{I}}\text{R}]_n$ to monomeric $[\text{M}^{\text{I}}\text{R}]$ units (M = Cu, Ag)

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Abstract

This paper deals with the breakdown of polymeric organo-copper(I) and -silver(I) compounds of general type $[M^IR]_n$ (M = Cu, Ag; R = singly bonded organic or inorganic ligand) to aggregates with lower polynuclearity and to mononuclear M^IX species. For the breakdown of the polynuclear structures of organo-copper(I) and -silver(I) compounds, main-group element substituted and organometallic substituted alkynes, diynes, and triynes are used. The synthesis, reactivity and structural features of $[M^IR]_x$ ($x = 1$–4) compounds are discussed.

Keywords: Copper(I) compounds; silver(I) compounds; Alkynes; Diynes; Triynes

1. Introduction

Organo-copper(I) and organo-silver(I) compounds of general type $[M^IR]_n$ (M = Cu, Ag; R = singly bonded organic ligand) possess wide potential as reagents for the stereoselective and regiospecific introduction of organic building blocks in organic and organometallic synthesis [1]. In most of these reactions the organo-copper(I) or organo-silver(I) reagents have been prepared in situ and used in excess. Therefore, the yield, based on organo-group 11 metal reagents, is sometimes low and depends on the reaction conditions used.

At present, it is still not clear whether $[M^IR]_n$ compounds have any relation to the reactive species in copper(I)- or silver(I)-mediated organic reactions. One of the reasons is that organo-group 11 metal compounds do not exist as single discrete aggregates in solution: the $[M^IR]_n$ compounds synthesized and characterized in the solid state are in equilibrium in solution with species with lower association.

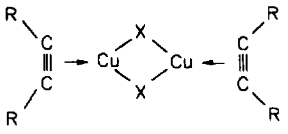
One approach to this problem is to use mononuclear and therefore well defined organo-copper(I) and organo-silver(I) species.

So far, it has been found that nitrogen-, phosphorus-, oxygen- or sulphur-containing molecules are suitable for breaking down polynuclear structures of organo-copper(I) and organo-silver(I) compounds to aggregates with a lower polynuclearity [2]. However, only a few examples of mononuclear organo-copper(I) and organo-silver(I) species $[M^IR]$ (M = Cu, Ag; R = singly bonded organic ligand, e.g. 2,4,6-$Ph_3C_6H_2$ or 2,4,6-$^tBu_3C_6H_2$) are known [3]. Recently, it was shown that main-group element and organometallic substituted alkynes and 1,4-diynes are also very capable of breaking down polynuclear copper(I) and silver(I) compounds to mononuclear compounds.

This paper focuses on the synthesis and reactivity of (η^2-alkyne)-copper(I) and -silver(I) species and is divided into two parts: (1) the synthesis and reactivity of main-group element substituted alkyne, diyne and triyne copper(I) and silver(I) compounds (Section 2) and (2) the synthesis and reactivity of organometallic substituted alkyne and 1,4-diyne copper(I) and silver(I) compounds (Section 3).

2. Main-group element substituted η^2-alkyne copper(I) and silver(I) compounds

Depending on the nature of the main-group substituted alkynes and of the copper(I) compounds $[\mathrm{Cu^IX}]_n$ (X = singly bonded organic or inorganic ligand) used, different coordination modes are observed. This section describes the synthesis of structural type **A**–**E** molecules.



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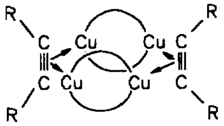

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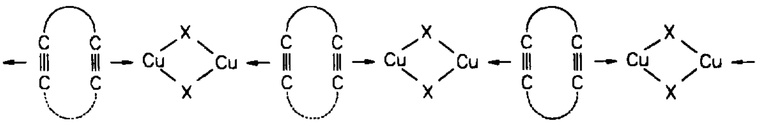

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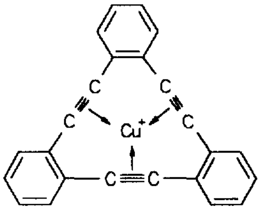

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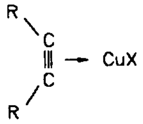

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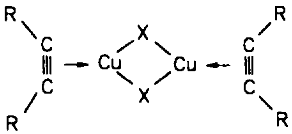
In compounds of structural types **A**–**E**, alkyne units are η^2-coordinated to $\mathrm{Cu^IX}$ fragments.

So far, it has been found that alkynes RC≡CR, cyclic monoalkynes and cyclic triynes are able to form monomeric (type **D** and **E**), dimeric (type **A**) and tetrameric (type **B**) copper(I) alkyne complexes, while main-group bridged 1,4-diynes or cyclic diynes form polymers of type **C**.

2.1. *Type A molecules,* $[(\eta^2\text{-RC}{\equiv}\text{CR})\mathrm{Cu^IX}]_2$

Structural type **A** molecules are dimers, which contain two copper atoms and two bridging X units in a centrosymmetric $\mathrm{Cu_2X_2}$ ring [4–17]. Each copper atom possesses a trigonal planar geometry.



A

The C_2 unit of the alkyne ligand RC≡CR is symmetrically η^2-coordinated to one copper atom; the Cu_2X_2 ring is coplanar with the CuC_2 fragments.

2.1.1. Synthesis

There are two methods for the synthesis of type **A** molecules: (a) direct synthesis from alkynes and (b) nucleophilic substitution of $[(\eta^2\text{-alkyne})Cu^IX]_2$ (X = Cl, Br, I) compounds.

(a) Direct synthesis route. The dimeric compounds **2** are best synthesized by treatment of RC≡CR (**1a**, R = $SiMe_3$; **1b**, R = Et; **1c**, R = Ph) or tmtch (3,3,6,6-tetramethyl-1-thia-4-cycloheptyne, $C_{10}H_{16}S$; **1d**) with $[Cu^IX]_n$ (X = Cl, Br, I, OSO_2CF_3, ...) (Table 1) [4–17].

1 **2**

(b) Nucleophilic substitution route. Compounds of type **A** are also formed by the reaction of $[(\eta^2\text{-tmtch})Cu^ICl]_2$ (**2j**) and NaX (X = OPh, O^{t}Bu) in thf; the dimeric complexes **2m** and **2n** are formed in ≈50% yield (Table 1) [10].

2.1.2. Reactivity

An overview of the diverse reactivity of type **A** compounds (**2a**, **2b** and **2j**–**2l**) is given in Scheme 1.

The nucleophilic substitution reaction of $[(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)CuX]_2$ (**2a**, X = Cl; **2b**, X = Br) and $[\eta^2\text{-tmtch})CuX]_2$ (**2j**, X = Cl; **2k**, X = Br; **2l**, X = I) with $[AgO_2CR]_n$ (route (a)), Na[acac] (acac = acetylacetonate) (route (b)), $Li[(Me_3SiN)_2CPh]$ (route (c)) or LiC_5H_5 (route (d)) leads to the formation of type **B** and **E** molecules (Scheme 1) [13,14,18].

With the Lewis bases SMe_2 (route (e)) and PPh_3 (route (f)), the monomeric adduct $[(\eta^2\text{-tmtch})Cu(I)(SMe_2)]$ (a type **E** molecule) [9,11] or the dimeric complexes $\{(\eta^2\text{-tmtch})[Cu(\mu\text{-}X)]_2(PPh_3)_2\}$ (**3a**, X = Cl; **3b**, X = Br; **3c**, X = I) are formed (Scheme 1) [12].

In a similar manner, **2a** and **2b** react with the organometallic chelate $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$ to yield the monomeric bimetallic compounds $\{(\eta^5\text{-}$

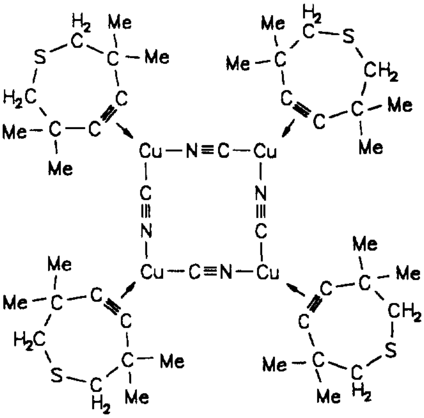
Table 1
Compounds $[(\eta^2\text{-RC}{\equiv}\text{CR})\text{CuX}]_2$ (**2**)

Compound	R[a]	X	Ref.
2a	$SiMe_3$	Cl	[5–7,13,14]
2b	$SiMe_3$	Br	[5,7,13,14]
2c	$SiMe_3$	OSO_2CF_3	[13,14]
2d	Et	O_2CCF_3	[15]
2e	Ph	O_2CCF_3	[15]
2f	Ph	O_2CPh	[16]
2g	Ph	$O_2C(2\text{-ClC}_6H_4)$	[17]
2h	Ph	$O_2C(2\text{-BrC}_6H_4)$	[17]
2i	$SiMe_3$	O_2CCH_3	[13,14]
2j	tmtch	Cl	[9–11]
2k	tmtch	Br	[9]
2l	tmtch	I	[9]
2m	tmtch	OPh	[10]
2n	tmtch	O^tBu	[10]
2o	tmtch	SPh	[8,10]
2p	tmtch	C≡CPh	[10]

[a] tmtch = 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne.

$C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}CuX$ (X = Cl, Br) as shown by route (g) (Scheme 1) [13,19]. However, with $LiC{\equiv}CSiMe_3$ dimeric **2b** yields the copper(I) acetylide $[CuC{\equiv}CSiMe_3]_n$ (**4**) (route (h), Scheme 1) [13]. The formation of a compound of structural type **A** in which the $Me_3SiC{\equiv}C$ ligands are σ, π bridging two $(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)Cu$ building blocks was not observed [13].

When isoelectronic CN^- is used instead of $Me_3SiC{\equiv}C^-$, the products formed are $[CuCN]_n$ and $Me_3SiC{\equiv}CSiMe_3$ (**1a**). Whereas the substitution of Cl^- in $[(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)CuCl]_2$ (**2a**) by CN^- was not successful, the direct reaction of the



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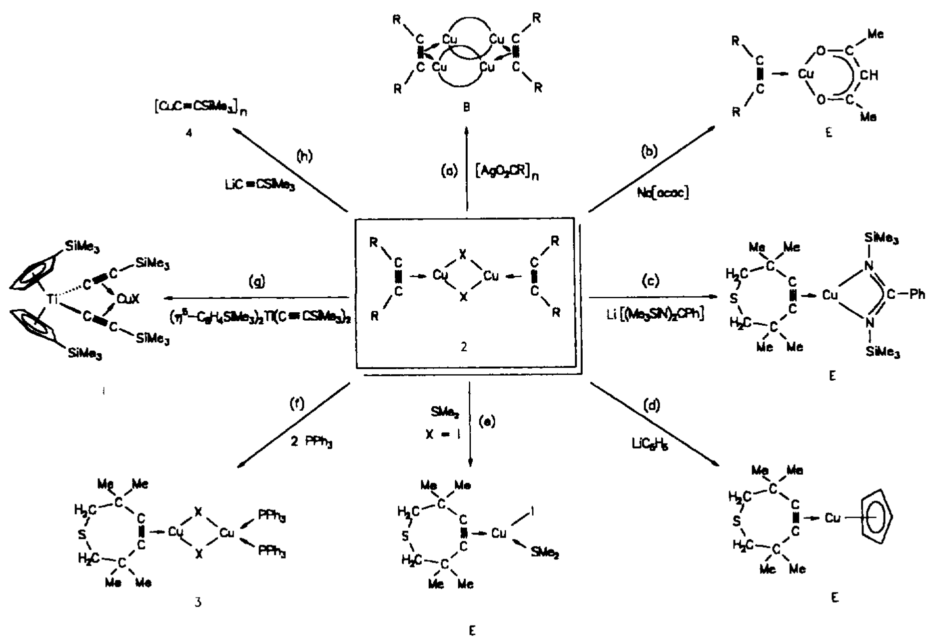


Scheme 1. Reaction of **2a**, **2b**, **2j**, **2k** and **2l** with different substrates.

highly strained cycloalkyne tmtch with $[CuCN]_n$ affords the tetranuclear complex $[(\eta^2\text{-tmtch})CuCN]_4$ (**5**) in high yields [11].

Complex **5** contains a slightly puckered $[CuCN]_4$ ring. Each cyanide ion is σ and dative bonded to two different copper atoms, thus forming an almost linear $Cu-CN{\rightarrow}Cu$ unit [11]. This coordination mode is typical for copper(I) cyanide [20–22]. A similar compound containing CuCl building blocks instead of CuCN units can be isolated by the reaction of $MeC{\equiv}CMe$ with $[CuCl]_n$ [4].

For a detailed discussion of type **B**, **E** and **I** molecules (Scheme 1), see Sections 2.2, 2.4 and 3.3.

2.1.3. Spectroscopy and bonding

In the binuclear compounds $[(\eta^2\text{-}RC{\equiv}CR)CuX]_2$ ($R = SiMe_3$, Et, Ph) and $[(\eta^2\text{-tmtch})CuX]_2$ (type **A** molecules), the alkyne ligands are η^2-coordinated to Cu^IX moieties. This is evidenced by the IR and ^{13}C NMR data (Table 2). In the IR spectra the $\nu(C{\equiv}C)$ absorption decreases from 2200/2170 or 2110 cm^{-1} in the free acetylenes tmtch and $Me_3SiC{\equiv}CSiMe_3$ to 2015/1950 cm^{-1} in **2j**–**2o** and **3a**–**3c** or 1940–1960 cm^{-1} in **2a**–**2c** (Table 2) [5–14]. The same behaviour is found for all other compounds of type **A** (Tables 1 and 2).

It is found that the copper–alkyne bond is stronger in the $[(\eta^2\text{-tmtch})CuX]_2$ compounds **2j**–**2o** than in the analogous $Me_3SiC{\equiv}CSiMe_3$ substituted compounds **2a**–**2c**, as given by the $\Delta\nu$ value of ~190 cm^{-1} (**2j**–**2o**) or ~150 cm^{-1} (**2a**–**2c**) (Table 2). In addition, the η^2-coordination of the alkyne ligands in compounds **2**

Table 2
Selected IR and $^{13}C\{^{1}H\}$ NMR data for compounds **2** and **3**

Compound	IR $\nu(C\equiv C)$ (cm^{-1})	$^{13}C\{^{1}H\}$ NMR $\delta(C\equiv C)$ (ppm)	Ref.
2a	1949	115.2	[5–7,13,14]
2b	1953	116.4	[5,13,14]
2c	1953	–	[13]
2d	2070	88.2	[15]
2e	–	95.7	[15]
2j	2007; 1981	109.1	[9–12]
2k	2005; 1981	110.5	[12]
2l	2015; 1980	112.2	[12]
2m	1955	107.8	[10]
2o	1970; 1950		[8,10]
3a	2001; 1980	109.5	[12]
3b	2000; 1979	110.5	[12]
3c	2011; 1980	112.5	[12]

and **3** to a $Cu^{I}X$ building block leads to changes in the ^{13}C NMR feature of the $RC\equiv CR$ ligands (Table 2), the carbon signals of the $RC\equiv CR$ units in type **A** molecules being shifted slightly to lower field compared with the corresponding starting materials (Table 2) [8–19].

The lengthening of the $C\equiv C$ triple bond and the bending of the $R-C\equiv C-R$ units from the linear arrangement in the free ligands, due to η^2-coordination of the alkyne ligand to a $Cu^{I}X$ building block, is corroborated by X-ray structure analysis (Table 3).

A typical example of a type **A** molecule (complex **2b**) is shown in Fig. 1 [7,13].

Fig. 1 shows that compounds of type **A** are dimeric. Each C_2 unit of the acetylene group is symmetrically π bonded to one copper atom. The CuC_2 building block is coplanar with the four-membered Cu_2Br_2 ring and each copper atom possesses a trigonal planar environment. As a result of the η^2-coordination of the $Me_3SiC\equiv CSiMe_3$ ligand to $Cu^{I}Br$, the $Si-C\equiv C-Si$ unit is distorted compared with the non-coordinated $Me_3SiC\equiv CSiMe_3$ ligand (Table 3). At the same time, the $C\equiv C$ triple bond of the alkyne is lengthened from 1.182 Å in $Me_3SiC\equiv CSiMe_3$ to 1.24 Å in **2b** (Table 3). The copper–copper distance of 3.05 Å is significantly larger than the sum of the van der Waals radii (1.54 Å) [23], implying that there is no copper–copper bond.

2.2. *Type **B** molecules, $[(\eta^2\text{-}RC\equiv CR)(Cu^{I}X)_2]_2$*

As shown in Section 2.1, acetylenes can be used to break down the oligomeric structure of copper(I) carboxylates to a dimeric structure (type **A** molecules) (Table 1) [14–17]. However, depending on the nature of the R and R′ groups on the alkynes $RC\equiv CR'$ and on the stoichiometry of the copper(I) carboxylate and alkyne used,

Table 3
X-ray data for compounds **2** and **3**

Compound	Ref.	Cu···Cu (Å)	Cu–X (Å)	Cu←‖‖ (Å)	C≡C (Å)	X–Cu–X (°)	Cu–X–Cu (°)	C≡C–R (°)
2a	[5]	–	2.279(1)	2.017(3)	1.227(5)	96.64(3)	93.36(3)	166.3(3)
			2.281(1)	2.020(3)				164.2(3)
2b	[7,13]	3.05	2.407(1)	2.043(7)	1.24(1)	89.9	–	165.0(6)
				2.045(7)				162.9(6)
2f	[16]	2.782(3)	1.99(1); 1.93(1)	1.93(2); 1.94(1)	1.28(2)	100.4(4)		157(1); 158(2)
			1.99(1); 1.95(1)	1.95(1); 1.93(1)	1.21(2)	99.6(4)		158(1); 160(1)
2j	[10]	3.021(1)	2.267(2)	1.937(5)	1.220(6)	96.8(1)	83.2(1)	147.9(5)
			2.283(2)	1.951(5)				147.3(5)
2m	[10]	2.940(2)	1.945(2)	1.929(3)	1.247(5)	81.8(2)	98.2(2)	146.9(3)
2o	[8]	2.904(1)	2.293(1); 2.284(1)	1.970(3); 1.962(3)	1.230(5)	91.89(4)	78.53(3)	147.8(4); 147.1(4)
			2.295(1); 2.283(1)	1.962(3); 1.969(3)	1.223(4)	91.87(4)	78.95(4)	145.9(4); 147.7(4)
2p	[10]	2.386(1)	2.014(3); 2.022(3)	1.940(4)	1.220(5)	107.5(1)	72.5(1)	147.2(4)
				1.951(4)				148.1(4)
3a[a]	[12]	3.134(2)	2.244(2); 2.242(3)	1.942(7)	1.22(1)	100.1(1)	84.5(1)	148.1(7)
			2.414(3); 2.416(2)	1.946(6)		90.8(1)		147.3(6)
3b[b]	[12]	3.186(2)	2.370(2); 2.384(2)	1.95(1)	1.22(2)	103.4(1)	79.4(1)	149(1)
			2.610(2); 2.586(2)	1.97(1)		91.7(1)	79.6(1)	148(1)
3c[c]	[12]	3.157(1)	2.544(1); 2.541(1)	1.989(8)	1.23(1)	108.6(1)	73.9(1)	146.1(8)
			2.704(1); 2.714(1)	1.982(8)		99.3(1)	73.8(1)	149.3(8)

[a] Cu–P 2.255(3)/2.254(2) Å; P–Cu–P 125.9(1)°.
[b] Cu–P 2.264(3)/2.264(3) Å; P–Cu–P 126.8(1)°.
[c] Cu–P 2.268(2)/2.261(2) Å; P–Cu–P 125.7(1)°.

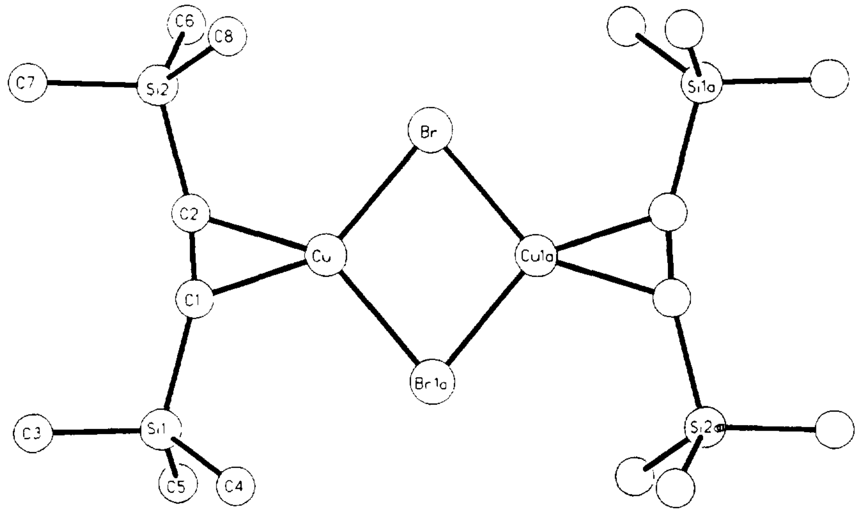
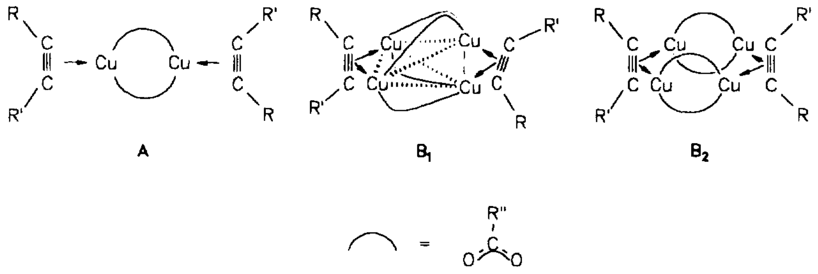


Fig. 1. Molecular geometry and atom labelling scheme for **2b**. Selected bond distances and angles are given in Table 3 [7,13].



other coordination modes can be realized, i.e. structural type **B** molecules [10,13–17,24,25].

The reaction of the alkynes $RC{\equiv}CR'$ (R, R' = Me, Et, CO_2Me, CO_2Et, tmtch) with $[CuO_2CR'']_n$ yields the tetranuclear complexes $[(\eta^2\text{-}RC{\equiv}CR')(CuO_2CR'')_2]_2$ (**6**) (Table 4) together with dimeric $[(\eta^2\text{-}RC{\equiv}CR')CuO_2CR'']_2$ (**2d**–**2h**) (Section 2.1; Table 1).

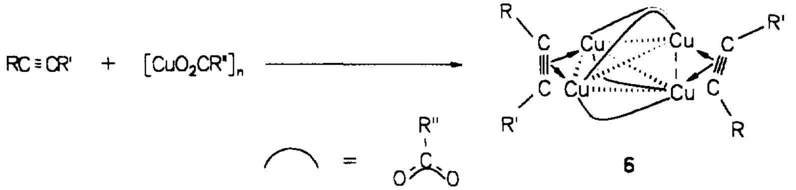
The formation of the dimeric compounds $[(\eta^2\text{-}RC{\equiv}CR')CuO_2CR'']_2$ (**2d**–**2h**) (R = R' = Et, Ph) (Section 2.1; Table 1) and the tetranuclear compounds $[(\eta^2\text{-}RC{\equiv}CR')(CuO_2CR'')_2]_2$ (**6**) (Table 4) clearly depends on the donor strength of the acetylenes used; weak donor ligands, such as dimethylacetylene dicarboxylate and diethylacetylene dicarboxylate, lead to the formation of coordination compounds in which the initial tetrameric copper(I) carboxylate moiety is retained.

With electron-donating substituents, such as Ph or Et, on the alkyne, the dimeric compounds described in Section 2.1 (type **A** molecules) are formed (Table 1).

Table 4
Compounds **6** and 7

Compound	R	R′	R″	Ref.
6a	Et	Et	CF_3	[15,24]
6b	CO_2Me	CO_2Me	CF_3	[15]
6c	CO_2Me	Me	CF_3	[15]
6d	CO_2Me	CO_2Me	Ph	[17]
6e	CO_2Me	CO_2Me	2-ClC_6H_4	[17]
6f	CO_2Me	CO_2Me	2-BrC_6H_4	[17]
6g	CO_2Et	CO_2Et	Ph	[17]
6h	CO_2Et	CO_2Et	2-ClC_6H_4	[17]
6i	CO_2Et	CO_2Et	2-BrC_6H_4	[17]
6j	tmtch[a]		Me	[10]
6k	tmtch[a]		Ph	[10]
7	$SiMe_3$	$SiMe_3$	Me	[13,25]

[a] tmtch = 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne.

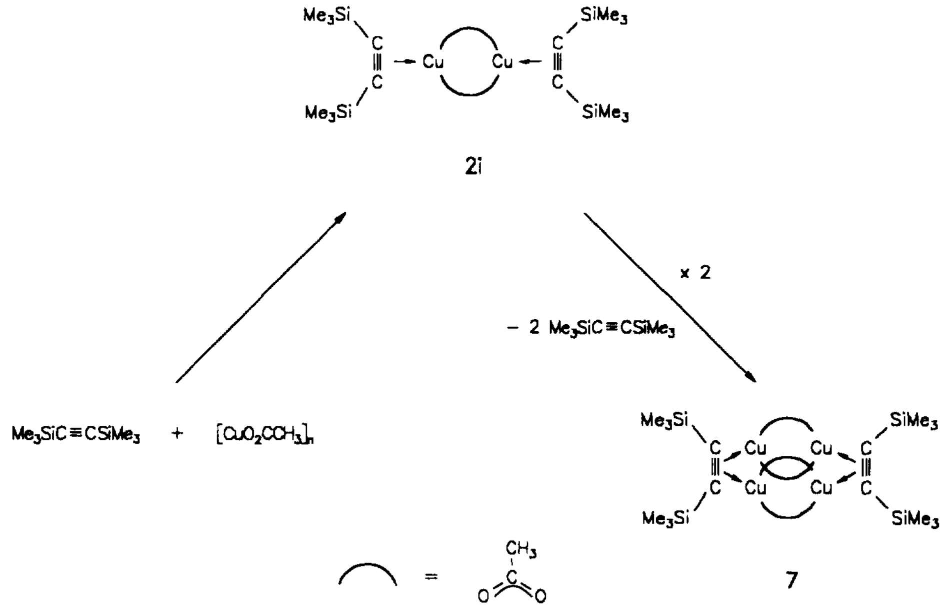


When the tetrameric starting compound $[CuO_2CPh]_4$ is reacted with isocyanates, azo compounds and quinoline as nitrogen donor ligands, the $[Cu(\mu\text{-}O_2CPh)]_2$ building block is also formed [26].

As expected, the reaction of $[CuO_2CCF_3]_n$ with $EtC{\equiv}CEt$ yields both types of compound (type **A** and **B** molecules) [15,24]. The product obtained can be controlled by the stoichiometry of the starting materials used: with an excess of 3-hexyne in the reaction mixture the only product isolated is the dinuclear compound $[(\eta^2\text{-}EtC{\equiv}CEt)CuO_2CCF_3]_2$ (**2d**), whereas with no excess of 3-hexyne the tetranuclear compound $[(\eta^2\text{-}EtC{\equiv}CEt)(CuO_2CCF_3)_2]_2$ (**6a**) is formed [15,24].

In one special case it could be shown that tetrameric compounds of type **B** are formed from dimeric structural type **A** complexes. Treatment of etheral solutions of $[CuO_2CCH_3]_n$ with $Me_3SiC{\equiv}SiMe_3$ (**1a**) yields together with dimeric $[(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)CuO_2CCH_3]_2$ (**2i**) the tetrameric coordination compound $[(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)(CuO_2CCH_3)_2]_2$ (**7**) [13,25].

It has been confirmed independently that compound **2i** dimerizes in solution, by $Me_3SiC{\equiv}CSiMe_3$ elimination, to form 7. This dimerization is evidenced by the IR spectroscopic data: the $\nu(C{\equiv}C)$ vibration of **2i** at 1952 cm^{-1} is shifted to 1731 cm^{-1} in 7 [13,25]. These data are consistent with the η^2-coordination of the $Me_3SiC{\equiv}CSiMe_3$ unit to one copper atom in **2i** and to two copper atoms in 7. Similar IR



spectroscopic data for the $C \equiv C$ stretching vibration are found for other alkyne-bridged dicopper(I) complexes containing macrocycles such as tropocoronand-6,6 [27,28].

The solid-state structures of selected examples of compounds **6** and **7** have been determined by X-ray diffraction studies (Fig. 2, Table 5).

Fig. 2 shows two structural isomers (**B**$_1$ and **B**$_2$) of type **B** molecules. The formation of these two products is surprising, since the reaction conditions for the synthesis of type **B** molecules used are identical. The common feature of compounds **6** and **7** is that each of the two acetylenes, and also each of the four carboxylate units, act as a four-electron donor, bridging two adjacent copper atoms. The two structural isomers of type **B** compounds (**B**$_1$ and **B**$_2$) differ in the arrangement of the four copper atoms with respect to each other. In the tetrameric compounds **6** the four copper atoms form a distorted tetrahedral core, whereas in **7** a square-planar arrangement is found. In **6** two short (2.76–3.00 Å) and four long (3.00–3.17 Å) Cu···Cu distances are found [10]; in **7** the Cu···Cu distances are 3.02 Å [13,25].

The observed bond weakening by IR spectroscopy (see above) of the $C \equiv C$ triple bonds in compounds **6** and **7**, relative to the starting materials $RC \equiv CR'$, was confirmed by X-ray diffraction studies (Fig. 2, Table 5). The $C \equiv C$ distances of 1.26–1.30 Å found in compounds **6** and **7** are significantly longer than in the free acetylenes $RC \equiv CR'$, but they are shorter than in the alkyne-bridged dinuclear copper(I) tropocoronand-6,6 compound $[Cu_2(\eta^2\text{-}RC \equiv CR)(TC\text{-}6,6)]$ ($R = CO_2Me$, CO_2Et; TC-6,6 = tropocoronand-6,6) [27,28]. The longer $C \equiv C$ distances found in tetrameric **6** and **7** (Table 5) compared with dimeric **2** (Table 3) are consistent with

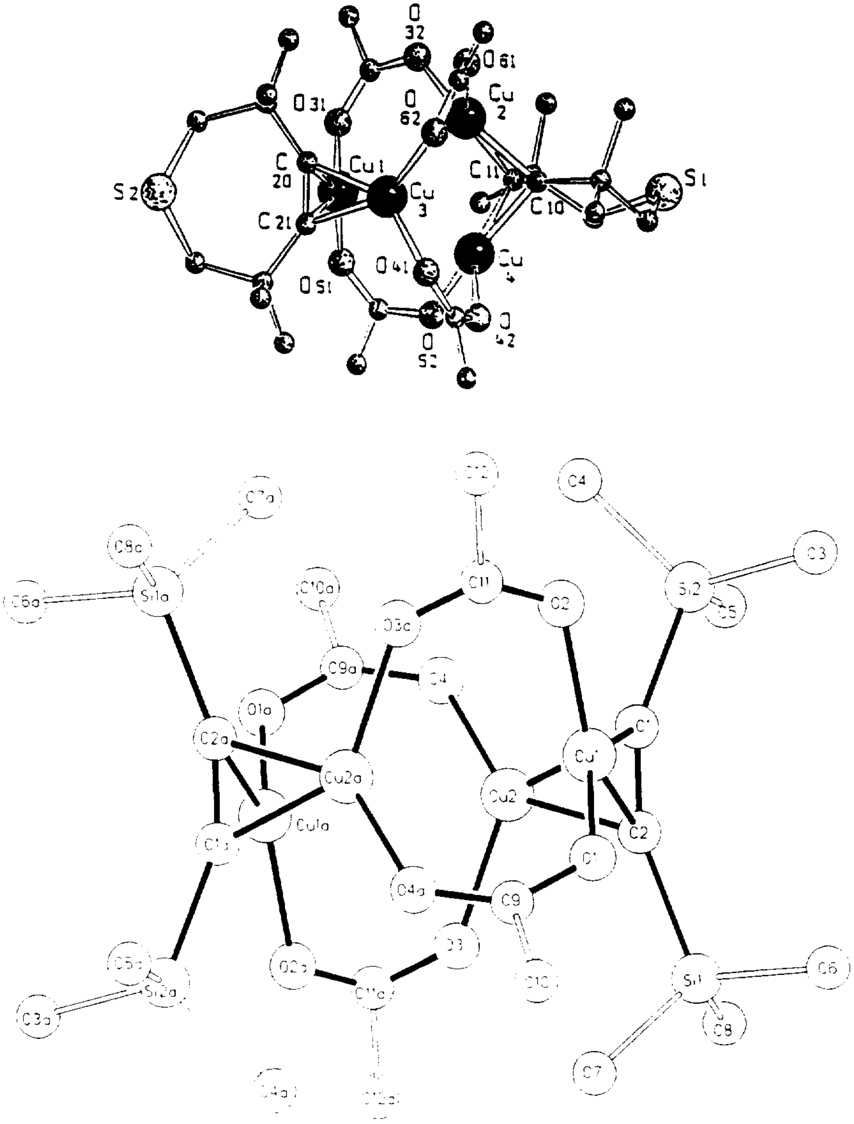
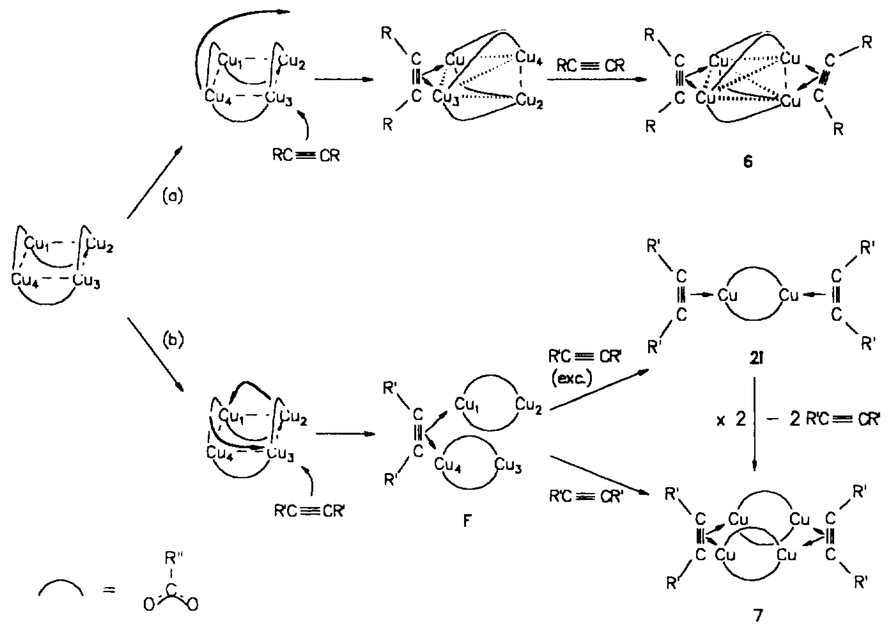


Fig. 2. Molecular geometry and atom labelling scheme for **6j** (top) and **7** (bottom) [10,13,25]. Selected bond distances (Å) and angles (°) are given in Table 5.

bridging alkyne units serving as 'four-electron donor' ligands, π-bonded to two copper(I) centres. As a result of the η^2-coordination of the alkyne ligands to the copper atoms in **6** and **7**, the angles R—C≡C—R are considerably reduced (143–158°) (Table 5). In comparison with the dinuclear $Cu_2(\eta^2$-$RC{\equiv}CR)(TC$-$6,6)$ compounds (R—C≡C—R angles 139.0°, 138.2°), both structural features imply that π back-bonding in compounds **6** and **7** is less important.

Table 5
X-ray data for compounds **6** and **7**

Compound	Ref.	Cu···Cu (Å)	Cu–O (Å)	Cu←‖‖ (Å)	C≡C (Å)	O–Cu–O (°)	C≡C–R (°)
6a	[24]	2.820(3); 3.136(3)	-	1.97(2); 1.99(2)	1.26(2)	-	152(2)
		3.130(3); 3.079(3)		1.97(3); 2.00(2)	1.26(2)		155(2)
		3.166(3); 2.799(3)		1.98(2); 2.00(2)			148(2)
				1.92(2); 1.98(2)			156(2)
6h	[17]	2.960(2); 2.998(2)	1.927(3); 1.899(4)	1.976(4); 1.968(4)	1.280(5)	98.3(2)	147.1(4)
		2.980(2); 3.001(2)	1.914(3); 1.922(3)	1.951(3); 1.950(4)	1.295(4)	96.6(2)	146.4(4)
		3.129(3); 2.941(2)	1.915(3); 1.910(3)	1.948(3); 1.950(3)		96.2(2)	148.5(3)
			1.915(3); 1.907(3)	1.963(3); 1.952(3)		96.6(2)	151.6(3)
6j	[10]	3.103(3); 3.151(3)	1.932(4)	1.974(5)	1.259(7)		142.7(5)
		2.774(3); 2.762(3)					
		3.131(3); 3.157(3)					
7	[13,25]	3.02(1); 3.02(1)	1.941(3); 1.99(1)	1.982(4); 1.985(4)	1.278(6)	106.2(6)	158.6(4)
			1.99(1); 1.945(3)	1.995(4); 2.007(5)		111.8(5)	157.0(4)



Scheme 2. Possible routes for the formation of type **B** compounds: (a) weak donors (type $\mathbf{B}_1$ molecules); (b) strong donors (type **A** and $\mathbf{B}_2$ molecules).

The formation of compounds **2d**–**2i**, **6** and **7** from copper carboxylates and alkynes is best explained by the two possible reaction pathways given in Scheme 2. The reaction of copper(I) carboxylates with acetylenes proceeds most likely via initial attack of the acetylene at one of the copper atoms (Scheme 2).

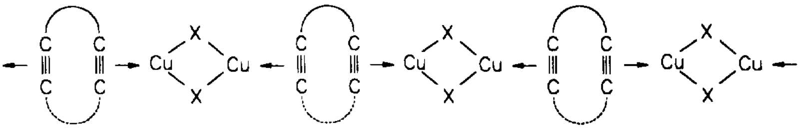
With weak donor ligands, such as $RO_2CC{\equiv}CCO_2R$ (R = Me, Et) the formation of tetrameric **6** proceeds via route (a) (Scheme 2). The donor strength of these acetylenes is not large enough to break copper–oxygen bonds in the tetrameric copper(I) carboxylate starting compounds, thus generating a three-coordinated copper(I) centre. The π-bonded acetylene moiety then interacts with the opposite copper atom in the Cu_4 core in the starting compound; a perpendicularly oriented acetylene bridging unit is formed. Subsequent complexation of a second acetylene ligand then yields complex **6** (Scheme 2).

The formation of the dimeric complex **2i** and the tetrameric compound **7** is explained by pathway (b) by using a strong donor acetylene ligand (Scheme 2): the donor strength of $RC{\equiv}CR$ (R = Ph, Et, $SiMe_3$) is large enough to break copper–oxygen bonds in tetrameric copper(I) carboxylates. Thus, bond breaking of Cu(1,3)—O and simultaneous inverse bond rebuilding yields the intermediate **F** (Scheme 2); **F** then reacts further with alkynes to form dimeric **2i** or tetrameric **7** [13,25].

2.3. *Type* **C** *molecules,* $\{[E(\eta^2\text{-}C{\equiv}CR)_2](M^IX)_2\}_n$

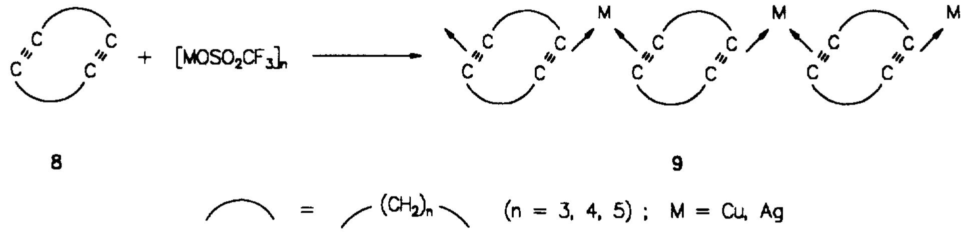
In general, alkynes can be used to break down the polymeric structures of Cu^IX compounds, $[Cu^IX]_n$ (X = singly bonded organic or inorganic ligand) (Sections 2.1

and 2.2) [4–25]. Similarly, diynes can be used. However, oligomers are obtained in which the diyne units are linked together by Cu^IX building blocks, thus forming type **C** molecules [13,29–33].



C

Polymers containing $M^IOSO_2CF_3$ (M = Cu, Ag) entities can be obtained, as shown by Gleiter et al. [29], when cyclic diynes, such as 1,6-cyclodecadiyne (**8a**), 1,7-cyclododecadiyne (**8b**) and 1,8-cyclotetradecadiyne (**8c**) are reacted with $[M^IOSO_2CF_3]_n$ in thf [29]. Compounds **9** (**9a**, M = Cu, $n=3$; **9b**, M = Ag, $n=3$; **9c**, M = Cu, $n=4$; **9d**, M = Ag, $n=4$; **9e**, M = Ag, $n=5$) are formed in high yields.



8 **9**

The spectroscopic data (IR, ^{13}C NMR) for polymeric **9** indicate a weak interaction between the C≡C triple bonds and the copper(I) or silver(I) ions [29].

The solid-state structures of compounds **9** were elucidated by X-ray crystallographic studies, carried out on **9b–e** [29]. The molecular structure of **9b** is shown in Fig. 3 [29]. In the crystal structure of **9b** the double strands of the 1,6-cyclodecadiyne rings are in a chair conformation and linked by $Ag(OSO_2CF_3)_2Ag$ units (Fig. 3, right) to form a two-dimensional network (Fig. 3, left).

In compounds **9c–e** the twelve-membered rings of the cyclododecadiynes are coupled by copper(I) or silver(I) ions. Since each trifluoromethanesulphonate ligand in these compounds uses two oxygen atoms to coordinate two different metal centres, a three-dimensional network is formed [29].

In contrast to the above-described reaction of cyclic diynes with $M^IOSO_2CF_3$, the reaction of the Me_2Si-bridged 1,4-diyne $Me_3SiC{\equiv}C{-}Me_2Si{-}C{\equiv}CSiMe_3$ (**10**) with $[Cu^IX]_n$ (X = Cl, Br) in CH_2Cl_2 yields the polymer $\{Me_2Si(C{\equiv}CSiMe_3)_2(CuX)_2\}_n$ (**11a**, X = Cl; **11b**, X = Br) of structural type **C** [13,30].

In polymeric **11** each $Me_3SiC{\equiv}C$ building block is η^2-coordinated to a Cu^IX unit and the Cu^IX moieties dimerize to form Cu_2X_2 rings. As a result of the formation of Cu_2X_2 units, two $Me_2Si\ (C{\equiv}CSiMe_3)_2$ building blocks are linked together, thus yielding a polymeric structure.

The η^2-coordination of the $Me_3SiC{\equiv}C$ units to Cu^IX is indicated by the IR

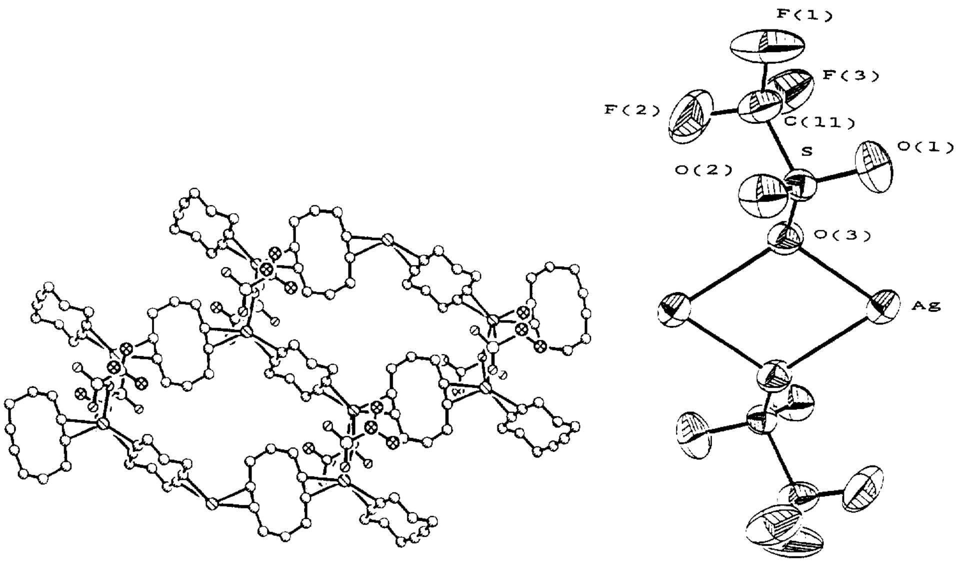


Fig. 3. Molecular geometry and atom labelling scheme for **9b** (left, polymer; right, $Ag_2(OSO_2CF_3)_2$ bridge) [29]. Selected bond distances (Å) and angles (°) are as follows: C1—C2/C6—C7 1.211, Ag—C1/Ag—C2/Ag—C6/Ag—C7 2.410; C1—C2—C3 170.7, D1—Ag—D2 131.2 (D = mid-point of the C_2 units).

$$n\ Me_2Si(C{\equiv}CSiMe_3)_2 \xrightarrow{2\ [CuX]_n} \{Me_2Si[(\eta^2\text{-}C{\equiv}CSiMe_3)CuX]_2\}_n$$

10 **11**

spectroscopic data. In the IR spectra of **11a** and **11b** the $\nu(C{\equiv}C)$ vibration decreases to 1960 cm^{-1} compared with 2104 cm^{-1} in **10** [13,30].

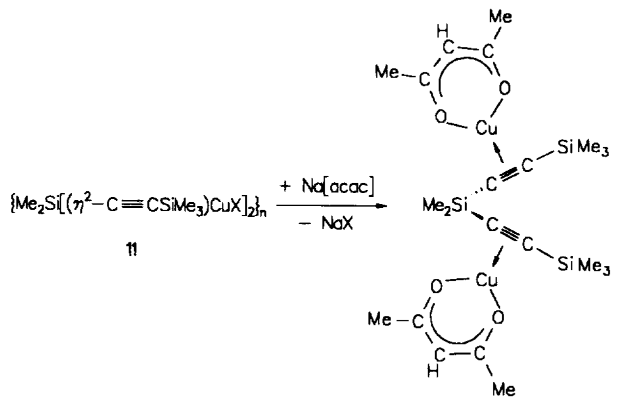
A similar structure to that of compounds **11a** and **11b** is found in $\{Hg(C{\equiv}CPh)_2(CuCl)_2\}_n$ (**11c**) in which the Me_2Si bridge head of the 1,4-diyne in compounds **11a** and **b** is replaced with a mercury atom [31].

Another polymer, containing Cu_2Cl_2 units, can be prepared by the reaction of $[Cu^ICl]_n$ with $HC{\equiv}C(CH_2)_4C{\equiv}CH$ (**12**) [32]. The resulting $\{C_8H_{10}(CuCl)_2\}_n$ polymer (**13**) was characterized by IR spectroscopy and a crystal structure determination. In **13**, layers of fused four- and eight-membered Cu^ICl rings are cross-linked by **12** to form a three-dimensional network [32].

The polymeric structures of **11a** and **11b** can be depolymerized using the organic chelate acetylacetonate (acac); monomeric **14** is formed in quantitative yields [13,30]. For a detailed discussion of monomeric (η^2-alkyne)copper(I) β-diketonates see Section 2.4.

2.4. *Type **D** and **E** molecules*

The breakdown of polymeric copper(I) and silver(I) compounds into dimeric or tetrameric compounds by alkynes is described in Sections 2.1 and 2.2 [4–25]. In

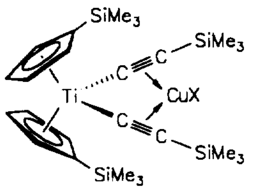


11

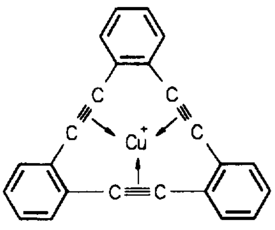
14

contrast, monomeric copper(I) building blocks can be stabilized using the chelate effect of organometallic 1,4-diynes (type **L** molecules) (Section 3) [13,34–40] or cyclic triynes (type **D** molecules) [41–43]. In addition, monomeric η^2-alkyne copper(I) compounds (structural type **E** molecules) are formed when mono-, di- or tridentate N-, O- and S-ligands are used [11,18,27,28,44–49].

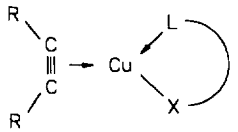
For a detailed discussion of structural type **I** molecules, see Section 3.



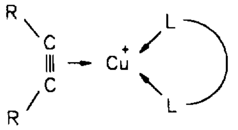
I



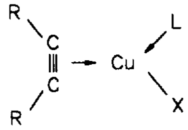
D



E₁



E₂

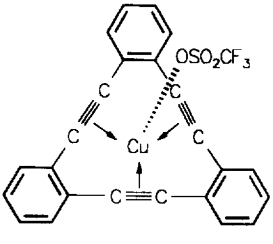


E₃

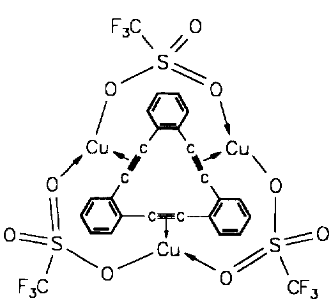
X = Singly bonded ligand; L = dative bonded ligand.

2.4.1. *Type* **D** *molecules,* $[(TBC)(M^1OSO_2CF_3)_n]$ $(n=1,3)$; $[(TBC)_2AgOSO_2CF_3]$

The reaction of TBC (1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne) (**15**) with $[CuOSO_2CF_3]_n$ yields $[(TBC)\text{-}CuOSO_2CF_3]$ (**16**) and $[(TBC)\text{-}(CuOSO_2CF_3)_3]$ (**17**) [41,43].



16

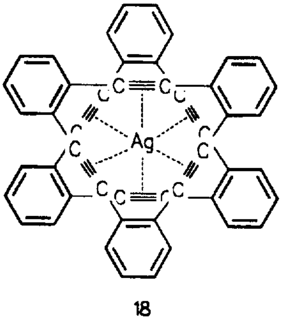


17

In **16**, the copper(I) ion is chelated by the three C_2 building blocks of TBC and semi-coordinated by an oxygen of the triflate anion (Cu—O 2.549 Å) [41].

In **17**, each C≡C triple bond of the macrocyclic trialkyne ligand TBC is η^2-coordinated to a copper(I) triflate building block. Complex **17** can best be described as a cofacial bimacrocycle: the TBC ligand is π-bonded to a cyclic trimer of $CuOSO_2CF_3$ moieties in which the three copper atoms are bridged by an O—S—O building block, thus forming a 12-membered macrocyclic ring with Cu—O—S—O as a repeat unit [43].

In contrast, when $[AgOSO_2CF_3]_n$ instead of $[CuOSO_2CF_3]_n$ is reacted with TBC, the silver(I) trifluoromethanesulphonate sandwich complex $[(TBC)_2AgOSO_2CF_3]$ (**18**) is formed [42].



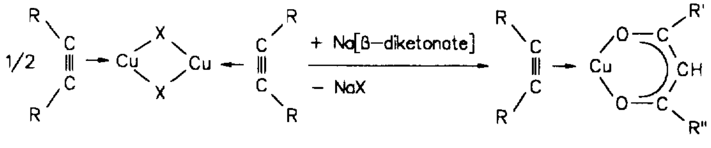
18

Compound **18** is the first example of a 12-membered macrocyclic sandwich complex [42]. A single X-ray diffraction study of **18** (Table 7) shows that the asymmetric unit contains one $(TBC)_2Ag^+$ eclipsed sandwich together with one $(TBC)_2Ag^+$ staggered sandwich. The Ag—C distances in the eclipsed conformation range from 2.5 to 2.9 Å, whereas in the staggered conformation they are 2.7–2.8 Å. The much smaller range of the Ag—C interatomic distances in the latter indicate that in the staggered situation the six C_2 units are each donating 1.33 electrons, or that there is an electrostatic interaction [42]. In contrast, in the eclipsed conformation four of the six alkynes behave as a two-electron donor while two C_2 building blocks are non-interacting. Similar metal to ligand interactions are found in ruthenium and rhodium bis(arene) complexes [50–52].

2.4.2. *Type* **E** *molecules, (η^2-RC≡CR)Cu^{I}X*

2.4.2.1. Synthesis. As shown in Section 2.3, polymeric $\{Me_2Si(C{\equiv}CSiMe_3)_2(CuX)_2\}_n$ (**11a**, X = Cl; **11b**, X = Br) reacts with Na[acac] to form the monomeric compound $[Me_2Si(C{\equiv}CSiMe_3)_2][Cu(acac)]_2$ (**14**) [13,30].

Using similar reaction conditions, the dimeric complexes $[(\eta^2\text{-}RC{\equiv}CR)CuX]_2$ (X = Cl, Br) (type **A** molecules) can be cleaved by β-diketonates to afford the monomeric (η^2-RC≡CR)Cu(β-diketonate) compounds **19** in high yields [13,14,53–55].



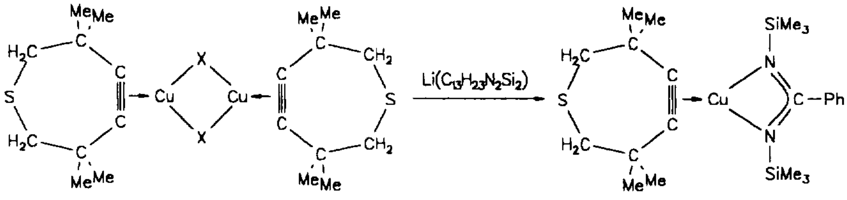
19

19a: R = $SiMe_3$, R' = R'' = Me
19b: R = Ph, R' = R'' = CF_3
19c: R = $SiMe_3$, R' = R'' = CF_3
19d: R = Me, R' = R'' = CF_3
19e: R = $SiMe_3$, R' = ^{t}Bu, R'' = $(CF_2)_2CF_3$
19f: R = Me, R' = ^{t}Bu, R'' = $(CF_2)_2CF_3$

The spectroscopic data for compounds **19a**–**19f** are consistent with chelation of the β-diketonate ligand through both oxygens to the copper atom (Section 2.4.2.2).

Recently, it was found that compounds **19** deposit copper films by chemical vapour deposition (CVD) through a thermally induced disproportionation reaction that generates Cu^0, Cu^{II}(β-diketonate)$_2$ and RC≡CR [13,14,53,55].

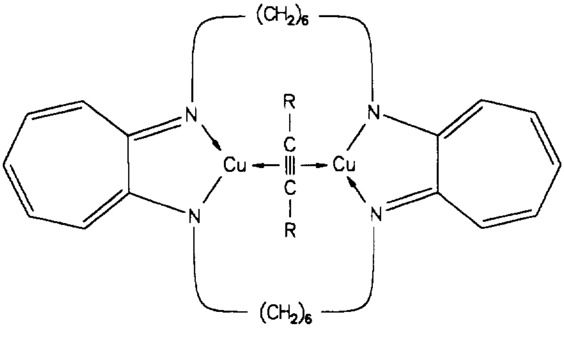
Further, Olbrich et al. [18] have shown that dimeric $[(\eta^2\text{-tmtch})CuCl]_2$ (**2j**) (tmtch = 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne) reacts with lithium *N,N'*-bis(trimethylsilylbenzaminidate) to yield the monomeric compound **20** [18].



2j **20**

Compound **20** is monomeric in the solid state and the copper atom possesses a trigonal planar environment, where the nitrogen atoms of the $PhC(NSiMe_3)_2$ ligand and the C_2 unit of the tmtch group are considered to occupy the three coordination sites (see Table 7) [18].

However, using the dimetallated macrocyclic tropocoronand-6,6 instead of $Li[PhC(NSiMe_3)_2]$, the alkyne-bridged dicopper(I) complexes **21a–21d** can be isolated in moderate yields [27,28].



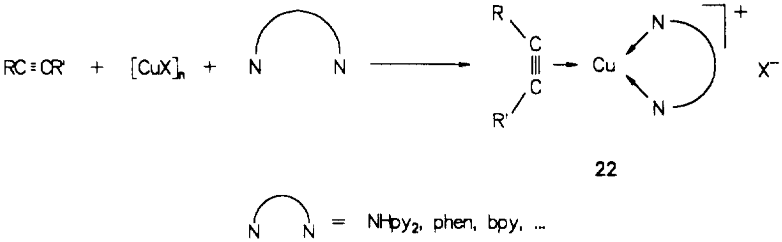
21a: R = Me
21b: R = Ph
21c: R = CO_2Me
21d: R = CO_2Et

21

There are three routes for the synthesis of complexes **21**: two methods employing labile copper(I) acetonitrile or carbon monoxide intermediates, and a third route in which the formation of complex **21** was achieved by generating the dicopper(I) tropocoronand unit in the presence of an excess of RC≡CR [27,28].

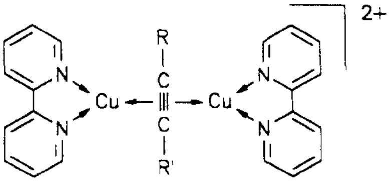
The structures in the solid state of compounds **21c** and **21d** have been determined by X-ray diffraction (see Table 7) [27,28]. It was found that the C≡C triple bond lengths of the RC≡CR groups are 1.314 Å (**21c**) and 1.320 Å (**21d**), substantially longer than the values found in other copper(I) alkyne complexes (see above). These larger C≡C distances are consistent with the bridging alkyne unit RC≡CR serving as a four-electron donor. Similar C≡C bond lengths were found in complexes of the type $(\eta^2\text{-RC}{\equiv}\text{CR})Co_2(CO)_6$ [56–60].

Complexes of type **E** are also formed by the addition of bidentate neutral chelating ligands such as 1,10-phenanthroline, 2,2′-bipyridine or di-2-pyridylamine to $[Cu^IX]_n$ ($X = BF_4$, ClO_4, PF_6, SbF_6) compounds in the presence of an excess of RC≡CR′ (Table 6) [44–47].



22

Reger and Huff [47] showed that compounds $\{(\eta^2\text{-RC}{\equiv}\text{CR}')[\text{Cu(bpy)}]_2\}X_2$ (**23**) can be isolated by repeated precipitation from solutions which initially contain $[(\eta^2\text{-RC}{\equiv}\text{CR}')\text{Cu(bpy)}]X$ (**22q**–**22s**) (bpy = 2,2′-bipyridine) and no additional RC≡CR′ (Table 6).



23

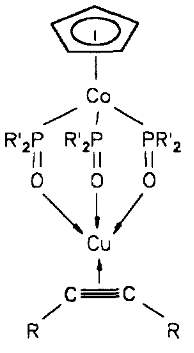
Whereas in compounds **22** the C_2 unit of the alkyne is η^2-coordinated to one copper atom in complexes **23** the C_2 building block is π-bonded to two (bpy)Cu fragments. The bonding situation in compounds **23** is similar to that found in the alkyne-bridged dicopper(I) complexes of tropocoronand-6,6 [27,28].

Table 6
Compounds **22** and **23**

Compound	RC≡CR′		X	NN[a]	Ref.
	R	R′			
22a	H	H	BF_4	$NHpy_2$	[44,45]
22b	H	H	ClO_4	phen	[46]
22c	H	Ph	ClO_4	phen	[46]
22d	H	CO_2Et	ClO_4	phen	[46]
22e	H	OEt	ClO_4	phen	[46]
22f	H	n-C_7H_{15}	ClO_4	phen	[46]
22g	Ph	Ph	ClO_4	phen	[46]
22h	CO_2Me	CO_2Me	ClO_4	phen	[46]
22i	H	Ph	ClO_4	5-NO_2-phen	[46]
22j	H	Ph	ClO_4	5-Cl-phen	[46]
22k	H	Ph	ClO_4	5-Me-phen	[46]
22l	H	Ph	ClO_4	5,6-Me_2phen	[46]
22m	Et	Et	PF_6	bpy	[47]
22n	H	^{n}Pr	PF_6	bpy	[47]
22o	Me	CO_2Me	PF_6	bpy	[47]
22p	Ph	Ph	PF_6	bpy	[47]
22q	CO_2Et	CO_2Et	PF_6	bpy	[47]
22r	H	Ph	SbF_6	bpy	[47]
22s	CO_2Et	CO_2Et	SbF_6	Me_2bpy	[47]
23a	CO_2Et	CO_2Et	PF_6	bpy	[47]
23b	CO_2Et	CO_2Et	SbF_6	Me_2bpy	[47]
23c	H	Ph	SbF_6	bpy	[47]

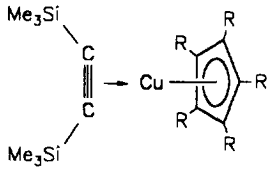
[a] $NHpy_2$ = 2-pyridylamine; phen = 1,10-phenanthroline; bpy = 2,2′-bipyridine.

In compounds **19**–**23** a bidentate chelating ligand is used for the stabilization of monomeric η^2-alkyne copper(I) moieties. In addition, the tris-chelating oxygen ligand $\{(\eta^5\text{-}C_5H_5)Co[P(O)R'_2]_3\}^-$ (R′ = OMe, O^{i}Pr) reacts with $[Cu(CH_3CN)_4]PF_6$ and RC≡CR (R = Ph, CO_2Me) to yield the η^2-alkyne copper(I) complexes of composition $(\eta^2\text{-}RC{\equiv}CR)Cu\{(\eta^5\text{-}C_5H_5)Co[P(O)R'_2]_3\}$ (**24a**, R = Ph, R′ = O^{i}Pr; **24b**, R = CO_2Me, R′ = OMe), as shown by Lenders and Kläui [48]. The η^2-bonded RC≡CR ligand in **24** can be easily exchanged by carbon monoxide and alkenes [48].

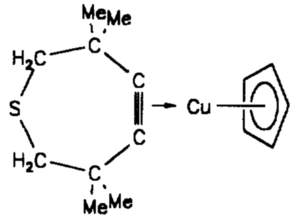


24

Another type of a monomeric η^2-alkyne copper(I) compound can be obtained by the nucleophilic cleavage of dimeric type **A** molecules. Thus, the reaction of $[(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)CuCl]_2$ (**2a**) and $[(\eta^2\text{-}tmtch)CuCl]_2$ (**2j**) with $Li[C_5R_5]$ (R = H, CH_3) leads to the formation of monomeric **25a**–**25c** [6,18,49].



25a: R = H
25b: R = Me

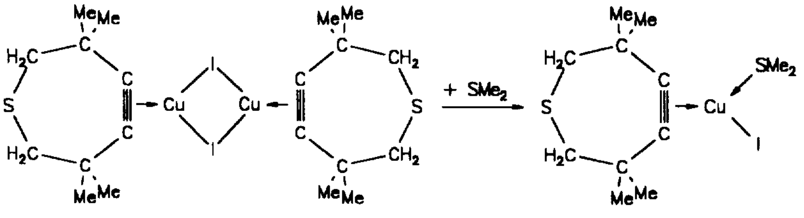


25c

The species **25a**–**c** represent the first "mixed sandwich" compounds of copper(I), as members of a long isoelectronic series in which $(\eta^5\text{-}C_5R_5)M$ building blocks interact with 2–5-electron donor ligands [6].

With the Lewis base SMe_2, the breakdown of the dimeric structure of $[(\eta^2\text{-}tmtch)CuI]_2$ (**21**) could be induced, forming the monomeric base-stabilized compound $[(\eta^2\text{-}tmtch)Cu(I)SMe_2]$ (**26**) [11].

Compound **26** is the first example of a type **E** molecule in which the η^2-alkyne copper(I) moiety is not stabilized by a bi- or tridentate chelating ligand.



21

26

2.4.2.2. *Spectroscopy and bonding.* As already pointed out in Section 2.1.3, the most remarkable feature in the IR spectra of the η^2-alkyne copper(I) complexes **16**–**26** is that these compounds all exhibit a significant $\nu(C{\equiv}C)$ absorption band shifted to lower wavenumbers than the corresponding $\nu(C{\equiv}C)$ vibration in the free acetylenes $RC{\equiv}CR'$ [4–21,24–49,53–55]. This phenomenon is typical of $C{\equiv}C$ triple bonds η^2-coordinated to transition metal centres [34,58–60].

In compounds **21** and **23**, the C_2 unit of the alkyne ligands is η^2-coordinated to two copper(I) centres, thus acting as a four-electron donor. Hence the $\nu(C{\equiv}C)$ vibration is shifted to lower wavenumbers (1630–1750 cm^{-1}) as compared with compounds **16**–**20**, **22** and **24**–**26** (1700–2000 cm^{-1}) in which the C_2 unit acts as a two-electron donor. This is consistent with the lengthening of the $C{\equiv}C$ triple bond of the alkyne ligands from 1.20–1.25 Å in compounds **16**–**20**, **22** and **24**–**26** to ~1.32 Å in compounds **21** and **23** (Fig. 4, Table 7).

Some selected examples of compounds **16**–**26** are shown in Fig. 4.

Fig. 4 shows that compounds of type **E** are monomeric. The copper atoms possess essentially a trigonal planar environment. As a result of the η^2-coordination of the alkyne ligands to copper(I), the $R{-}C{\equiv}C{-}R'$ units are distorted compared with the free situation in which they are almost linear (Table 7) [11,18,27,28,41,43–46].

3. Organometallic substituted η^2-alkyne copper(I) and silver(I) compounds

As shown in Section 2, alkynes ($RC{\equiv}CR'$), 1,4-diynes ($RC{\equiv}C{-}E{-}C{\equiv}CR$; E = main-group element building blocks such as $SiMe_2$) and cyclic triynes (TBC) can be used for the breakdown of polymeric $[Cu^IX]_n$ compounds to discrete $[Cu^IX]_x$ (x = 1–4) aggregates. However, the application of organometallic substituted acetylides $L_nM{-}C{\equiv}CR$ or organometallic bridged 1,4-diynes $RC{\equiv}C{-}ML_n{-}C{\equiv}CR$ (R = singly bonded organic ligand; ML_n = organometallic building block) afford other coordination modes, i.e. type **G**–**K** molecules.

As shown schematically in Scheme 3, cluster **G** contains as substructures type **H**, **J** and **K** molecules (routes (a)). Structural type **H** molecules can formally be broken down in to type **I** or **J**-molecules (route (b)). The reversion/re-building of this breakdown is the formation of a type **A** molecule from two structural type **K** compounds (route (c)).

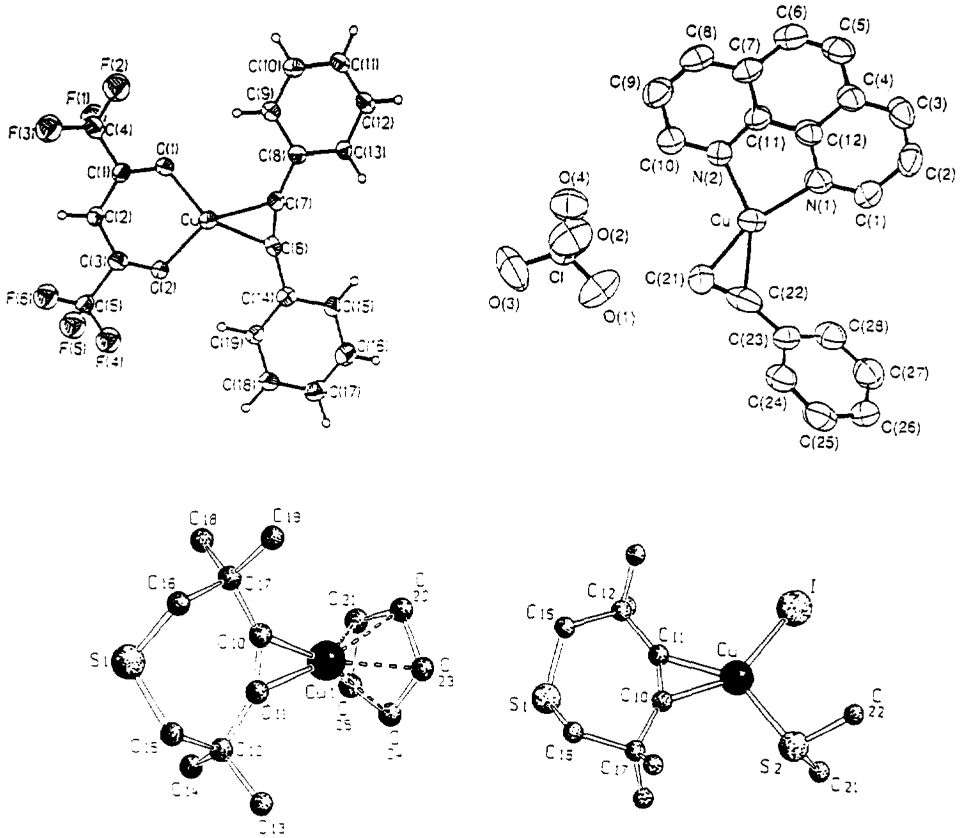


Fig. 4. Selected X-ray structures of type **E** molecules. The interatomic bond distances and angles are given in Table 7.

This Section describes the synthesis and reactivity of all compounds of these structural types.

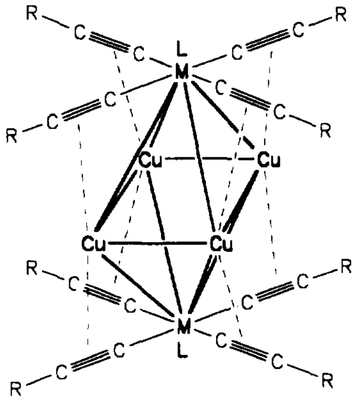
3.1. *Type* **G** *molecules,* $M_2M^I_4(C{\equiv}CR)_8(PPh_3)_2$ *(M = Ir, Rh, Pt; M^I = Cu, Ag)*

The reaction of Vaska's complex *trans*-$(PPh_3)_2(CO)IrCl$ (**27a**) or $(PPh)_3RhCl$ (**27b**) with $[M^IC{\equiv}CR]_n$ yields $\{[(PPh_3)_2(RC{\equiv}C)_2]M[(\eta^2\text{-}C{\equiv}CR)_2\}M^I[PPh_3]$ (M = Ir, M^I = Cu; M = Rh, M^I = Ag) (type **I** molecules; see Section 3.3) as byproducts, together with the hexanuclear clusters $M_2M^I_4(C{\equiv}CR)_8(PPh_3)_2$ (**28**) (M = Ir, Rh; M^I = Cu, Ag) of type **G** [61–66].

In clusters of type **G** the six metal atoms (four Cu (Ag) and two Ir or Rh atoms) define an octahedron in which each iridium or rhodium atom is bonded apically to a phosphine ligand PR_3. Four $RC{\equiv}C$ ligands are σ-bonded to each iridium or rhodium atom, and two $RC{\equiv}C$ ligands (one from each Ir, Rh) form a π linkage with one of the four equatorial copper or silver atoms on the octahedron meridian.

Table 7
X-ray data for compounds **16**, **17**, **19**–**22**, **25** and **26**

Compound	Ref.	Cu–X (Å)	Cu←||| (Å)	C≡C (Å)	X–Cu–X (°)	C≡C–R (°)
16	[41]	2.549(5)	2.060(4)	1.22(1)	–	177.8(6)
17	[43]	1.955(5)–2.006(5)	1.991(8)–2.001(7)		94.4(3)–101.5(3)	163.0(8)–166.0(8)
19b	[54]	1.969(6)	1.959(8)	1.25(1)	93.8(2)	158.4(8)
		1.954(6)	1.956(8)			160.4(8)
20	[18]	2.004(2)	1.928(2)	1.248(3)		146.0(2)
		2.019(2)	1.942(2)			144.3(2)
21c	[27,28]	1.912(5); 1.901(5)	1.946(7); 1.938(7)	1.314(9)	84.5(2)	139.0(7)
		1.910(6); 1.926(6)	1.935(7); 1.952(7)		84.1(2)	138.2(4)
21d	[27]	1.912(3); 1.907(3)	1.937(4); 1.955(4)	1.320(6)	83.7(2)	138.7(4)
		1.907(3); 1.910(3)	1.961(4); 1.939(4)		84.0(2)	136.9(4)
22a	[44,45]	1.968(3)	1.971(4)	1.19(1)	96.8(2)	–
22b	[46]	1.979(4); 1.978(4)	1.930(5); 1.961(5)	1.190(7)	84.9(2)	–
22c	[46]	1.997(8); 2.000(7)	1.92(1); 1.99(1)	1.22(1)	85.3(3)	163(1)
22d	[46]	1.978(6); 1.977(6)	1.925(9); 1.934(7)	1.19(1)	84.5(2)	154.7(8)
25c	[18]	2.247(3); 2.168(2)	1.954(3); 1.937(2)	1.236(4)		148.1(2)
		2.251(3); 2.180(2)				146.4(2)
		2.169(3)				
26	[11]	2.508(1) (Cu–I)	1.975(6); 1.971(6)	1.241(8)	107.1(1)	148.9(6)
		2.278(2) (Cu–S)				147.0(6)



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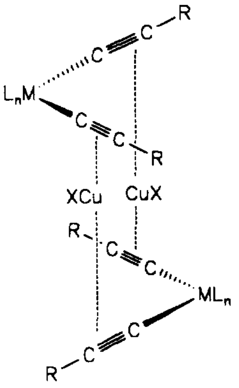

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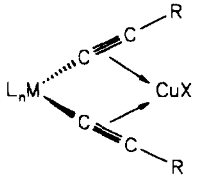
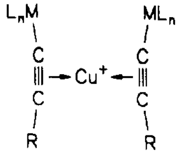


I



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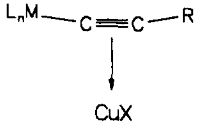


K

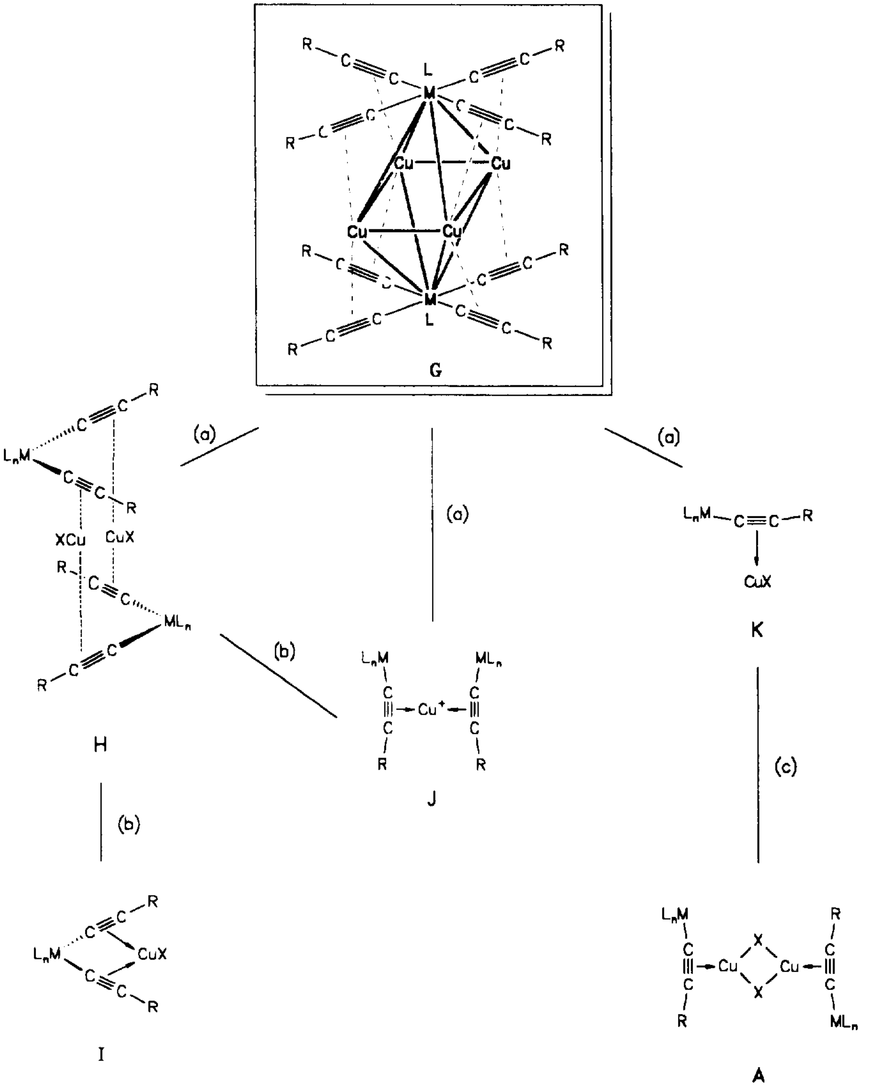
Complexes **28**, i.e. clusters of type **G**, can be prepared in good yields by the nucleophilic substitution of the transition metal halides *trans*-$(PPh_2R)_2(CO)MCl$ (**27a**, M = Ir, R = Ph; **27c**, M = Ir, R = Me; **27d**, M = Rh, R = Me; **27e**, M = Rh, R = Ph), $(PPh_3)_3RhCl$ (**27b**) or $(tht)_2PtCl_2$ (tht = tetrahydrothiophene) (**27f**) with $[M^IC{\equiv}CR]_n$ (M^I = Cu, Ag) (Table 8) [61–66].

Conspicuous in this method of synthesis is that the yields of clusters **28** decrease on changing from iridium to rhodium and from copper to silver. The clusters **28g**–**28n**, **28s** and **28t** (Table 8), containing rhodium, are apparently less stable than the corresponding iridium clusters. The lower stability of the rhodium clusters gives rise to acetylide couplings of two $RC{\equiv}C$ ligands, generating symmetrically substituted 1,3-diynes [61–66]. It is possible to replace the PPh_3 ligand with PPh_2Me in order to increase the solubility of clusters **28** (Table 8).

The hexanuclear clusters $Ir_2Cu_4(PPh_3)_2(C{\equiv}CR)_8$ (**28a**, R = Ph; **28b**, R = 4-MeC_6H_4) react with $Fe_2(CO)_9$ in benzene to yield the octanuclear clusters $Ir_2Cu_4Fe_2(C{\equiv}CR)_8(PPh_3)_2(CO)_8$ (**29a**, R = Ph; **29b**, R = 4-MeC_6H_4) [64,65]. In **29** the Ir_2Cu_4 skeleton is retained. A possible coordination mode of **29** is shown.

By the reaction of **27b** with $[M^IC{\equiv}CC_6F_5]_n$ (M^I = Ag) two further products, $\{[(PPh_3)_2(C_6F_5C{\equiv}C)_2]Rh(\eta^2\text{-}C{\equiv}CC_6F_5)_2\}Ag(PPh_3)$ **39e** (type **I** molecule; see Section 3.3) and the trinuclear compound $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ (**30**), are formed [61,63–65].

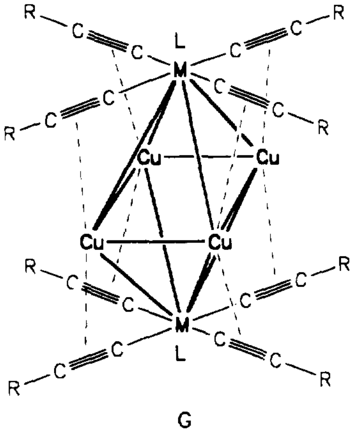
The synthesis and reactivity of compound **39e** is described in Section 3.3.



Scheme 3. Substructural features of cluster **G**.

The structures of the heteronuclear clusters $M_2M^1_4(C{\equiv}CR)_8(PPh_3)_2$ (M = Ir, Rh; M^1 = Cu, Ag) (**28**) and $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ (**30**) were established by X-ray diffraction studies (Fig. 5) [61,63–65].

The four copper and two iridium atoms in **28a** form a distorted octahedron with the four copper atoms taking equatorial positions. Each iridium atom is surrounded by an apically bonded PPh_3 group and four coplanar σ-bonded $RC{\equiv}C$ ligands. It is also found that each acetylenic fragment simultaneously participates in an asymmetric π interaction with a copper atom on the octahedral meridian. Thus, each



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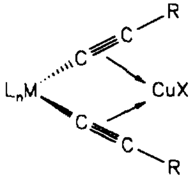


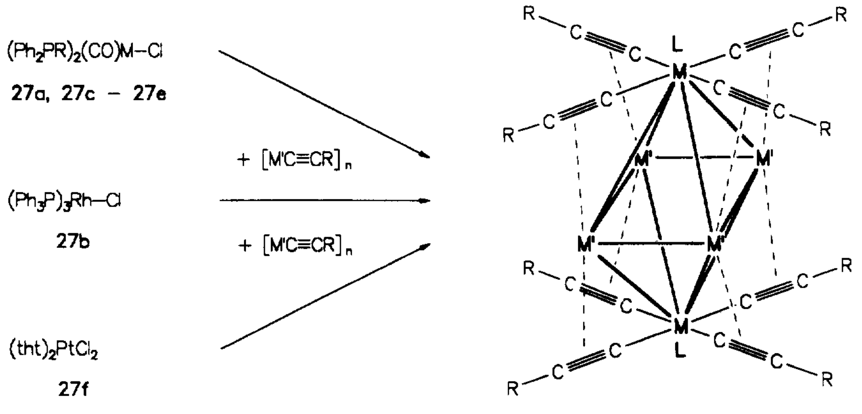
I

Table 8
Clusters **28**

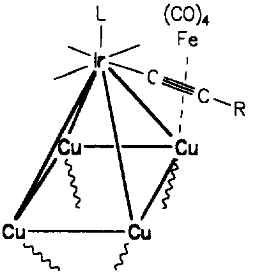
Compound	ML	M^I	R	Ref.
28a	Ir(PPh$_3$)	Cu	Ph	[61,62,64]
28b	Ir(PPh$_3$)	Cu	4-MeC$_6$H$_4$	[64]
28c	Ir(PPh$_3$)	Cu	4-FC$_6$H$_4$	[64]
28d	Ir(PPh$_3$)	Cu	C$_6$F$_5$	[64]
28e	Ir(PPh$_2$Me)	Cu	Ph	[64]
28f	Ir(PPh$_2$Me)	Cu	C$_6$F$_5$	[64]
28g	Rh(PPh$_3$)	Cu	Ph	[64]
28h	Rh(PPh$_3$)	Cu	4-MeC$_6$H$_4$	[64]
28i	Rh(PPh$_3$)	Cu	4-FC$_6$H$_4$	[64]
28j	Rh(PPh$_3$)	Cu	C$_6$F$_5$	[64]
28k	Rh(PPh$_2$Me)	Cu	C$_6$H$_5$	[64]
28l	Rh(PPh$_2$Me)	Cu	4-MeC$_6$H$_4$	[64]
28m	Rh(PPh$_2$Me)	Cu	4-FC$_6$H$_4$	[64]
28n	Rh(PPh$_2$Me)	Cu	C$_6$F$_5$	[64]
28o	Pt	Cu	Ph	[66]
28p	Pt	Cu	^{t}Bu	[66]
28q	Ir(PPh$_3$)	Ag	Ph	[65]
28r	Ir(PPh$_3$)	Ag	C$_6$F$_5$	[65]
28s	Rh(PPh$_3$)	Ag	Ph	[63,65]
28t	Rh(PPh$_3$)	Ag	C$_6$F$_5$	[63,65]
28u	Pt	Ag	Ph	[66]
28v	Pt	Ag	^{t}Bu	[66]
28w	Pt	Au	^{t}Bu	[66]

copper atom is π-bonded to two acetylenic ligands, one below and one above the equatorial Cu_4 plane.

As a result of the η^2-coordination of the alkynyl units to a copper atom, the $C{\equiv}C$ triple bonds of the $RC{\equiv}C$ building blocks are lengthened from approximately 1.20 Å in $L_nMC{\equiv}CR$ compounds to 1.23 Å in **28a**. This fits to the IR spectroscopically



28



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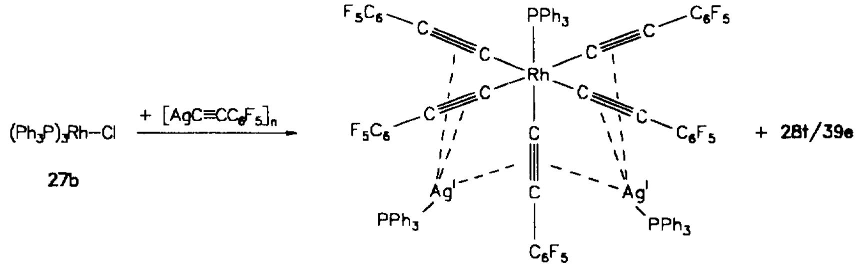


made observation that all clusters **28** show absorption bands due to $\nu(C\equiv C)$ vibrations in the 2000 cm^{-1} region [61–66].

The formal oxidation states of the metal atoms in the heteronuclear clusters **28** are Ir^{IV}/Rh^{IV} combined with Cu^0/Ag^0, hence these clusters are electron rich, containing six electrons more than required to fill the metal bonding and non-bonding orbitals. These six electrons are assumed to be located in metal–metal antibonding orbitals, thus giving an overall bond order of 3/4 [61–67].

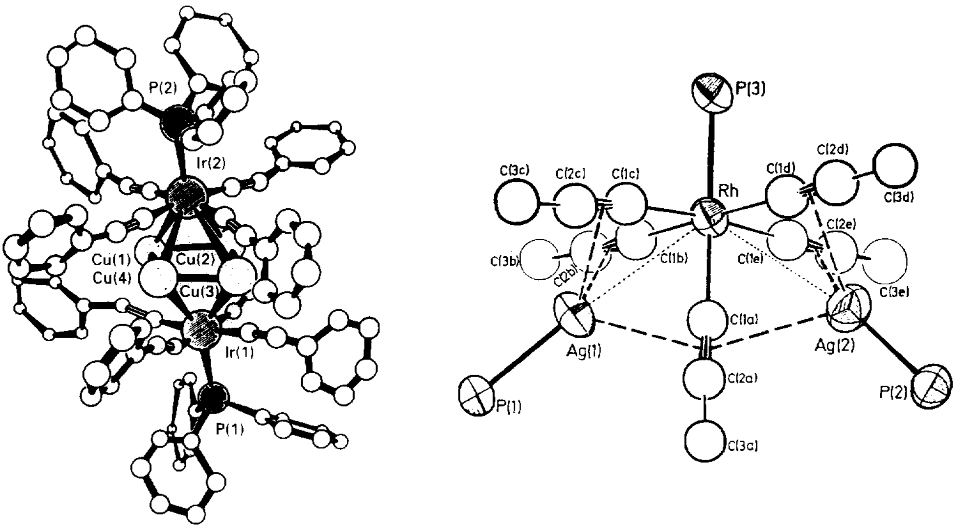


Fig. 5. Molecular geometry and atom labelling scheme for **28a** (left) and **30** (right) [61,63–65]. Selected bond distances (Å) and angles (°) are as follows. **28a**: Ir—Cu (av. (average)) 2.87(5), Cu—Cu (av.) 2.74(7), Ir—P (av.) 2.26(1), Ir—C (av.) 2.04(4), Cu—C_α (av.) 1.99(4), Cu—C_β (av.) 2.19(4), C≡C (av.) 1.23(5); C_α—Ir—C_α (av.) 89.6(1), Ir—C_α—C_β (av.) 170(4), C≡C—Ph (av.) 165(3). **30**: Rh—Ag1 3.1021(8), Rh—Ag2 3.0871(8), Ag1—Ag2 5.087(1), Rh—C_α (av.) 2.02, C≡C (av.) 1.21(8), Ag1—C≡C(A) 2.642, Ag1—C≡C(B) 2.572, Ag1—C≡C(C) 2.534, Ag2—C≡C(A) 2.822, Ag2—C≡C(D) 2.751, Ag2—C≡C(E) 2.396; P3—Rh—C1A 173.8, C_α—Rh—C_α (av.) 89.6, C≡C(A)—Ag1—C≡C(B) 93.75, C≡C(B)—Ag1—C≡C(C) 89.79, C≡C(C)—Ag1—C≡C(A) 83.30, C≡C(A)—Ag2—C≡C(D) 81.77, C≡C(D)—Ag2—C≡C(E) 89.40, C≡C(E)—Ag2—C≡C(A) 94.20.

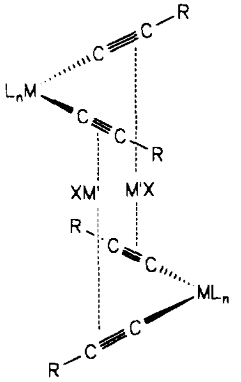
According to Fig. 5, the trinuclear complex $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ (**30**) prepared from $(Ph_3P)_3RhCl$ (**27b**) and $[AgC{\equiv}CC_6F_5]_n$ contains a central rhodium atom, which is octahedrally coordinated by one PPh_3 ligand (apical position) and five σ-bonded alkynyl moieties [61,63–65]. Three alkynyls are η^2-coordinated to an $Ag[PPh_3]$ building block, one being involved with both silver atoms.

The rhodium–silver distances of 3.1021(8) and 3.0871(8) Å in **30** are considerably larger than those expected for rhodium–silver single bonds (2.79 Å) [61,67]. In the absence of a metal–metal bond, the metal atoms appear to be present in their most common oxidation states, i.e. Rh^{III} and Ag^{I}. Thus, the rhodium atom shows its expected regular octahedral coordination geometry and the silver atoms are tetrahedrally coordinated. Consequently, it seems that the compound $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ (**30**) is zwitterionic, consisting of a $[(Ph_3P)Rh^{III}(C{\equiv}CC_6F_5)_5]^{2-}$ unit and two $[(Ph_3P)Ag^{I}]^+$ moieties. These components are kept together by η^2-coordination of the alkynyl units to $[Ag(PPh_3)]^+$ building blocks.

3.2. *Type **H** molecules, $\{[L_nM(C{\equiv}CR)_2]M^IX\}_2$*

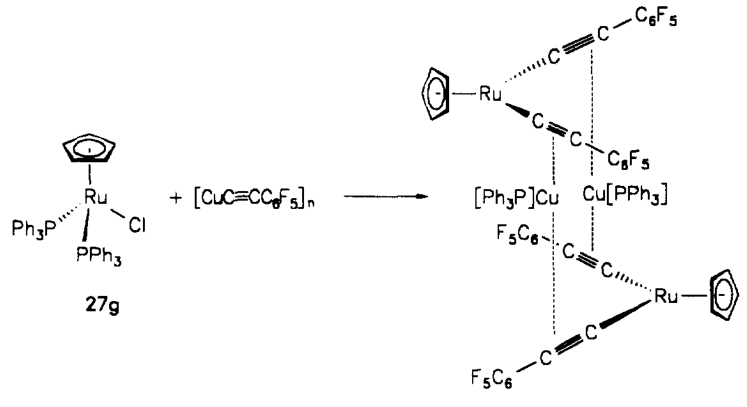
Another common feature of complexes isolated from reactions involving transition metal halides L_nMCl and copper(I) or silver(I) acetylides $[M^IC{\equiv}CR]_n$ (M = Cu, Ag) (Section 3.1) are molecules of structural type **H**.

Type **H** molecules can be considered as substructures of clusters **28** (type **G** molecules, Section 3.1) in which the two bis(alkynyl) complex fragments $L_nM(C{\equiv}CR)_2$ are bridged by two M^IX ($M = Cu$, Ag) building blocks.



H

A procedure for the synthesis of a type **H** molecule containing ruthenium and copper as metal atoms is given by the reaction of $(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCl$ (**27g**) with $[CuC{\equiv}CC_6F_5]_n$ [68].



27g

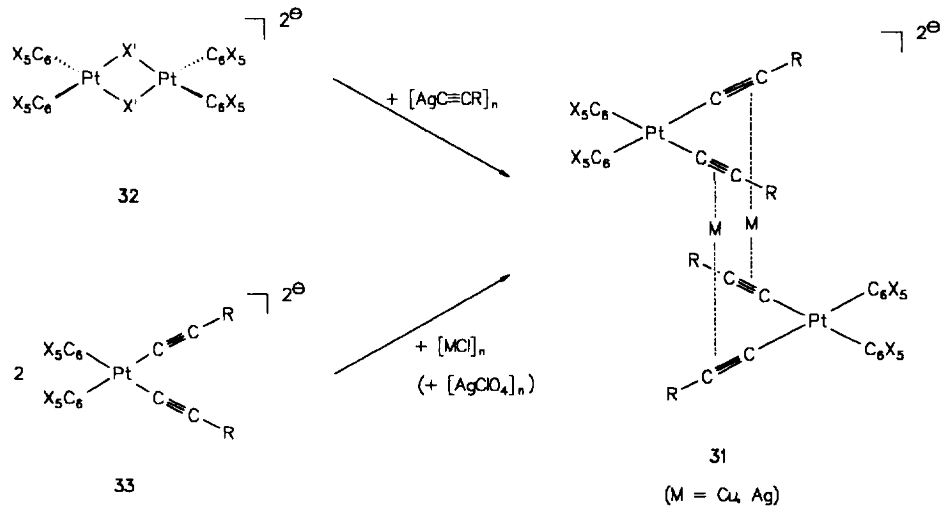
31

Another route to structural type **H** molecules is the reaction of the square-planar d^8 platinum (Pt^{II}) compounds $A_2[Pt_2(\mu\text{-}X')_2(C_6X_5)_4]$ (**32**) ($A = NBu_4$, $PMePh_3$; $X' = Cl$, I; $X = F$, Cl) with $[AgC{\equiv}CR]_n$ ($R = Ph$, ${}^tBu$) [69,70].

Compounds **31a**–**31g** can also be synthesized by treatment of $A_2[cis\text{-}(C_6X_5)_2Pt(C{\equiv}CR)_2]$ (**33**) ($A = NBu_4$, $PMePh_3$; $R = Ph$, ${}^tBu$; $X = F$, Cl) with $[Cu^ICl]_n$, $[Ag^ICl]_n$ or $[Ag^IClO_4]_n$ [70].

All compounds synthesized by these methods are listed in Table 9.

The most remarkable feature in the IR spectra of compounds **31a**–**31g** is that they



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31

(M = Cu, Ag)

Table 9
Compounds **31a**–**31g** [70]

Compound	M	X	R	A
31a	Ag	F	Ph	NBu$_4$
31b	Ag	F	^{t}Bu	NBu$_4$
31c	Ag	Cl	Ph	NBu$_4$
31d	Ag	Cl	^{t}Bu	NBu$_4$
31e	Ag	F	Ph	PMePh$_3$
31f	Cu	F	Ph	PMePh$_3$
31g	Cu	F	^{t}Bu	NBu$_4$

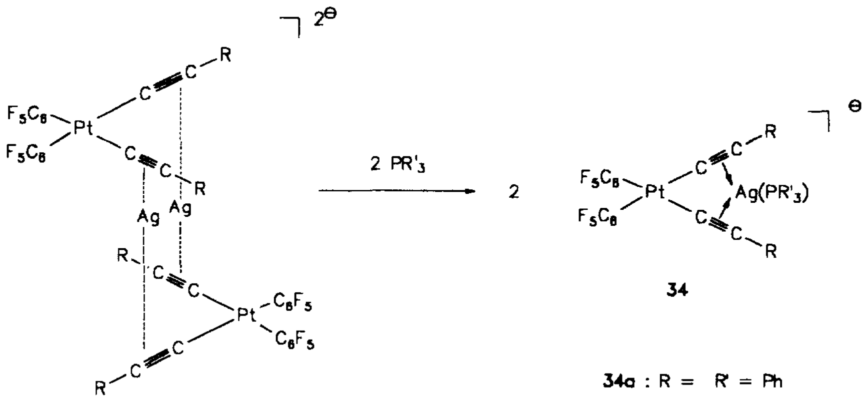
all exhibit a $\nu(C{\equiv}C)$ absorption band in the 2035–2000 cm^{-1} region [70]. This is typical for C≡C triple bonds η^2-coordinated to a copper(I) or silver(I) fragment (see above).

The X-ray crystal structure analysis which was carried out on representative compound **31a** shows that two square-planar platinum building blocks, *cis*-$(C_6F_5)_2Pt(C{\equiv}CPh)_2$, are linked together by two silver atoms. The C_2 units of the phenylethynyl ligands are η^2-coordinated to the silver atoms in such a way that these two PhC≡C ligands are asymmetrically π-bonded to each silver atom.

As a consequence of the η^2-coordination of the PhC≡C group to silver, the alkynyl ligands are not linear (Pt–C≡C, 176.3°, 176.6°; C≡C–Ph, 173.4°, 172.8°) [70]. The C_2 units, associated with each silver atom, are oriented perpendicular to one another. The Pt···Ag distances of 3.10 and 3.15 Å are consistent with the absence of bonding character. Furthermore, the Ag···Ag distance of 2.939 Å is at the high end of the range observed for silver–silver systems (2.740–3.085 Å) [71].

Molecules of structural type **H** can be considered as dimeric species of type **I** molecules (for a detailed discussion of structural type **I** molecules, see Section 3.3).

Thus, the anionic tetranuclear platinum–silver compounds **31a** and **31b** react with PR'_3 ($R' = Ph$, Et) to give the anionic platinum–silver compounds **34** in which the alkynyl groups act as σ,π bridges between platinum and silver atoms [69].



31a, b

34

34a : R = R' = Ph

34b : R = Ph; R' = Et

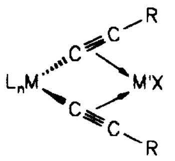
34c : R = ^{t}Bu; R' = Ph

34d : R = ^{t}Bu; R' = Et

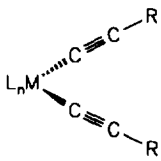
The structures of compounds **34** were established by a single-crystal diffraction study of **34a** [69]. The structure of complex **34a** reveals that the two metal atoms (platinum and silver) are asymmetrically bridged by two phenylethynyl groups, each of which forms a σ bond to platinum and a π bond to silver.

3.3. *Type **I** molecules, $\{L_nM(C{\equiv}CR)_2\}M^IX$ ($n^I = Cu$, Ag)*

In general, organometallic bis(σ-alkynyl) compounds of type **L** can be used for the synthesis of binuclear complexes (type **I** molecules) containing σ,π-alkynyl ligands as bridging groups between two metal atoms.

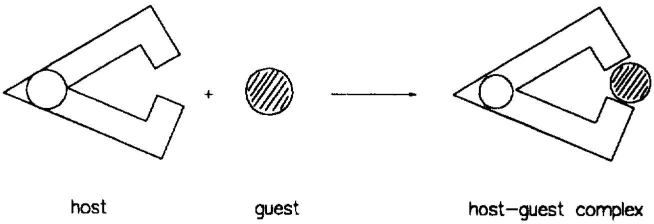


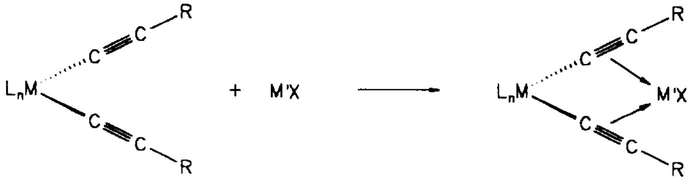
I



L

Compounds of type $RC{\equiv}C{-}L_nM{-}C{\equiv}CR$ ($L_nM = (\eta^5\text{-}C_5H_4R')_2Ti$, etc.) (**L**) can be considered as organometallic π tweezers [34,72,73]. In compounds of type **I**, the $RC{\equiv}C{-}L_nM{-}C{\equiv}CR$ fragments act as host molecules with the M^IX ($M = Cu$, Ag) building blocks as guests. The aim is to use simultaneously the steric stabilization of the organic groups R and the chelating effect of type **L** compounds for the preparation of stable type **I** molecules.



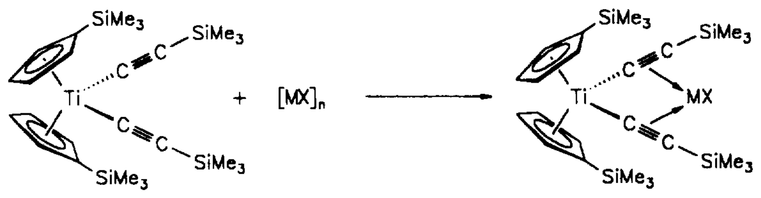


L I

3.3.1. Synthesis

There are three general routes for the synthesis of type **I** molecules: (a) direct synthesis from complexes of type **L**, (b) nucleophilic substitution of $L_nM(PPh_3)Cl$ and $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Cu^IX$ (X = Cl, OSO_2CF_3) compounds and (c) breakdown of dimeric complexes $(NBu_4)_2[Pt_2Ag_2(C{\equiv}CR)_4(C_6F_5)_4]$ under the influence of Lewis bases.

(a) Direct synthesis route. The bis(alkynyl) titanocenes $Me_3SiC{\equiv}C{-}L_2Ti{-}C{\equiv}CSiMe_3$ ($L = \eta^5\text{-}C_5H_4SiMe_3$) (**35**) [74] have been used as organometallic chelating ligands (organometallic π tweezers) for the synthesis of $\{L_2Ti(C{\equiv}CSiMe_3)_2\}M^IX$ compounds (**36**, M^I = Cu; **37**, M^I = Ag; X = singly bonded ligand) (Table 10) [13,25,30,34–40]. They are best synthesized using the appropriate $[M^IX]_n$ starting materials at 25 °C in thf or Et_2O (Table 10).



35

36: M = Cu
37: M = Ag

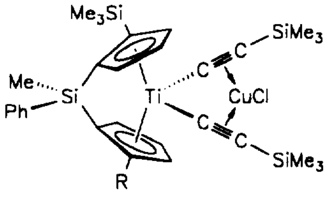
In a similar manner, ansa-[bis(alkynyl)] titanocenes react with $[CuCl]_n$ to yield the binuclear complexes **38a**–**38c** [75].

In general, the chelate effect of type **L** compounds, $RC{\equiv}C{-}L_nM{-}C{\equiv}CR$ [76], is suitable for stabilizing low-valent M(CO), $M[PR_3]$ (M = Ni [77–79], Co [79,80],

Table 10
Compounds $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}M^IX$ (**36**, **37**)

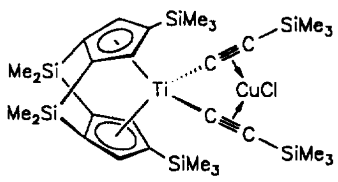
Compound	M^IX	Ref.	Compound	M^IX	Ref.
36a	CuCl	[82,85]	**37a**	AgCl	[36]
36b	CuBr	[40,85]	**37b**	AgBr	[36]
36c	CuI	[40,85]	**37c**	AgI	[36]
36d	CuCN	[40,85]	**37d**	AgCN	[36]
36e	CuSCN	[40,85]	**37e**	AgSCN	[36]
36f	CuOC(O)Me	[13,14]	**37f**	$AgNO_2$	[36]
36g	CuOC(O)Ph	[13,14]	**37g**	$AgNO_3$	[36]
36h	$CuC{\equiv}CPh$	[37,40]	**37h**	$AgClO_4$	[36]
36i	$CuC{\equiv}CSiMe_3$	[37,40]	**37i**	$AgS_2C(NEt_2)$	[36]
36j	$CuC{\equiv}C^tBu$	[37,40]	**37j**	AgO_2CMe	[13,14]
36k	CuPh	[38]	**37k**	AgO_2CPh	[13,14]
36l	CuTol[a]	[38]	**37l**	AgMes[b]	[38]
36m	CuMes[b]	[38]	**37m**	AgOTf[d]	[38]
36n	$CuCH_2SiMe_3$	[86]	**37n**	$AgBF_4$	[13]
36o	CuSR[c]	[86]			
36p	CuOTf[d]	[38,40]			
36q	$CuBF_4$	[38,40]			
36r	$CuPF_6$	[38,40]			
36s	Cu(acac)	[13]			

[a] Tol = $4\text{-}MeC_6H_4$.
[b] Mes = $2,4,6\text{-}Me_3C_6H_2$.
[c] R = $2\text{-}Me_2NC_6H_4$.
[d] OTf = trifluoromethanesulphonate, OSO_2CF_3.



38a: R = H

38b: R = SiMe3



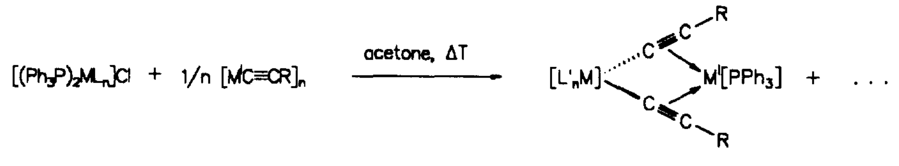
38c

Pt [81]) and $M(C_6F_5)_2$ (M = Pd, Pt) [69] moieties. In addition, the organometallic 1,4-diynes $RC{\equiv}C{-}L_nM{-}C{\equiv}CR$ can be used for the stabilization of monomeric MCl_2 (M = Fe, Co, Ni) [82,83] and Mg(Cl)(thf) [84] units.

(b) Nucleophilic substitution route. Compounds of type **I** are also formed by the reaction of $[(Ph_3P)_2ML_n]Cl$ (**27a**, $ML_n = Ir(CO)$ [64,65]; **27b**, $ML_n = Rh(PPh_3)$ [64,65]; **27h**, $ML_n = Re(CO)_3$ [87,88]; **27g**, $ML_n = Ru(\eta^5\text{-}C_5H_5)$ [87,88]) with $[M^IC{\equiv}CR]_n$ (M = Cu, Ag) (Table 11).

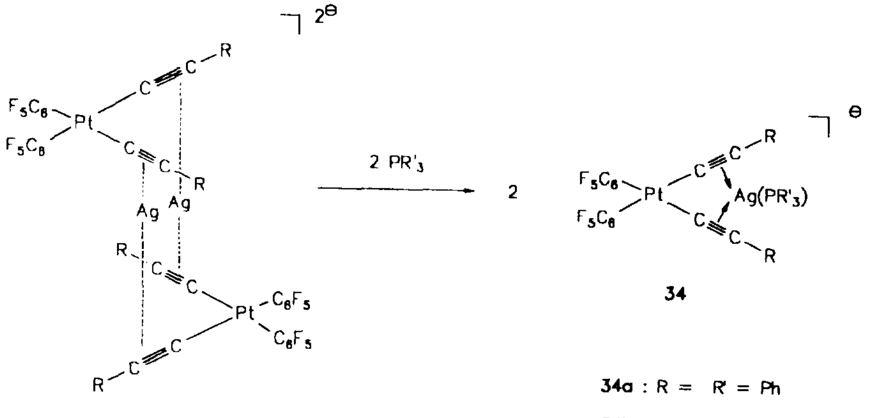
Table 11
Compounds **39**

Compound	$[ML'_n]$	R	M^I	Ref.
39a	$Re(CO)_3(PPh_3)$	C_6F_5	Cu	[87,88]
39b	$Ru(\eta^5\text{-}C_5H_5)$	$p\text{-}C_6H_4Me$	Cu	[87,88]
39c	$Ru(\eta^5\text{-}C_5H_5)$	$p\text{-}C_6H_4F$	Cu	[87,88]
39d	$Ir(PPh_3)_2(C{\equiv}CR)_2$	C_6F_5	Cu	[64,65]
39e	$Rh(PPh_3)_2(C{\equiv}CR)_2$	C_6F_5	Ag	[64,65]
39f	$Ir(PPh_3)_2(C{\equiv}CR)_2$	C_6F_5	Ag	[64,65]



27 **39**

(c) Breakdown of dimeric complexes with Lewis bases. Another route to type **I** molecules is given by the reaction of the tetranuclear platinum–silver complex $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ (**31a**, R = Ph; **31b**, R = ^tBu) with PR'_3 (R' = Ph, Et) [69]. The binuclear complexes **34** are formed in good yields (see also Section 3.2).



31a, b

34

34a : R = R' = Ph
34b : R = Ph; R' = Et
34c : R = ^{t}Bu; R' = Ph
34d : R = ^{t}Bu; R' = Et

In general, the organometallic 1,4-diynes $RC{\equiv}C{-}L_nM{-}C{\equiv}CR$ (L_nM = see above) can be used as organometallic chelating ligands for the stabilization of M^IX (M = Cu, Ag) units (Tables 10 and 11).

The binuclear compounds $\{L_nM(C{\equiv}CR)_2\}MX$ (**34** and **36**–**39**) are the first examples of stable molecules containing monomeric bis(η^2-alkyne)M^IX (M = Cu, Ag) species.

3.3.2. Spectroscopy and bonding

In binuclear compounds of type $\{L_nM(C{\equiv}CR)_2\}M^IX$ (**34** and **36–39**), the organometallic bis(alkynyl) building blocks $L_nM(C{\equiv}CR)_2$ [$L_nM = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$, $Re(CO)_3(PPh_3)$, $(\eta^5\text{-}C_5H_5)Ru$, $Ir(PPh_3)_2(C{\equiv}CC_6F_5)_2$, $Rh(PPh_3)_2(C{\equiv}CC_6F_5)_2$] act, through their alkynyl groups, as organometallic chelating ligands to the Cu^IX and Ag^IX entities. Spectroscopic data (IR, ^1H, ^{13}C NMR) of compounds **34** and **36–39** also indicate that both alkynyl ligands are η^2-coordinated to M^IX moieties (Table 12).

In the IR spectra, the $\nu(C{\equiv}C)$ absorption decreases from 2012 cm^{-1} in the parent compound $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$ (**35**) to 1850–1960 cm^{-1} in compounds **36** and **37** (Table 12). This is in agreement with the increasing participation of the backbonding component in alkyne to copper (silver) bonding.

As Table 12 shows, changing the monoanionic ligand X in $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}M^IX$ (M = Cu, **36**; M = Ag, **37**) from a weaker (e.g. $X = OSO_2CF_3$) to a stronger σ donor (e.g. $X = 2,4,6\text{-}Me_3C_6H_2$) increases the back-donation component of the η^2-alkyne–metal interaction in the total bonding. The reduction of the $Ti{-}C{\equiv}C$ and $C{\equiv}C{-}Si$ angles from 177/176.5° in the parent compound $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti\ (C{\equiv}CSiMe_3)_2$ (**35**) to 171.8/167° in **37m**, 166.6/162.9° in **37l**, 166.8/157.4° in **36p** and 163.7/155.5° in **36m** also supports this conclusion, i.e. bending of the substituents of the C_2 unit increases with increasing σ donation of the ligand X in $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}M^IX$. Further, it is found that

Table 12
Selected IR and $^{13}C\{^1H\}$ NMR data for compounds **35–37**

Compound	IR $\nu(C{\equiv}C)$ (cm^{-1})	$^{13}C\{^1H\}$ NMR $\delta C{\equiv}C$ (ppm)	Ref.
35	2012	C_β 135.4; C_α 172.5	[74]
36d	1901	C_β 132.8; C_α 173.6	[13,85]
36f	1901	C_β 132.4; C_α 170.9	[13,14]
36g	1903	–	[13,14]
36m	1856	C_β 125.0; C_α 201.8	[38]
36n	1930	C_β 125.4; C_α 202.9	[86]
36o	1897	C_β 120.5; C_α 180.4	[86]
36p	1923	C_β 140.2; C_α 162.2	[86]
36r	1934	C_β 136.2; C_α 163.2	[38,40]
37j	1944	C_β 137.5; C_α 155.8	[13,14]
37k	1951	C_β 137.4 (d, $J_{AgC} = 15$ Hz) C_α 156.3 (d, $J_{AgC} = 15$ Hz)	[13,14]
37l	1902	C_β 125.8 (d, $J_{AgC} = 7$ Hz) C_α 184.5 (d, $J_{AgC} = 3$ Hz)	[38]
37m	1956	C_β 144.8; C_α 151.8	[38]
37n	1948	C_β 127.2; C_α 149.3	[13]

the η^2-alkyne–copper bonding interaction is stronger than the corresponding η^2-alkyne–silver bonding interaction (Table 12) [38]: complexes **37** readily exchange silver(I) for copper(I) building blocks, thus forming compounds **36** [38].

The ^{1}H and ^{13}C{^{1}H} NMR spectra of compounds **36** and **37** remain essentially unchanged in the temperature range 200–317 K and the data are consistent with monomeric species in solution (as confirmed by molecular weight determinations in solution by cryoscopy).

The silver compound $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}AgMes$ (Mes = 2,4,6-$Me_3C_6H_2$) (**37l**) provides direct information concerning the Ag—C bonding of the η^1-bonded C_{ipso} atom of the mesityl unit. The C_{ipso} mesityl resonance is observed at 168.3 ppm as two doublets due to coupling with ^{107}Ag and ^{109}Ag: $^1J(^{107}\text{Ag}, ^{13}\text{C}) =$ 142 Hz and $^1J(^{109}\text{Ag},^{13}\text{C}) = 164$ Hz [38]. The fact that these J(Ag,C) couplings are observed indicates that the Ag—C_{ipso} bond is stable and does not dissociate on the NMR time-scale. These data are the first ^{107,109}Ag coupling constant values for a two-electron, two-centre (2e–2c) silver–carbon bond; ^3J(Ag,C) of 7 Hz is also observed for the hydrogen-bearing carbon atoms of the mesityl ligands. Examples of ^1J(Ag,C) values have been reported for two-electron, three-centre bonded aryl silver compounds (118.3, 136.9 Hz in $[Ag_2Li_2(2\text{-}NMe_2CH_2C_6H_4)_4]$ and 115.0, 132.0 Hz in $[Ag_2Li_2(C_6H_5)_4]$ for ^{107}Ag and ^{109}Ag, respectively [89,90]). The larger silver–carbon coupling constant found in **37l** reflects the anticipated higher degree of s-orbital participation in the silver–carbon bond in this complex than in the electron-deficient Ag—C interactions in $[Ag_2Li_2(2\text{-}NMe_2CH_2C_6H_4)_4]$ and $[Ag_2Li_2(C_6H_5)_4]$ [89,90]. Interestingly, Ag—^{13}C couplings are also seen for the two carbon signals of the η^2-bonded alkynyl ligands. The signal at 184.5 ppm (Ti—$C{\equiv}$C) occurs as a doublet resulting from a $^1J(\text{Ag},^{13}\text{C})$ splitting of 3 Hz, while the doublet at 125.8 ppm (C$\equiv C$—Si) has a $^1J(\text{Ag},^{13}\text{C})$ splitting of 7 Hz [38,86].

The structure in the solid state of selected examples from compounds **34**–**39** have been determined by X-ray diffraction (Table 13).

Fig. 6 shows that compounds of type **I** are monomeric. The metal atoms M (M = Cu, Ag) of the M$^{\text{I}}$X building blocks (where X is a unidentate ligand) show essentially a trigonal planar environment comprising η^2-coordination of both alkynyl groups from the $L_nM(C{\equiv}CR)_2$ fragment and η^1-bonding of the ligand X. In complexes **36s** and **37f** (Table 13), where X is a bidentate ligand, the copper or silver atoms have a tetrahedral environment in which the ligand X, i.e. X = acetylacetonate (acac) (**36s**) or NO_2 (**37f**), is almost perpendicular to the titanium–alkynyl–copper (**36s**) or the titanium–alkynyl–silver (**37f**) plane (interplanar angle ~87°).

As a result of the η^2-coordination of the alkynyl units in **36**–**38** to the M$^{\text{I}}$X moiety, the angle C_α—Ti—$C_{\alpha'}$ between the σ-bonded alkynyl ligands is considerably smaller than that in $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$ (**35**), where it is 102.8° (Table 13). The Ti—C$\equiv$C—$SiMe_3$ units are distorted compared with the starting compounds, in which they are linear (Table 13).

The η^2-coordination of the alkynyl ligands to the M$^{\text{I}}$X moiety in **36** and **37** is accompanied by a bond lengthening of the C$\equiv$C triple bonds of the $Me_3SiC{\equiv}C$ building blocks from 1.203 and 1.214 Å in **35** to 1.23–1.27 Å in **36** and **37** (Table 13). It is found that the C$\equiv$C triple bond is not significantly lengthened upon changing

Table 13
X-ray data for compounds $\{L_nM(C{\equiv}CR)_2\}M'X$, **35**, **36**, **37** and **39**

Compound	Ref.	M···M′ (Å)	$M-C_{C\equiv C}$ (Å)	$M'-C_{C\equiv C}$ (Å)	C≡C (Å)	C–M–C (°)	M–C≡C (°)	C≡C–R (°)
35	[74]		2.124(5), 2.103(5)	–	1.214(6)	102.8(2)	175.8(4)	174.8(4)
					1.203(9)		178.2(5)	178.3(5)
36a	[82,85]	290.9(3)	209(1), 210.4(9)	C_α: 205.5(9), 218(1)	123(2)	89.6141	167.8(9)	161(1)
				C_β: 204(1), 221(1)	124(2)		168.6(9)	163(1)
36f	[13,14]	2.930(3)	2.10(1), 2.09(1)	C_α: 2.08(1); 2.07(1)	1.25(2)	90.3(4)	163.6(9)	164.1
				C_β: 2.15(1); 2.12(1)	1.23(2)		166(1)	165.1
36m	[38]	2.941(2)	2.079(2)	C_α: 2.067(2); C_β: 2.083(2)	125.0(3)	89.30(9)	163.6(2)	155.5(2)
36p	[38,40]	2.998(1)	2.105(4), 2.110(4)	C_α: 2.066(4); 2.066(4)	1.233(6)	87.4(2)	166.7(3)	156.18(4)
				C_β: 2.143(5); 2.158(5)	1.238(5)		166.9(3)	158.1(4)
36s	[13]	2.920(1)	2.081(4), 2.091(4)	C_α: 2.079(4); 2.088(3)	1.235(5)	90.7(1)	164.7(3)	163.8(3)
				C_β: 2.171(4); 2.145(3)	1.227(5)		165.8(3)	164.9(3)
37f	[36]	3.162(5)	2.12(2), 2.10(2)	C_α: 2.29(2); 2.33(2)	1.26(2)	93.8(1)	171(2)	170(2)
				C_β: 2.41(2); 2.43(2)	1.27(3)		170(2)	171(2)
37l	[38]	3.104(7)	2.090(8)	C_α: 2.270(9)	1.24(1)	94.0(3)	166.6(6)	162.9(7)
				C_β: 2.305(9)				
37m	[38]	3.156(2)	2.141(6), 2.159(7)	C_α: 2.291(6); 2.311(6)	1.22(1)	93.8(2)	170.8(5)	163.7(3)
				C_β: 2.417(7); 2.478(7)	1.225(8)		172.7(5)	170.2(5)
37n	[38]	3.096(2)	2.114(7), 2.128(7)	C_α: 2.294(7); 2.293(7)	1.23(1)	95.6(3)	170.7(6)	168.8(6)
				C_β: 2.472(8); 2.447(7)	1.222(9)		171.0(6)	166.8(7)
39a	[87,88]	3.078(3)	2.39(2), 2.26(2)	C_α: 1.98(2); 2.12(2)	–	–	–	–
				C_β: 2.33(2); 2.34(2)				

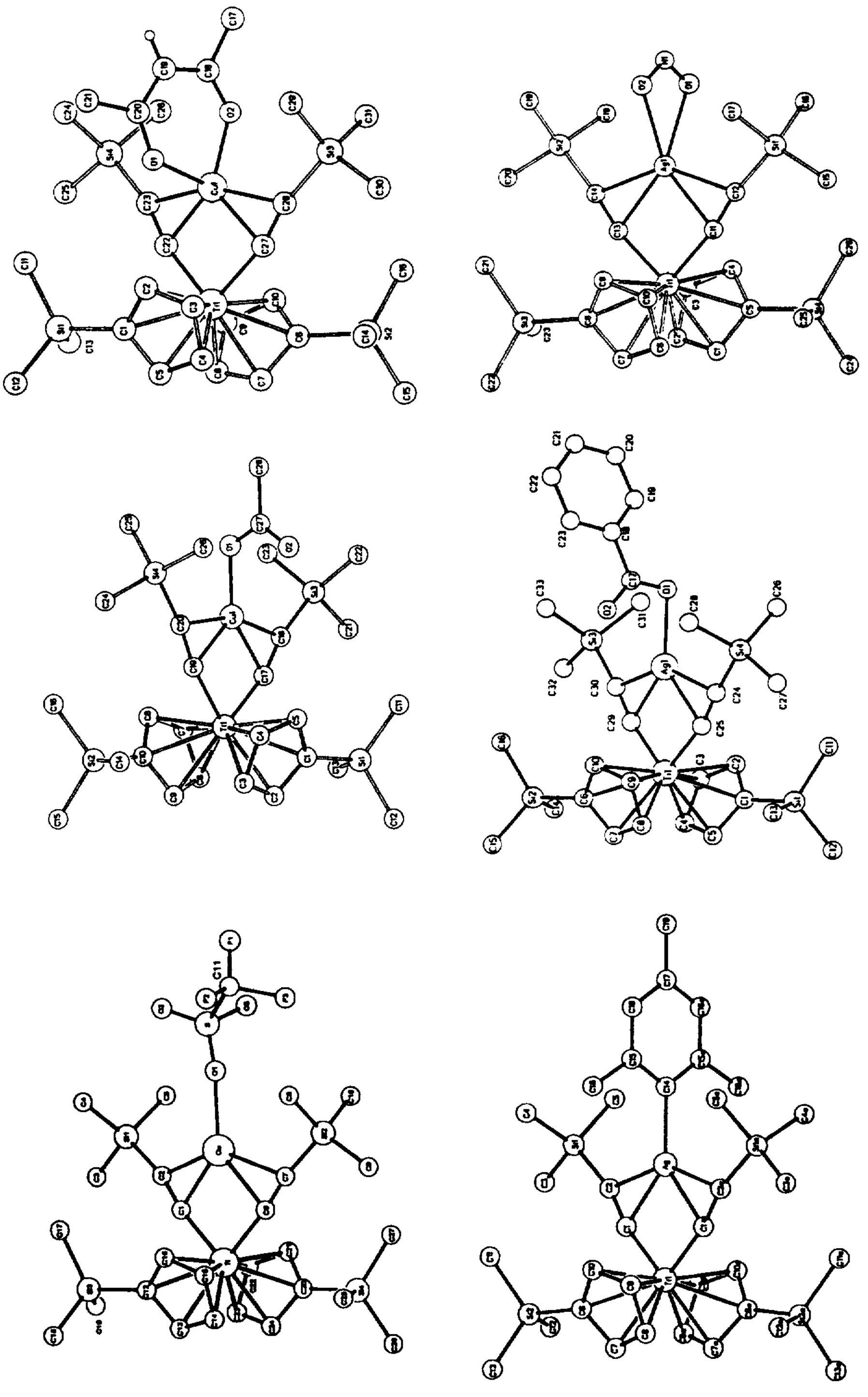


Fig. 6. Selected X-ray structures of type **I** molecules. The interatomic bond distances and angles are given in Table 13.

the σ-donating properties of the ligand X (Table 13). However, spectroscopic studies (IR and ^{13}C NMR) show a clear correlation: the ^{13}C chemical shift of the alkyne units is almost linear with the C≡C stretching frequency [38,86].

As a result of the steric constraints, and also the overlap of the orbitals participating in the bonding of the group 11 metal atoms with the alkynyl groups of the $Ti(C{\equiv}CSiMe_3)_2$ entity, the two alkynyl ligands are in-plane bonded [38,86]. A similar bonding arrangement is present in the structure of [cyclo(o-$C_6H_4C{\equiv}C)_3]Cu(OSO_2CF_3)$ (**16**) (C≡C 1.222 Å, Cu—C (mean) 2.060 Å, Cu 0.18 Å above the [(C≡C)$_3$] plane) (Section 2.4.1) [41–43].

In compounds **36** and **37** the central Group 11 metal has a formal 16-electron count and consequently the Ti—Cu and Ti—Ag distances (Ti—Cu, 2.92–2.99 Å; Ti—Ag, 3.10–3.26 Å) are considered to represent non-bonding situations [38,86].

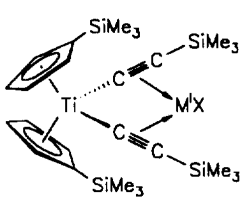
The titanium–copper distances in **36** (see above) are shorter than the similar titanium–silver distances in **37**, owing to the smaller ionic radius of copper(I) (0.96 Å) than that of silver(I) (1.26 Å). Similar observations have been made for the copper to alkyne and silver to alkyne distances in the isostructural compounds $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Cu(Mes)$ (**36m**)/$\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Ag(Mes)$ (**37l**) (Mes = 2,4,6-$Me_3C_6H_2$) and $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Cu(OSO_2CF_3)$ (**36p**)/$\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Ag(OSO_2CF_3)$ (**37m**) (Table 13). It was found that the copper to alkyne interatomic distances were approximately 0.25 Å shorter than the corresponding bond lengths in the silver complexes, reflecting the smaller ionic radius of Cu^I over that of Ag^I (see above). Similarly, the copper–carbon distance (C_{ipso}—Mes) in **36m** of 1.947 Å is 0.15 Å shorter than the corresponding silver–carbon (C_{ipso}—Mes) distance of 2.099 Å in **37l** (Table 13).

The Cu—C_{ipso} and Ag—C_{ipso} mesityl bond lengths are in the range expected for two-electron, two-centre (2e–2c) bonding of carbon to copper. Reported (2e–2c) Cu—C distances include that for sp^3-hybridized carbon atoms, 2.04(1) Å in $(Ph_3P)_3CuMe$ [3b], sp^2-hybridized carbon atoms, 2.020(4) Å in $MeC(CH_2PPh_2)_3CuPh$ [3a], 1.916(3) Å in Cu(2,4,6-$^tBu_3C_6H_2$)(Me_2S) [3c] and 1.890(6) Å in Cu(2,4,6-$Ph_3C_6H_2$) [3f], and sp-hybridized carbon atoms, 1.898(3) Å in $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Cu{-}C{\equiv}CSiMe_3$ (**36i**) [86]. A similar observation is valid for the analogous binding of carbon to silver (the Ag—C bond length for a sp^2-hybridized carbon is 1.902(5) Å in Ag(2,4,6-$Ph_3C_6H_2$) [3f].

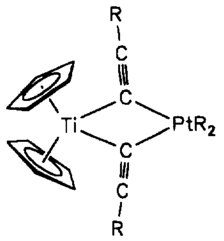
These results show that the striking property of $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$ (**35**) to bind mononuclear metal fragments gives access to a novel type of mononuclear organo-copper and -silver species (type **I** molecules) with an organometallic chelating bis(alkynyl) ligand $RC{\equiv}C{-}L_2Ti{-}C{\equiv}CR$. It is important that in the $L_2Ti(C{\equiv}CR)_2{-}CuX$ interaction (see above) copper represents a metal with a low Lewis acidity (electrophilicity). Metals with a higher electrophilicity (e.g. R_2Pt) tend to coordinate preferentially to the C_α atom of the $Ti(C{\equiv}CR)_2$ fragment, giving rise to a bonding, better described as asymmetric bridging of C≡CR between the titanium and the platinum centres (a type **M** molecule) [91].

3.3.3. *Reactivity*

The binuclear compounds $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}M^IX$ (**36a**, M = Cu, X = Cl; **36p**, M = Cu, X = OSO_2CF_3; **37m**, M = Ag, X = OSO_2CF_3) contain, as func-



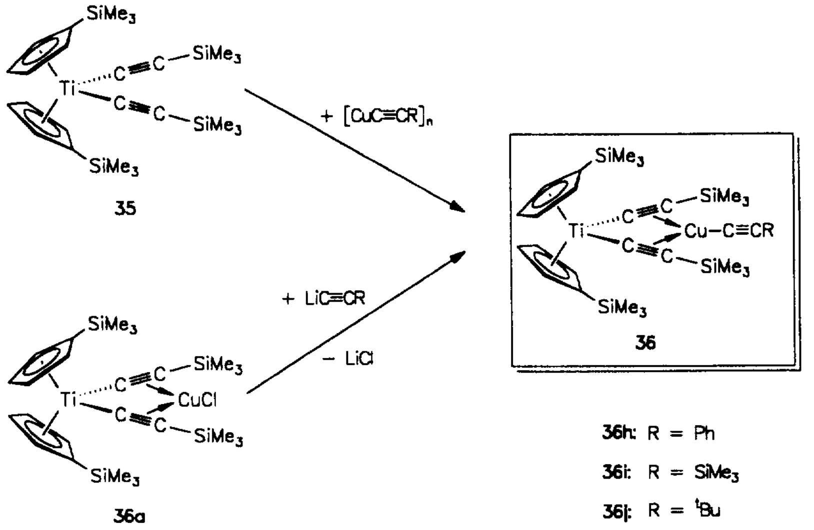
I



M

tional ligands, a chloride or trifluoromethanesulphonate (OTf) group at the copper or silver atom. Substitution of these groups should lead to a versatile reaction chemistry.

3.3.3.1. {(η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡CSiMe$_3$)$_2$}CuCl. To study intermolecular vs. intra-molecular alkyne to copper coordination, the mononuclear bis(η^2-alkyne)-η^1-acetylide copper(I) compounds {(η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡CSiMe$_3$)$_2$}CuC≡CR (**36h**, R = Ph; **36i**, R = SiMe$_3$; **37j**, R = ^{t}Bu; **36t**, R = 4-C_6H_4C≡CSiMe$_2$H) were prepared: addition of (η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡CSiMe$_3$)$_2$ (**35**) to a solution or suspension of oligomeric or polymeric alkynyl copper(I) compounds, [CuC≡CR]$_n$, in a 1 : 1 molar ratio yields the quantitative formation of the monomeric compounds **36h**–**36j** and **36t** [37,40]. An alternative preparative route is the metathesis reaction of {(η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡CSiMe$_3$)$_2$}CuCl (**36a**) with LiC≡CR (R = Ph, ^{t}Bu, SiMe$_3$, 4-C_6H_4C≡CSiMe$_2$H).

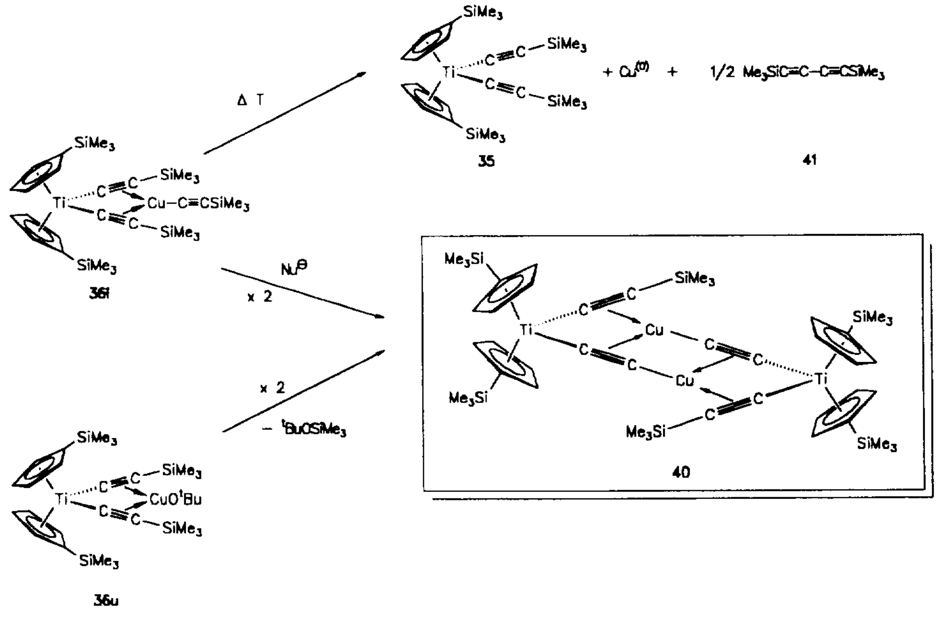


36h: R = Ph
36i: R = SiMe$_3$
36j: R = ^{t}Bu
36t: R = 4–C_6H_4C≡CSiMe$_2$H

The presence of both η^2-bonded alkyne ligands and a η^1-bonded acetylide in compounds **36h**–**36j** and **36t** is shown by two different C≡C stretching frequencies in their IR spectra: through the η^2-coordination of the trimethylsilylethynyl moieties in **35** to a copper atom in **36h–36j** and **36t** the $\nu(C{\equiv}C)$ vibration is shifted from $2012\ cm^{-1}$ in **35** to $1905\ cm^{-1}$ in **36h**, $1902\ cm^{-1}$ in **36i**, $1896\ cm^{-1}$ in **36j** and $1899\ cm^{-1}$ in **36t** [37,40]. The σ-bonded acetylide ligand $C{\equiv}CR$ absorbs in the infrared region at $2095\ cm^{-1}$ in **36h**, $2095\ cm^{-1}$ in **36i**, $2035\ cm^{-1}$ in **36j** and $2152/2090\ cm^{-1}$ in **36t** for $\nu(C{\equiv}C)$, and these data clearly indicate that the copper acetylide ligand is not π coordinated.

Surprisingly, compound **35** reacts selectively with $1/4[CuO^tBu]_4$ in diethyl ether to yield quantitatively the dimeric complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)(C{\equiv}CCu)]_2$ (**40**) [37,40]. In this case, the binuclear compound $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}CuO^tBu$ (**36u**) could not be isolated; elimination of $^tBuOSiMe_3$ (detected by GC–MS) and formation of **40** are instantaneous and quantitative.

Other nucleophiles show a similar reactivity towards compounds **36h–36j**, although the reaction is much slower and less selective owing to competitive cleavage of the $Ti{-}C{\equiv}C$ σ bond [37,40].



However, when $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}CuC{\equiv}CSiMe_3$ (**36i**) is heated homolytic cleavage of the copper–carbon σ bond of the $CuC{\equiv}CSiMe_3$ fragment is observed [13]. The formation of $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$ (**35**), copper(0) together with $Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3$ (**41**) takes place. This observation represents the well known Glaser reaction in which two acetylenes are oxidative coupled to symmetrical 1,3-diynes in presence of copper(I).

Compound **40** has a decomposition point of 157 °C; this high thermal stability is remarkable, since bimetallic acetylide species of copper(I), e.g. $CuC{\equiv}CCu$, are usually very reactive or even explosive [92].

Cryoscopic molecular weight determination of **40** in benzene indicates that **40** is dimeric in solution. Variable-temperature ^{1}H NMR experiments confirm that **40** maintains this aggregation state in solution; in the temperature range 207–353 K the ^{1}H NMR spectra remain essentially identical [37,40].

To establish the solid-state structure of **40**, an X-ray crystallographic study was carried out [37,40].

The molecular structure of **40** (Fig. 7) consists of a dimer of the bimetallic acetylide $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)(C{\equiv}CCu)]$. The C≡C bond length of the alkynyl ligands within this building block is lengthened from 1.208 Å (av.) in **35** to 1.234 Å (TiC≡CSi) and 1.243 Å (TiC≡CCu) in **40**. Each copper atom exhibits a distorted trigonal planar geometry with two η^2- and one η^1-bonded alkynyl ligands. The Ti—C≡C—Cu unit is non-linear (Ti1—C22—C23 = 163.4°; Cu1—C23—C22 = 165.0°), since this acetylide unit is η^2-coordinated to a second copper atom.

Formally, the structural arrangement of the CuC_2 building blocks in **40** corresponds to that realized in polymeric $[Cu^IC{\equiv}CR]_n$ in which the alkynyl units C≡CR are both σ- and π-bonded to copper atoms, thus forming an infinite zigzag chain [1]. Similar structural observations were made for tetrameric $[(PMe_3)Cu(C{\equiv}CPh)]_4$ [93].

Further examples of transmetallation $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}CuCl$

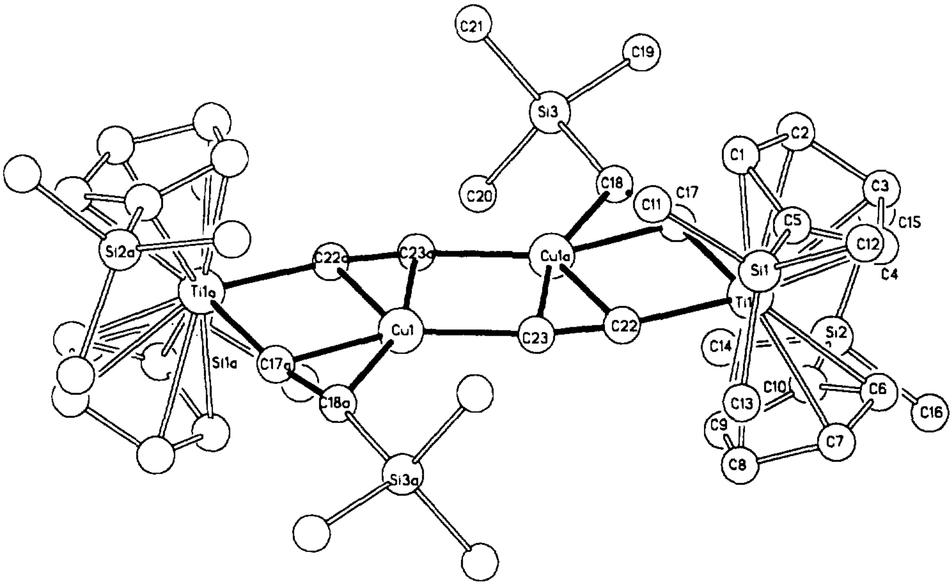


Fig. 7. Molecular geometry and atom labelling scheme for **40** [37,40]. Selected bond distances (Å) and angles (°) are as follows: Ti1—Cu1 2.911(1), Cu1—Cu1a 2.998(1), Cu1—C22 2.107(2), Cu1a—C23 2.162(2), Cu1—C23 1.920(3), Cu1a—C17 2.031(3), Cu1a—C18 2.087(3), C17—C18 1.234(3), C22—C23 1.243(4), Ti1—C17 2.098(2), Ti—C22 2.080(3); Ti1—C17—C18 164.5(2), C17—C18—Si3 164.9(3), Ti1—C22—C23 163.4(2), C22—C23—Cu1 165.0(2), C17—Ti1—C22 90.5(1), Cu1—C23—Cu1a 39.7(1).

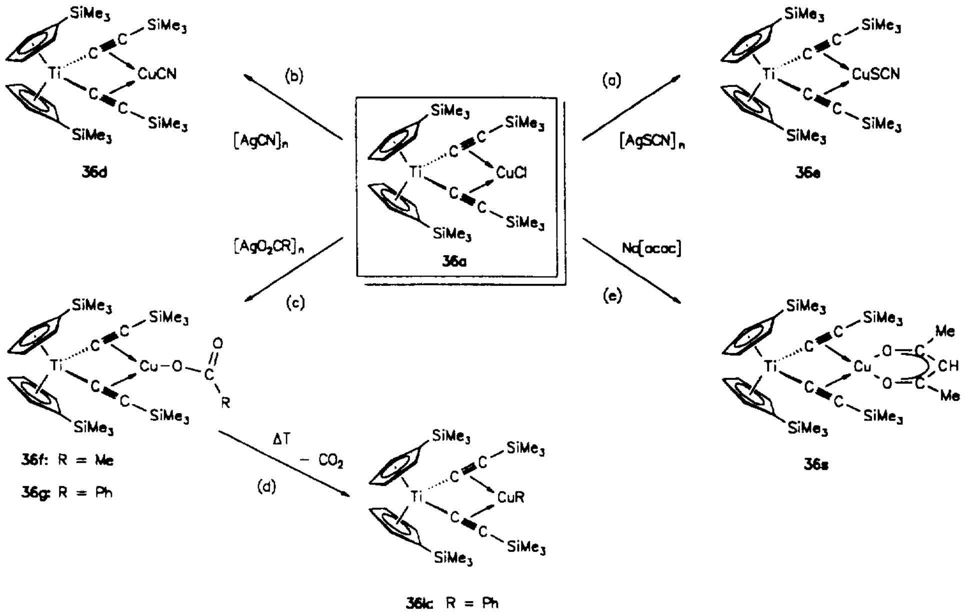
(**36a**) with $[AgX]_n$ [X = SCN, route (a); X = CN, route (b); X = O_2CMe, O_2CPh, route (c), or Na[acac] (acac = acetylacetonate), route (e)] are given in Scheme 4.

$\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Cu[OC(O)Ph]$ (**36g**) eliminates CO_2 if heated in high-boiling solvents and yields $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}CuPh$ (**36k**) (Scheme 4), in which a monomeric CuPh fragment is stabilized by the chelating effect of the organometallic ligand $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$ [13].

Another procedure for the synthesis of **36k** was discussed earlier (addition of $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$ (**35**) to polymeric $[Cu^IPh]_n$) (Section 3.3.1, Table 10) [38,40,86].

These results as a whole show that the striking property of the organometallic chelate $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$ (**35**) to bind mononuclear metal fragments gives access to a novel type of mononuclear organo-copper(I) species with a chelating bisalkynyl ligand. Studies are currently being undertaken in which this property of a fixed bidentate alkynyl ligand is exploited for the isolation of mononuclear aryl copper fragments from heterocopper and cuprate reagents and, as an example, the quantitative isolation of $\mathbf{35}\cdot Cu\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}$ from $Cu_4\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}_2Br_2$ has been achieved [38,86].

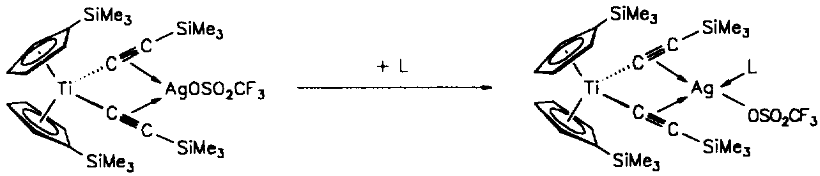
Finally, spectroscopic and chemical properties of these compounds, with an extended ligand to ligand electronic communication (alkyne-to-aryl), are being investigated by variation of the mesomeric and inductive properties of the aryl para substituents [94].



Scheme 4. Synthesis of compounds **36d**, **36e**, **36f**, **36g**, **36k** and **36s**.

3.3.3.2. *$\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}M(OSO_2CF_3)$ $(M{=}Cu,$ $Ag)$.* The complexes $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}M^IX$ (M = Cu, **36**; M = Ag, **37**) contain a monomeric M^IX moiety in which the copper or silver atom possesses a trigonal planar environment. There are several complexes known in which copper or silver atoms show a tetrahedral coordination sphere [1,95]. Hence, $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti\text{-}(C{\equiv}CSiMe_3)_2\}Cu(OSO_2CF_3)$ (**36p**) was reacted with N≡CR (R = Me; R = Ph) in an attempt to produce a copper complex with a copper atom in a tetrahedral environment. The compounds $[\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Cu\text{-}(N{\equiv}CR)]\text{-}(OSO_2CF_3)$ were formed in high yields [40].

However, $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Ag(OSO_2CF_3)$ (**37m**) reacts even at low temperature with thf, N≡CR (R = Me, Ph), PR_2R' (R = R′ = Ph; R = C≡CPh, R′ = CH_2Ph) or $P(OMe)_3$ to afford compounds **42**, **43** and **44** in quantitative yields [13].



37m

42a: L = thf

43a: L = N≡CMe

43b: L = N≡CPh

44a: L = $P(OMe)_3$

44b: L = PPh_3

44c: L = $P(C{\equiv}CPh)_2(CH_2Ph)$

As a result of the coordination of the Lewis bases thf, N≡CR and PR_2R' to the silver(I) centre in the adducts **42**, **43** and **44**, the $\nu(C{\equiv}C)$ vibration in the IR spectra decreases from 1956 cm^{-1} in $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Ag(OSO_2CF_3)$ (**37m**) to 1950–1870 cm^{-1} in **42**–**44**. This effect is in agreement with the increasing participation of the back-bonding components in the silver metal to alkyne bonding.

In order to establish the solid-state structure of compounds **42**–**44**, an X-ray diffraction study was carried out on a single crystal of representative $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Ag[(thf)(BF_4)]$ (**42b**) [13].

Fig. 8 shows that **42b** is monomeric, and that the silver atom possesses a pseudo-tetrahedral environment built up from two alkyne ligands, one BF_4 group and one thf molecule [13].

3.4. Type A, J and K molecules

Formally, type **J** and **K** molecules can be considered as sub-structures of type **H** molecules, which themselves are part of structural type **G** clusters (see above). Dimerization of **K** generates molecules of type **A** (see also Section 2.1).

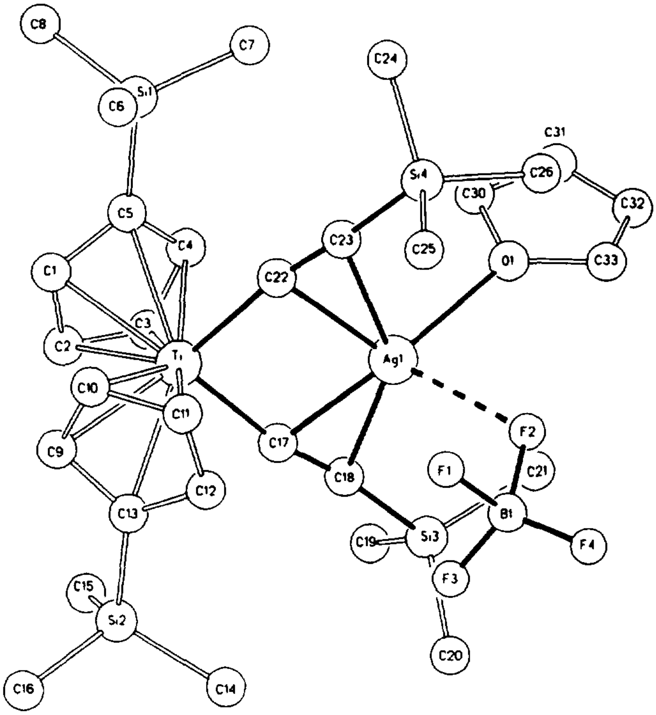
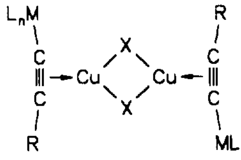
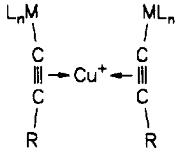


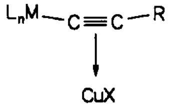
Fig. 8. Molecular geometry and atom labelling scheme for **42b** [13]. Selected bond distances (Å) and angles (°) are as follows: Ti1—Ag1 3.096(2), Ti1—C17 2.114(7), Ti1—C22 2.128(7), Ag1—C17 2.293(6), Ag1—C18 2.447(7), Ag1—C22 2.294(7), Ag1—C23 2.472(8), Ag1—O1 2.389(5), Ag1—F2 2.47(2), C17—C18 1.23(1), C22—C23 1.222(9); Ti1—C17—C18 170.7(6), Ti—C22—C23 171.0(6), C17—C18—Si3 168.8(6), C22—C23—Si4 166.8(7), Ti1—Ag1—O1 135.8(4), Ti1—Ag1—F2 138.7(3), C17—Ti1—C22 95.6(3).



A



J



K

3.4.1. *Type* **J** *and* **K** *molecules,* $[\eta^2\text{-RC}{\equiv}\text{CML}_n)_2]\text{Cu}^I\text{X}$ *(***J***),* $(\eta^2\text{-RC}{\equiv}\text{CML}_n)\text{Cu}^I\text{X}$ *(***K***)*

There are two general routes for the synthesis of type **K** molecules: (a) metathesis reaction of L_nMCl compounds and (b) direct synthesis from $L_nM{-}C{\equiv}CR$ complexes.

(a) Metathesis reaction route. The reaction of transition metal halides L_nMCl [**27g**, $L_nM = (\eta^5\text{-}C_5H_5)(PPh_3)_2Ru$; **27h**, $L_nM = (CO)_3(PPh_3)_2Re$] with copper(I) acetylides

$[CuC{\equiv}CR]_n$ ($R = Ph$, 4-MeC_6H_4, Me) affords the monomeric compounds **45** [68,96–99].

27 **45**

45a: $L_nM = (\eta^5\text{-}C_5H_5)(PPh_3)_2Ru$; R = Ph

45b: $L_nM = (\eta^5\text{-}C_5H_5)(PPh_3)_2Ru$; R = 4-$MeC_6H_4$)

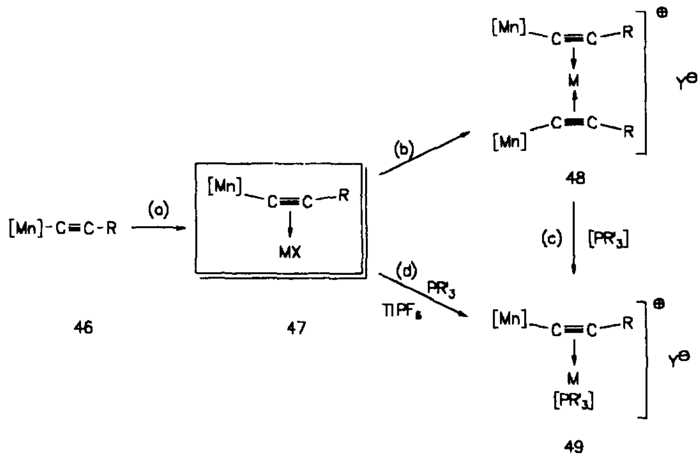
45c: $L_nM = (\eta^5\text{-}C_5H_5)(PPh_3)_2Ru$; R = Me

45d: $L_nM = (CO)_3(PPh_3)_2Re$; R = Ph

(b) Direct synthesis route. Another possibility for the synthesis of structural type **K** molecules is given by the reaction of $[Mn]{-}C{\equiv}CR$ ([Mn] = *fac*-$Mn(CO)_3$(dppe); **46a**, R = Ph; **46b**, $R = {}^tBu$; **46c**, $R = CH_2OMe$) with $[Cu^ICl]_n$ or $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) to yield compounds **47** (Scheme 5, route (a)] (Table 14) [97–99].

As shown in Scheme 5, complexes **47** are suitable for the synthesis of ionic compounds $[\{[Mn](\eta^2\text{-}C{\equiv}CR)\}_2M^I]Y$ (**48**) (type **J** molecules; route (b)) and $[\{[Mn](\eta^2\text{-}C{\equiv}CR)\}M^I(PR'_3)]Y$ (**49**) (type **K** molecules; route (c)) (Table 14) [97,98].

Compound **48a** is formed by the reaction of **47a** with **46** and $TlPF_6$ in CH_2Cl_2 (route (b)). Compounds **48c** and **48d** can be synthesized on addition of solid [AuCl(tht)] and $TlPF_6$ to the starting material **46**, whereas for the synthesis of **48b** the addition of $TlPF_6$ is not necessary [97,98]. On addition of Lewis bases, e.g. PR'_3, to solutions of **48**, one organometallic $[Mn]{-}C{\equiv}CR$ building block



Scheme 5. Synthesis of compounds **47**, **48** and **49**; [Mn] = *fac*-$Mn(CO)_3$(dppe); R' = *o*-tolyl [97–99].

is exchanged by PR'_3, yielding the monomeric ionic compounds $[\{[Mn](\eta^2\text{-}C{\equiv}CR)\}M^I(PR'_3)]Y$ (**49a**–**49d**) (type **K** molecules) (route (c)). A further possibility for preparing compounds **49a**–**49d** is given by route (d) [97–99].

All complexes prepared at present are summarized in Table 14 [96–99].

Compared with the starting compounds **46**, the $\nu(C{\equiv}C)$ frequencies of complexes **47**–**49** are significantly lower owing to the η^2-coordination of the $RC{\equiv}C$ ligands to M^IX (M = Cu, Ag, Au) building blocks [96–99]. This is the normal observation made for alkynes, changing from the uncoordinated to the η^2-coordinated state (see above).

The monomeric structures of compounds **45**, **47** and **49** are evidenced both by osmometric measurements and X-ray diffraction studies [68,96–99].

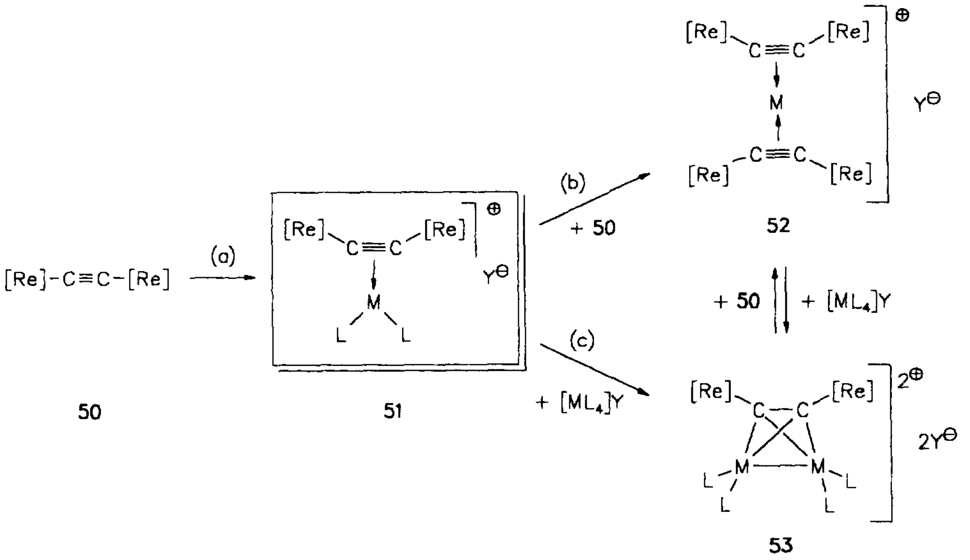
The X-ray diffraction studies additionally confirm the IR spectroscopically observed bond lengthening of the C_2 building blocks (see above). The $C{\equiv}C$ bond is lengthened from 1.20 Å in organometallic substituted alkynes to 1.23 Å in **47a**, 1.24 Å in **49b** and 1.25 Å in **45a** [68,96–99]. In addition, the η^2-coordination leads to a deformation of the $M{-}C{\equiv}C{-}R$ fragment (**47a**, 171.1°, 165.6°; **49b**, 171.0°, 164.0°; **45a**, 173.0°, 165.0°) [68,96–99].

On replacement of the organic group R in transition metal substituted alkynes $[M]{-}C{\equiv}CR$ with organometallic building blocks, bimetallic complexes of the type $[M]{-}C{\equiv}C{-}[M]$ are obtained. One example is $[Re]{-}C{\equiv}C{-}[Re]$ ($[Re] = (CO)_5Re$) (**50**), synthesized by Beck and co-workers [100]. Treatment of **50** with $[M^IL_4]Y$ (L = NCMe; M = Cu, Y = PF_6; M = Ag, Y = BF_4) yields the cationic compounds **51a** (M = Cu, Y = PF_6) and **51b** (M = Ag, Y = BF_4) (Scheme 6, route (a)) [101].

On addition of $[Re]{-}C{\equiv}C{-}[Re]$ (**50**) to **51**, the cationic complexes **52** (**52a**, M = Cu, Y = PF_6; **52b**, M = Ag, Y = BF_4) are formed (Scheme 6, route (b)), whereas with $[M^IL_4]Y$ the metalla-carbon tetrahedranes **53** (**53a**, M = Cu, Y = PF_6; **53b**, M = Ag, Y = BF_4) can be obtained (Scheme 6, route (c)) [101].

Table 14
Compounds **47**, **48** and **49** [97–99]

Compound	M	X	R	Y
47a	Cu	Cl	Ph	–
47b	Cu	Cl	^{t}Bu	–
47c	Cu	Cl	CH_2OMe	–
47d	Au	C_6F_5	^{t}Bu	–
47e	Au	C_6F_5	CH_2OMe	–
48a	Cu	–	^{t}Bu	PF_6
48b	Ag		^{t}Bu	BF_4
48c	Au	–	Ph	PF_6
48d	Au	–	^{t}Bu	PF_6
49a	Cu	–	^{t}Bu	PF_6
49b	Cu	–	CH_2OMe	PF_6
49c	Ag	–	^{t}Bu	BF_4
49d	Au	–	^{t}Bu	PF_6

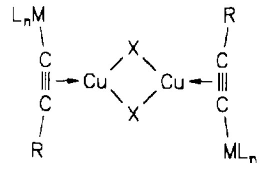


Scheme 6. Synthesis of compounds **51**–**53**; $[Re]=Re(CO)_5$; $L=N\equiv CMe$; M = Cu, Ag; $Y=PF_6$, BF_4 [100,101].

The η^2-coordination of the C_2 unit in **50** to a copper(I) or silver(I) fragment leads to C≡C stretching vibrations in the 1890–1950 cm^{-1} region, a phenomenon typical of this coordination mode (see above).

3.4.2. *Organometallic type A molecules,* $[(\eta)^2\text{-}RC\equiv CML_n)Cu^IX]_2$

In structural type **A** compounds, the C_2 unit of the organometallic group $L_nM-C\equiv CR$ is η^2-coordinated to a Cu^IX fragment and through the formation of copper–halide bridges (Cu_2X_2) a dimer is formed (for the synthesis of $[(\eta^2\text{-}RC\equiv CR)Cu^IX]_2$ compounds, see Section 2.1).



A

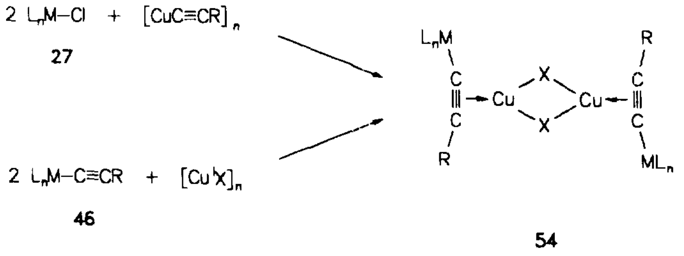
Type **A** molecules can be obtained by the reaction of L_nMCl (**27**) with $[CuC\equiv CR]_n$ or the reaction of $L_nM-C\equiv CR$ (**46**) with Cu^IX (Table 15) [68,96,102–106].

Compounds **54** are dimeric, as indicated by osmometric measurements [68,96,102–106].

In order to establish the solid-state structure of compounds **54a**–**54j**, an X-ray diffraction study was carried out on a single crystal of **54b** (Fig. 9) [102–104]. Fig. 9 shows that complex **54b** is dimeric and consists of two asymmetric units related by

Table 15
Compounds **54**

Compound	L_nM	*X*	*R*	*Ref.*
54a	$(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru$	Cl	C_6H_5	[87,96]
54b	$(\eta^5\text{-}C_5H_5)(CO)_2Fe$	Cl	C_6H_5	[102–104]
54c	$(\eta^5\text{-}C_5H_5)(CO)_2Fe$	Cl	$4\text{-}MeC_6H_4$	[102]
54d	$(\eta^5\text{-}C_5H_5)(CO)_2Fe$	Cl	$4\text{-}FC_6H_4$	[102]
54e	$(\eta^5\text{-}C_5H_5)(CO)_2Fe$	Cl	C_6F_5	[102]
54f	$(\eta^5\text{-}C_5H_5)(CO)_2Fe$	Cl	Me	[102]
54g	$(\eta^5\text{-}C_5H_5)(CO)_2Fe$	Cl	$SiMe_3$	[105,106]
54h	$(\eta^5\text{-}C_5H_5)(CO)_2Fe$	Br	C_6H_5	[102]
54i	$(\eta^5\text{-}C_5H_5)(CO)_3Mo$	Cl	$SiMe_3$	[105,106]
54j	$(\eta^5\text{-}C_5H_5)(CO)_3W$	Cl	$SiMe_3$	[105,106]



a centre of inversion. Each copper atom possesses a trigonal planar environment and is symmetrically η^2-coordinated by the C_2 unit of the phenylethynyl group. The Cu_2Cl_2 ring is coplanar with the CuC_2 moiety. The Cu···Cu distance of 3.075(4) Å indicates that there is no bonding character between these two metal atoms.

Through the η^2-coordination of the PhC≡C ligand to a Cu^ICl building block, the bond length of the C≡C unit is lengthened from approximately 1.20 Å in the starting material to 1.23 Å in **54b**. In addition, it is found that the Fe—C≡C—Ph building block is distorted from linearity (Fig. 9). The same kind of structure is present in a series of analogous compounds $[(\eta^2\text{-}RC{\equiv}CR)Cu^IX]_2$ (R = singly bonded organic ligand; X = Cl, Br, etc.) which contain an organic group R instead of an organometallic moiety ML_n (Section 2.1).

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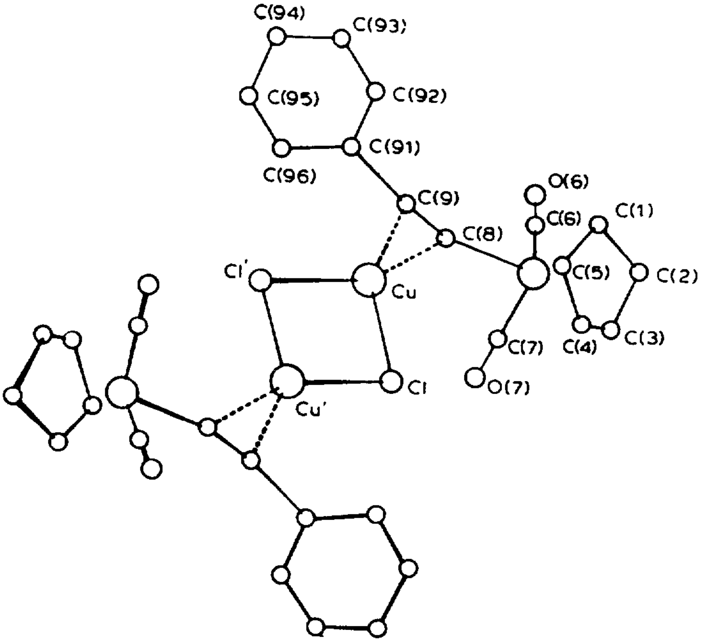

Fig. 9. Molecular geometry and atom labelling scheme for **54b** [102-104]. Important selected interatomic distances (Å) and angles (°) are as follows: Cu—Cl 2.283(3), Cu'—Cl' 2.291(3), Fel—C8 1.91(1), Cu—C8 2.02(1), Cu—C9 2.00(1), C8—C9 1.23(1), Fel—C8—C9 164.3(9), C8—C9—C91 161.1(1), Cu—Cl—Cu' 84.3(1), Cl—Cu—Cl' 95.7(1).

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References

[1] B.H. Lipshutz and S. Sengupta, Org. React., 41 (1992) 135; G.H. Posner, An Introduction to Synthesis Using Organocopper Reagents, Wiley-Interscience, New York, 1980; B.H. Lipshutz, Synthesis, (1987) 325; J.F. Normant, Synthesis, (1972) 63; W. Carruthers, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), Comprehensive Organometallic Chemistry, Vol. 7, Pergamon Press, Oxford, 1982, Chapter 49; C. Glaser, Liebigs Ann. Chem., 154 (1870) 137; T. Sandmeyer, Chem. Ber., 17 (1884) 1633; F. Ullman and J. Bielecki, Chem. Ber., 43 (1901) 2174; W.R.H. Hurtley, J. Chem. Soc., (1929) 1870; H. Gilman and J.M. Straley, Recl. Trav. Chim. Pays-Bas, 55 (1936) 821; M.S. Kharash and P.O. Tawney, J. Am. Chem. Soc., 63 (1941) 2308; H.O. House, W.L. Respess and G.M. Whitesides, J. Org. Chem., 31 (1966) 3138; G.M. Whitesides, W.F. Fischer, Jr., J. San Filippo, Jr., R.W. Bashe and H.O. House, J. Am. Chem. Soc., 91 (1969) 4871; L.I. Zakharkin and L.P. Sorokina, Zh. Org. Khim., 6 (1970) 2430; J. Org. Chem. (USSR), 6 (1970) 2482; J.F. Normant and M. Bourgain, Tetrahedron Lett., 11 (1970) 2659; H.O. House and M.J. Umen, J. Am. Chem. Soc., 94 (1972) 5495; G.M. Whitesides and P.E. Kendall, J. Org. Chem., 37 (1972) 3718; G.H. Posner, C.E. Whitten and J.J. Sterling, J. Am. Chem. Soc., 95 (1973) 7788; H.O. House and M.J. Umen, J. Org. Chem., 36 (1973) 3893; C.R. Johnson and G.A. Dutra, J. Am. Chem. Soc., 95 (1973) 7783; A. Bruggink and A. McKillop, Tetrahedron, 31 (1975) 2607; H.O. House, Acc.

Chem. Res., 9 (1976) 59; J. Berlan, J.P. Battioni and K. Koosha, Tetrahedron Lett., 17 (1976) 3355; T. Olsson, M.T. Rahman and C. Ullenius, Tetrahedron Lett., 18 (1977) 75; M. Nilsson, M.T. Rahman and C. Ullenius, Acta Chem. Scand., Sect. B, 31 (1977) 514; J. Berlan and K.J. Koosha, J. Organomet. Chem., 152 (1978) 359; J. Berlan, J.P. Battioni and K.J. Koosha, Bull. Soc. Chim. Fr., (1979) 183; C.P. Casey and M.C. Cesa, J. Am. Chem. Soc., 101 (1979) 4236; R.A.J. Smith and D.J. Hannah, Tetrahedron, 35 (1979) 1183; S.R. Krauss and S.G. Smith, J. Am. Chem. Soc., 103 (1981) 141; F. Leyendecker and D. Laucher, Tetrahedron Lett., 24 (1983) 3517; E.J. Corey and N.W. Boaz, Tetrahedron Lett., 25 (1984) 3063; B.H. Lipshutz, R.S. Wilhelm and J.A. Kozlowski, Tetrahedron, 40 (1984) 5005; F. Leyendecker and D. Laucher, Nouv. J. Chim., 9 (1985) 13; E.J. Corey and N.W. Boaz, Tetrahedron Lett., 26 (1985) 6015; J. Berlan and Y. Besace, Tetrahedron, 42 (1986) 4767; E.J. Corey, R. Naef and F.J. Hannon, J. Am. Chem. Soc., 108 (1986) 7114; Y. Yamamoto, Angew. Chem., 98 (1986) 956; Angew. Chem., Int. Ed. Engl., 25 (1986) 947; G.M. Villacorta, C. Pulla and S.J. Lippart, J. Am. Chem. Soc., 110 (1988) 3175; C. Ullenius and B. Christenson, Pure Appl. Chem., 60 (1988) 57; S.H. Bertz and R.A.J. Smith, J. Am. Chem. Soc., 111 (1989) 8276; A.E. Dorigo and K. Morokuma, J. Am. Chem. Soc., 111 (1989) 6524; A.E. Dorigo and K. Morokuma, J. Am. Chem. Soc., 111 (1989) 4635; D.M. Knotter, A.L. Spek and G. van Koten, J. Chem. Soc., Chem. Commun., (1989) 1738; D.M. Knotter, G. van Koten, L.H. van Maaren, D.M. Grove and A.L. Spek, Angew. Chem., 101 (1989) 351; Angew. Chem., Int. Ed. Engl., 28 (1989) 341; B.H. Lipshutz, Synlett, (1990) 119; B.H. Lipshutz, E.L. Ellsworth and S.H. Dimock, J. Am. Chem. Soc., 112 (1990) 5869.

[2] P.P. Power, Prog. Inorg. Chem., 39 (1991) 76; A.J. Jukes, Adv. Organomet. Chem., 12 (1974) 215; G. van Koten and J.G. Noltes, in F.G.A. Stone and E.W. Abel (eds.), Comprehensive Organometallic Chemistry, Vol. II/14, Pergamon Press, Oxford, 1982, p. 709; A.M. Sladkov and I.R. Gol'ding, Russ. Chem. Rev., 48 (1979) 868; A. Camus, N. Marsich, G. Nardin and L. Randaccio, Inorg. Chim. Acta, 23 (1977) 131; G. Bähr and P. Barba, in Houben-Weyl, Methoden der Organischen Chemie, Vol. XIII/1, Georg Thieme, Stuttgart, 1970, p. 735; D.W. Stephan, Coord. Chem. Rev., 95 (1989) 41; E. Wehman, G. van Koten, J.T.B.H. Jastrzebski, M.A. Rotteveel and C.H. Stam, Organometallics, 7 (1988) 1477; E. Wehman, G. van Koten, D.M. Knotter, H. Spelten, D. Heijdenrijk, N.S. Mak and C.H. Stam, J. Organomet. Chem., 325 (1987) 293; B. Lenders, D.M. Grove, W.J.J. Smeets, P. van der Sluis, A.L. Spek and G. van Koten, Organometallics, 10 (1991) 786; D.M. Knotter, W.J.J. Smeets, A.L. Spek and G. van Koten, J. Am. Chem. Soc., 112 (1990) 5895; S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Chem. Soc., Chem. Commun., (1983) 1156.

[3] S. Gambarotta, S. Strologo, C. Floriani, A. Chiesi-Villa and C. Guastini, Organometallics, 3 (1984) 1444; P.S. Coan, K. Folting, J.C. Huffmann and K.G. Caulton, Organometallics, 8 (1989) 2724; P.W. Corfield and H.M.M. Shearer, Acta Crystallogr., 20 (1966) 502; R. Uson, A. Laguna, A. Uson, P.G. Jones and K. Meyer-Base, J. Chem. Soc., Dalton Trans., (1988) 341; X. He, M.M. Olmstead and P.P. Power, J. Am. Chem. Soc., 114 (1992) 9668; R. Lingnau and J. Strähle, Angew. Chem., 100 (1988) 409; Angew. Chem., Int. Ed. Engl., 27 (1988) 436; T.A. Wark and D.W. Stephan, Inorg. Chem., 26 (1987) 363; D.W. Stephan, J. Chem. Soc., Chem. Commun., (1991) 129; T.T. Nadasdi and D.W. Stephan, Organometallics, 11 (1992) 116; P.S. Braterman and V.A. Wilson, J. Organomet. Chem., 31 (1971) 131; H.J. Küppers, K. Wieghardt, Y.-H. Tsay, C. Krüger, B. Nuber and J. Weiss, Angew. Chem., 99 (1987) 583; Angew. Chem., Int. Ed. Engl., 26 (1987) 575; H. Maelger, F. Olbrich, J. Kopf, D. Abeln and E. Weiss, Z. Naturforsch., Teil B, 47 (1992) 1276; A. Haaland, K. Rypdal, H.P. Verne, W. Scherer and W.R. Thiel, Angew. Chem., 106 (1994) 2515; Angew. Chem., Int. Ed. Engl., 33 (1994) 2443.

[4] F.L. Carter and E.W. Hughes, Acta Crystallogr., 10 (1974) 801.

[5] G.G. Aleksandrov, I.R. Gol'ding, S.R. Sterlin, A.M. Sladkov, Yu.T. Struchkov, I.A. Garbuzova and V.T. Aleksanyan, Izv. Akad. Nauk SSR, Ser. Khim., 12 (1980) 2679 (Engl. Transl., p. 1857).

[6] D.W. Macomber and M.D. Rausch, J. Am. Chem. Soc., 105 (1983) 5325, and references cited therein.

[7] G. Maier, M. Hoppe, H.P. Reisenauer and C. Krüger, Angew. Chem., 94 (1982) 445; Angew. Chem., Int. Ed. Engl., 21 (1982) 437; Angew. Chem., Suppl., (1982) 1061.

[8] F. Olbrich, J. Kopf, E. Weiss, A. Krebs and S. Müller, Acta Crystallogr., Sect. C, 46 (1990) 1650.

[9] F. Olbrich, G. Schmidt, U. Behrens and E. Weiss, J. Organomet. Chem., 418 (1991) 41.

[10] F. Olbrich, U. Behrens, G. Gröger and E. Weiss, J. Organomet. Chem., 448 (1993) C10; F. Olbrich, U. Behoens and E. Wiess, J. Organomet Chem., 472 (1994) 365.
[11] F. Olbrich, J. Kopf and E. Weiss, J. Organomet. Chem., 456 (1993) 293.
[12] F. Olbrich, U. Behrens, G. Schmidt and E. Weiss, J. Organomet. Chem., 463 (1993) 249.
[13] K. Köhler, Diplom-Thesis, University of Heidelberg, 1994.
[14] H. Lang, K. Köhler and L. Zsolnai, Chem. Ber., submitted for publication.
[15] D.L. Reger and M.F. Huff, Organometallics, 9 (1990) 2807.
[16] M. Pasquali, P. Leoni, C. Floriani and A. Gaetani-Manfredotti, Inorg. Chem., 21 (1982) 4324.
[17] H.L. Aalton, G. van Koten, E. Riethorst and C.H. Stam, Inorg. Chem., 28 (1989) 4140.
[18] F. Olbrich, G. Schmidt, E. Weiss and U. Behrens, J. Organomet. Chem., 456 (1993) 299.
[19] H. Lang and K. Köhler, J. Organomet. Chem., submitted for publication.
[20] J.C. Dyason, P.C. Healy, L.M. Engelhardt, C. Pakawatchai, V.A. Patrick and A.H. White, J. Chem. Soc., Dalton Trans., (1985) 839.
[21] D.T. Cromer, A.C. Larson and R.B. Roof, Acta Crystallogr., 20 (1966) 279.
[22] Holleman-Wiberg, Lehrbuch der Anorganischen Chemie, Walter de Gruyter, Berlin, 1976.
[23] N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1984, p. 1368.
[24] D.L. Reger, M.F. Huff, Th.A. Wolfe and R.D. Adams, Organometallics, 8 (1989) 848.
[25] H. Lang, K. Köhler and L. Zsolnai, Chem. Ber., in press.
[26] M. Pasquali, C. Floriani, G. Venturi, A. Gaetani-Manfredotti and A. Chiesi-Villa, J. Am. Chem. Soc., 104 (1982) 4092; A. Toth, C. Floriani, A. Chiesi-Villa and C. Guastini, Inorg. Chem., 26 (1987) 236.
[27] E.g. G.M. Villacorta, D. Gibson, I.D. Williams, E. Whang and S.J. Lippard, Organometallics, 6 (1987) 2426, and references cited therein.
[28] G.M. Villacorta, D. Gibson, I.D. Williams and S.J. Lippard, J. Am. Chem. Soc., 107 (1985) 6732.
[29] R. Gleiter, M. Karcher, D. Kratz, M.L. Ziegler and B. Nuber, Chem. Ber., 123 (1990) 1461.
[30] H. Lang, M. Herres, K. Köhler, S. Blau, S. Weinmann, M. Weinmann, G. Rheinwald and W. Imhof, J. Organomet. Chem., in press.
[31] I.A. Garbuzova, I.R. Gol'ding, N.N. Travkin, A.M. Sladkov and V.T. Aleksanyan, Koord. Khim., 5 (1979) 345.
[32] M. Hakansson, K. Wettström and S. Jagner, J. Organomet. Chem., 421 (1991) 347.
[33] A.C. Ukwueze and S.R. Landor, Spectrochim. Acta, Part A, 40 (1984) 433; A.C. Ukwueze and S.R. Landor, Synth. React. Inorg. Met.-Org. Chem., 14 (1984) 1013.
[34] H. Lang and M. Herres, Trends in Organometallic Chemistry, Council of Scientific Research Integration, India, 1995, and references cited therein.
[35] H. Lang, Angew. Chem., 106 (1994) 569; Angew. Chem., Int. Ed. Engl., 33 (1994) 547.
[36] H. Lang, M. Herres and L. Zsolnai, Organometallics, 12 (1993) 5008.
[37] M. Herres, M.D. Janssen, L. Zsolnai, D.M. Grove, H. Lang and G. van Koten, unpublished.
[38] M.D. Janssen, M. Herres, A.L. Spek, D.M. Grove, H. Lang and G. van Koten, J. Am. Chem. Soc., to be submitted.
[39] H. Lang, M. Herres, L. Zsolnai and W. Imhof, J. Organomet. Chem., 409 (1991) C7.
[40] M. Herres, Diplom-Thesis, University of Heidelberg, 1990; M. Herres, Ph.D. Thesis, University of Heidelberg, 1993.
[41] J.D. Ferrara, C. Tessler-Youngs and W.J. Youngs, Organometallics, 6 (1987) 676.
[42] J.D. Ferrara, A. Djebli, C. Tessler-Youngs and W.J. Youngs, J. Am. Chem. Soc., 110 (1988) 647.
[43] J.D. Ferrara, C. Tessler-Youngs and W.J. Youngs, Inorg. Chem., 27 (1988) 2201.
[44] J.S. Thompson and J.F. Whitney, J. Am. Chem. Soc., 105 (1983) 5488.
[45] J.S. Thompson and J.F. Whitney, Inorg. Chem., 23 (1984) 2813.
[46] M. Munakata, S. Kitagawa, I. Kawada, M. Maekawa and H. Shimono, J. Chem. Soc., Dalton Trans., (1992) 2225.
[47] D.L. Reger and M.F. Huff, Organometallics, 11 (1992) 69.
[48] B. Lenders and W. Kläui, Chem. Ber., 123 (1990) 2233.
[49] G.A. Carriedo, J.A.K. Howard and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1984) 1555.
[50] G. Huttner and K. Knoll, Angew. Chem., 99 (1987) 765; Angew. Chem., Int. Ed. Engl., 26 (1987) 743.

[51] G. Huttner, D. Lange and E.O. Fischer, Angew. Chem., 83 (1971) 579; Angew. Chem., Int. Ed. Engl., 10 (1971) 556.

[52] H. Wadepohl, Angew. Chem., 104 (1992) 253; Angew. Chem., Int. Ed. Engl., 31 (1992) 247.

[53] A. Jain, K.M. Chi, T.T. Kodas, M.J. Hampden-Smith, J.D. Farr and M.F. Paffett, Chem. Mater., 3 (1991) 995.

[54] K.M. Chi, H.K. Shin, M.J. Hampden-Smith, T.T. Kodas and E.N. Duesler, Inorg. Chem., 30 (1991) 4293.

[55] K.M. Chi, T.S. Corbitt, M.J. Hampden-Smith, T.T. Kodas and E.N. Duesler, J. Organomet. Chem., 449 (1993) 181.

[56] D.M. Hoffman, R. Hoffmann and C.R. Fisel, J. Am. Chem. Soc., 104 (1982) 3858.

[57] F. Baert, A. Guelzim and P. Coppens, Acta Crystallogr., Sect. B, 40 (1984) 590.

[58] H. Lang and L. Zsolnai, Chem. Ber., 124 (1991) 259, and references cited therein; H. Lang and L. Zsolnai, Z. Naturforsch., Teil B, 45 (1990) 1529; H. Lang, H. Keller, W. Imhof and S. Martin, Chem. Ber., 123 (1990) 417.

[59] R.S. Dickson and P.J. Fraser, Adv. Organomet. Chem., 12 (1974) 323.

[60] R. Nast, Coord. Chem. Rev., 47 (1982) 89.

[61] O.M. Abu Salah and M.I. Bruce, J. Chem. Soc., Chem. Commun., (1972) 858.

[62] M.R. Churchill and S.A. Bezman, Inorg. Chem., 13 (1974) 1418.

[63] M.R. Churchill and B.G. DeBoer, Inorg. Chem., 14 (1975) 2630.

[64] O.M. Abu Salah and M.I. Bruce, Aust. J. Chem., 29 (1976) 531; O.M. Abu Salah and M.I. Bruce, Aust. J. Chem., 30 (1977) 2639.

[65] O.M. Abu Salah and M.I. Bruce, J. Chem. Soc., Chem. Commun., (1974) 688.

[66] P. Espinet, J. Fornies, F. Martinez, M. Tomas, E. Lalinde, M. Moreno, A. Ruiz and A.J. Welch, J. Chem. Soc., Dalton Trans., (1990) 791.

[67] International Tables for X-Ray Crystallography, Vol. 3, Kynoch Press, Birmingham, 1962, p. 278 (based on $d(\mathrm{Rh-Rh})_{\min} = 2.690$ Å and $d(\mathrm{Ag-Ag})_{\min} = 2.889$ Å in the pure metals).

[68] O.M. Abu Salah and M.I. Bruce, J. Chem. Soc., Dalton Trans., (1975) 2311.

[69] J. Fornies, E. Lalinde, F. Martinez, M.T. Moreno and A.J. Welch, J. Organomet. Chem., 455 (1993) 271.

[70] P. Espinet, J. Fornies, F. Martinez, M. Sotes, E. Lalinde, M.T. Moreno, A. Ruiz and A.J. Welch, J. Organomet. Chem., 403 (1991) 253.

[71] R. Uson, J. Fornies, B. Menjon, F.A. Cotton, L.R. Falvello and M. Tomas, Inorg. Chem., 24 (1985) 4651, and references cited therein.

[72] C.W. Chen and H.W. Whitlock. Jr., J. Am. Chem. Soc., 100 (1978) 4921.

[73] F. Vögtle, Th. Papkalla, H. Koch and M. Nieger, Chem. Ber., 123 (1990) 1097; E. Weber and F. Vögtle, Chem. Unserer Zeit, 23 (1989) 210; F. Vögtle, H.G. Löhr, J. Franke and D. Worsch, Angew. Chem., 97 (1985) 721; Angew. Chem., Int. Ed. Engl., 24 (1985) 727; F. Vögtle and E. Weber, Angew. Chem., 91 (1979) 813; Angew. Chem., Int. Ed. Engl., 18 (1979) 753.

[74] H. Lang and D. Seyferth, Z. Naturforsch., Teil B, 45 (1990) 212, and references cited therein.

[75] H. Lang and S. Blau, in preparation; S. Blau, Ph.D. Thesis, University of Heidelberg, 1995.

[76] G.L. Wood, C.B. Knobler and M.F. Hawthorne, Inorg. Chem., 28 (1989) 382; A. Sebald, P. Fritz and B. Wrackmeyer, Spectrochim. Acta, Part A, 41 (1985) 1405; R. Jimenez, M.C. Barral, V. Moreno and A. Sandoz, J. Organomet. Chem., 174 (1979) 281; A.J. Jenkins, M.F. Lappert and R.C. Shrivastava, J. Oganomet. Chem., 23 (1970) 165; J.H. Teuben and H.J. Liefde Meijer, J. Organomet. Chem., 17 (1969) 87; H. Köpf and M. Schmidt, J. Organomet. Chem., 10 (1967) 383.

[77] K. Yasufuku and H. Yamazaki, Bull. Chem. Soc. Jpn., 45 (1972) 2664.

[78] H. Lang and W. Imhof, Chem. Ber., 125 (1992) 1307.

[79] H. Lang, M. Herres and L. Zsolnai, Bull. Chem. Soc. Jpn., 66 (1993) 429.

[80] H. Lang and L. Zsolnai, J. Organomet. Chem., 406 (1991) C5.

[81] M. Ciriano, J.A.K. Howard, J.L. Spencer, F.G.A. Stone and H. Wadepohl, J. Chem. Soc., Dalton Trans., (1979) 1749.

[82] H. Lang, M. Herres, L. Zsolnai and W. Imhof, J. Organomet. Chem., 409 (1991) C7.

[83] M. Herres and H. Lang, J. Organomet. Chem., 480 (1994) 235.

[84] S.I. Troyanov, V. Varga and K. Mach, Organometallics, 12 (1993) 2820.

[85] H. Lang, M. Herres, K. Köhler and L. Zsolnai, J. Organomet. Chem., in press.
[86] M.D. Janssen, M. Herres, A. Spek, D.M. Grove, H. Lang and G. van Koten, in preparation.
[87] O.M. Abu Salah, M.I. Bruce and A.D. Redhouse, J. Chem. Soc., Chem. Commun., (1974) 855.
[88] O.M. Abu Salah and M.I. Bruce, J. Chem. Soc., Dalton Trans., (1975) 2311.
[89] A.J. Leusink, G. van Koten, J.W. Marsman and J.G. Noltes, J. Organomet. Chem., 55 (1973) 419.
[90] J. Blenkers, H.K. Hofstee, J. Boersma and G.J.M. van der Kerk, J. Organomet. Chem., 168 (1979) 251.
[91] J.R. Berenguer, L.R. Falvello, J. Fornies, E. Lalinde and M. Thomas, Organometallics, 12 (1993) 6.
[92] G. Bähr and P. Barba, in Houben-Weyl, Methoden der Organischen Chemie, Vol. XIII/1, Georg Thieme, Stuttgart, 1970, pp. 738–741, and references cited therein.
[93] P.W.R. Corfield and H.M.M. Shearer, Acta Crystallogr., 21 (1966) 957; E.A. Jeffery and T. Mole, J. Organomet. Chem., 11 (1968) 393.
[94] M.D. Janssen, M. Herres, K. Köhler, H. Lang and G. van Koten, in preparation.
[95] G. van Koten, J. Organomet. Chem., 400 (1990) 283.
[96] M.I. Bruce, O.M. Abu Salah, R.E. Davis and N.V. Raghavan, J. Organomet. Chem., 64 (1974) C48.
[97] G.A. Carriedo, D. Miguel, V. Riera and X. Solans, J. Chem. Soc., Dalton Trans., (1987) 2867.
[98] G.A. Carriedo, D. Miguel, V. Riera, X. Solans, M. Font-Altaba and M. Coll, J. Organomet. Chem., 299 (1986) C43.
[99] X. Solans, J. Solans, C. Miravitlles, D. Miguel, V. Riera and J.M. Rubio-Gonzalez, Acta Crystallogr., Sect. C, 42 (1986) 975.
[100] W. Beck, B. Niemer, J. Breitmair and J. Heidrich, J. Organomet. Chem., 371 (1989) 79; J. Heidrich, M. Steinmann, M. Appel, W. Beck, J.R. Philipps and W.C. Trogler, Organometallics, 9 (1990) 1296.
[101] S. Mihan and W. Beck, unpublished results.
[102] O.M. Abu Salah and M.I. Bruce, J. Chem. Soc., Dalton Trans., (1974) 2302.
[103] M.I. Bruce, R. Clark, J. Howard and P. Woodward, J. Organomet. Chem., 42 (1972) C107.
[104] R. Clark, J. Howard and P. Woodward, J. Chem. Soc., Dalton Trans., (1974) 2027.
[105] H. Lang, S. Blau, G. Rheinwald and L. Zsolnai, J. Organomet. Chem., in press.
[106] G. Rheinwald, Diplom-Thesis, University of Heidelberg, 1990.