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(η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡C–SiMe$_2$–C≡CSiMe$_3$)$_2$: a unique entry to monomeric and oligomeric alkyne–copper(I) and alkyne–silver(I) halides

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Abstract

The reaction of [Ti]Cl$_2$ (**1**) {[Ti]=(η^5-$C_5H_4SiMe_3$)$_2$Ti} with two equivalents of LiC≡C–SiMe$_2$–C≡CSiMe$_3$ (**2**) produces [Ti](C≡C–SiMe$_2$–C≡CSiMe$_3$)$_2$ (**3**). On treatment with [MX] (M = Cu: **4a** X = Cl, **4b** X = Br; M = Ag: **5a** X = Cl, **5b** X = Br) the tweezer complexes {[Ti](C≡C–SiMe$_2$–C≡CSiMe$_3$)$_2$}MX (M = Cu: **6a** X = Cl, **6b** X = Br; M = Ag: **7a** X = Cl, **7b** X = Br) are formed in which the Ti–C≡C–Si units are η^2-coordinated to a monomeric copper(I) or silver(I) halide moiety. When **6b** is further reacted with [CuBr] (**4b**), oligomeric {[Ti](C≡C–SiMe$_2$–C≡CSiMe$_3$)$_2$(CuBr)$_3$}$_n$ (**8**) is formed. This molecule contains a (η^2-TiC≡CSi)$_2$CuBr entity next to two (η^2-SiC≡CSi)CuBr moieties, of which the latter building blocks are responsible for the oligomeric structure. In addition, **8** can be prepared by the direct reaction of **3** with an excess of **4b**, respectively. However, when an excess of [AgX] is used, the only formed products are **7**; no polymeric material is obtained. A Group 11 metal exchange reaction is noticed, when **7a** or **7b** are reacted with [CuX]: depending on the amount of [CuX] used, monomeric **6** or oligomeric **8** is produced. An explanation is given by a better bonding synergysmus for the alkyne-to-copper interaction. The result of the X-ray structure analysis of compound **7b** is reported. The compound **7b** crystallizes in the monoclinic space group $C2/c$ with cell constants $a = 25.097(8)$, $b = 11.327(3)$, $c = 19.014(6)$ Å, $\beta = 122.36(3)°$, $V = 4566(2)$ Å^3 and $Z = 4$. The compound **7b** contains a monomeric (η^2-alkyne)$_2$AgBr moiety in which the silver(I) center possesses a trigonal-planar environment, caused by the η^2-coordinated TiC≡CSi units as well as a η^1-bonded bromine atom. However this differs from the behavior of compounds **6** and **7** in solution, where all four C≡C building blocks of the TiC≡CSi as well as the SiC≡CSi units are complexed by the transition metal entities MX (M = Cu, Ag X = Cl, Br). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanocene; Diyne; Copper(I); Silver(I)

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1. Introduction

Bis(alkynyl) titanocenes of type RC≡C–[Ti]–C≡CR {[Ti] = (η^5-$C_5H_4SiMe_3$)$_2$Ti; R = singly bonded organic ligand) can successfully be applied as organometallic π-tweezers for the breakdown of oligomeric or polymeric copper(I) and silver(I) aggregates [MX] (M = Cu, Ag; X = singly bonded inorganic or organic ligand), to form monomeric alkyne-stabilized MX entities [1–7]. Depending on the nature of the ligands X in heterobimetallic {[Ti](C≡CR)$_2$}MX (type **A** molecule) a manifold reaction chemistry is observed, such as carbon–carbon coupling, M–X substitution and e.g. copper–X addition reactions [8].

For the formation of structural type **A** molecules the availability of the organometallic bridging unit [Ti] is essential, since main-group linked 1,4-diynes, such as RC≡C–SiMe$_2$–C≡CSiMe$_3$ (R = H, SiMe$_3$), only afford with [CuX] oligomeric species of general composition {(Me$_2$Si(C≡CR)(C≡CSiMe$_3$)]Cu$_2$X$_2$}$_n$ (X = Cl, Br, OSO$_2$CF$_3$, ...) [2,9–11].

Nevertheless, the organic group R in Me$_2$Si(C≡CR)(C≡CSiMe$_3$) possesses a significant influ-

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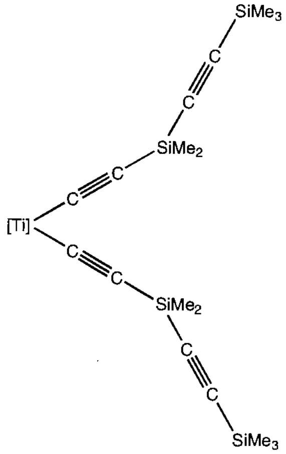
ence on the products formed: while the Me_3Si unit is a favourable group for the η^2-coordination of the C≡C triple bonds to copper, other organic groups only tend to bind or even show no tendency to coordinate to Group 11 metal atoms [2,10,13]. A similar finding is made for RC≡CR′ (R, R′ = singly bonded organic ligand or a hydrogen atom) [2,10,12,13].

In this paper we report the preparation of $[Ti](C{\equiv}C{-}SiMe_2{-}C{\equiv}CSiMe_3)_2$, a molecule, which features a titanocene moiety, [Ti], and a Me_2Si main-group fragment as bridging units between C≡C entities. This provides the possibility to directly compare the influence of the chemical behavior of the two different links towards copper(I) or silver(I) halides in one molecule.



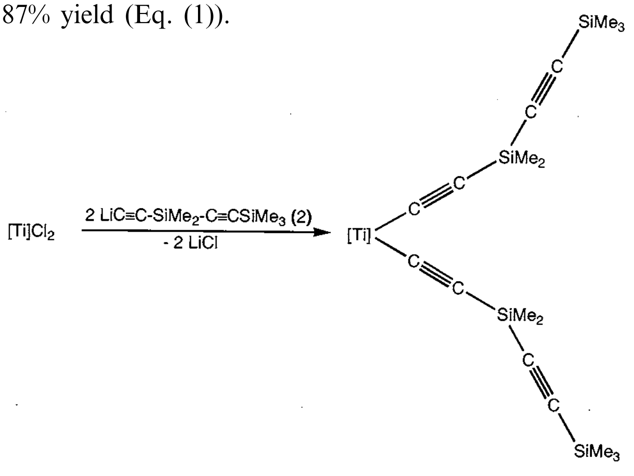
3

2. Results and discussion

2.1. Synthesis and reaction chemistry of *$[Ti](C{\equiv}C{-}SiMe_2{-}C{\equiv}CSiMe_3)_2$ (3)*

2.1.1. Synthesis

The titanocene dichloride $[Ti]Cl_2$ {[Ti] = η^5-$C_5H_4SiMe_3$) (**1**) [14] reacted at 0°C in diethyl ether with two molar equivalents of $LiC{\equiv}C{-}SiMe_2{-}C{\equiv}CSiMe_3$ (**2**) [15] produces $[Ti](C{\equiv}C{-}SiMe_2{-}C{\equiv}CSiMe_3)_2$ (**3**) in an 87% yield (Eq. (1)).

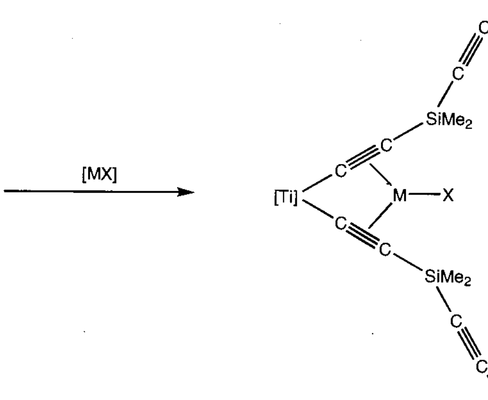


1 **3** (1)

Compound **3** after appropriate purification gave an deep red oily product, which is stable for months at 0°C. Compound **3** can be handled in air for short periods of time, whereas in solution a slow decomposition process takes place.

2.2. Reaction chemistry

Addition of **3** to an equimolar amount of [MX] (M = Cu, **4a** X = Cl, **4b** X = Br; M = Ag, **5a** X = Cl, **5b** X = Br) in toluene at 25°C resulted in the formation of heterobimetallic $\{[Ti](C{\equiv}C{-}SiMe_2{-}C{\equiv}CSiMe_3)_2\}MX$ (M = Cu: **6a** X = Cl, **6b** X = Br; M = Ag: **7a** X = Cl, **7b** X = Br), respectively (Eq. (2)).

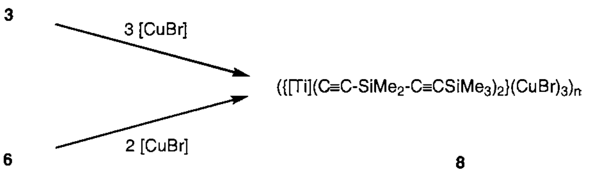


6, 7 (2)

Molecules **6** and **7** are highly soluble in common organic solvents, such as toluene, diethyl ether and THF and can be precipitated as bright orange (**6a**, **6b**) or orange–red solids (**7a**, **7b**) by cooling their diethyl ether/*n*-pentane solutions to − 30°C. While **3** only can be handled in air for short periods, complexes **6** and **7** are stable in air for months.

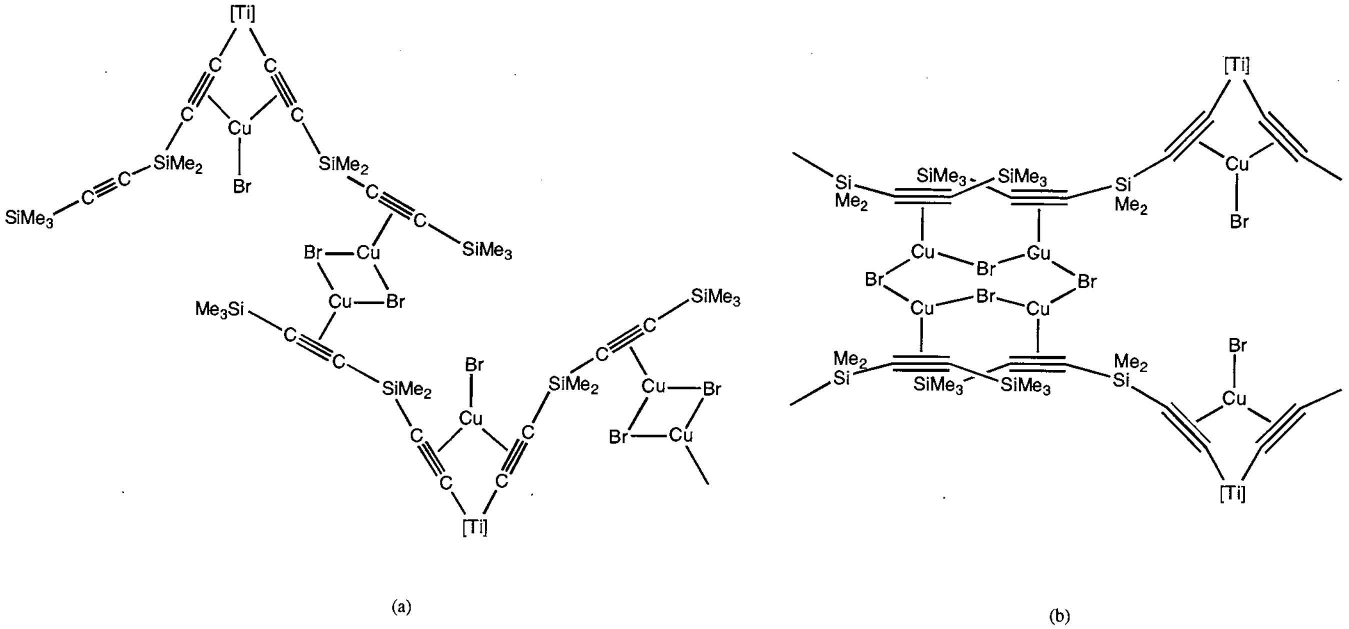
Compounds **6** and **7** feature a monomeric copper(I) or silver(I) halide moiety, which is η^2-complexed by the TiC≡CSi units, while the SiC≡CSi moieties are not coordinated.

When for example **6b** is further reacted with two equivalents of [CuBr] (**4b**) in toluene or diethyl ether at 25°C the titanium–copper oligomer $\{[Ti](C{\equiv}C{-}SiMe_2{-}C{\equiv}CSiMe_3)_2(CuBr)_3\}_n$ (**8**) is formed in quantitative yields (Eq. (3)). In addition **8** is also accessible by the reaction of **3** with three equivalents of (**4b**) in toluene at 25°C (Eq. (3)).



8 (3)

After appropriate work-up **8** can be obtained as a

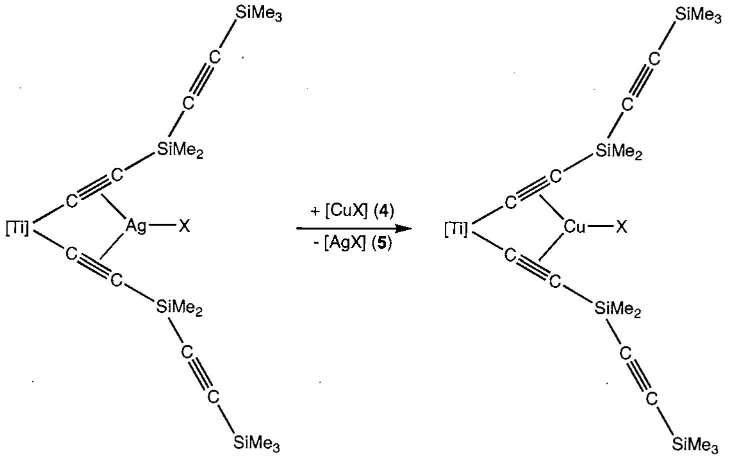


Scheme 1. Possible structural arrangements of oligomeric $\{[Ti](C{\equiv}C{-}SiMe_2{-}C{\equiv}CSiMe_3)_2(Cu_3Br_3)\}_n$ (**8**).

air-stable orange solid, which is nicely soluble in e.g. toluene or methylenchloride. In **8** a total of three CuBr entities are present of which one is chelate bonded by the inner $TiC{\equiv}CSi$ units, while the others are each η^2-coordinated by the outer C_2-moieties, $SiC{\equiv}CSi$, resulting in an oligomeric structure (Scheme 1).

A similar bonding situation is observed, when silicon containing diynes like $Me_2Si(C{\equiv}CR)(C{\equiv}CSiMe_3)$ (R = H, $SiMe_3$) or bis(alkynyl) functionalized phosphanes and sulfanes are used [2,9,10]. In addition, the obtained products show a similar chemical behavior with inorganic copper(I) compounds, producing oligomeric alkyne–copper(I) species.

Despite this finding, no reaction takes place when the latter alkynes or diynes are reacted with silver(I) aggregates [2,16]. The same behavior is found, when the titanium–silver complexes **7a** and **7b** are reacted with [AgX] (**5a** X = Cl, **5b** X = Br): no reaction with the $SiC{\equiv}CSi$ units is observed, even not when a ten-fold excess of [AgX] is used and/or the reaction mixture is kept under reflux. An explanation of this finding is given by a weaker alkyne-to-silver interaction compared to the appropriate copper(I) species. In addition, this could be clearly evidenced in the reaction of **7a** and **7b** with [CuX]: heterobimetallic **7a** and **7b** rapidly exchanges their monomeric AgX moieties when they are reacted with aggregated copper(I) halides [CuX] in diethyl ether at 25°C, while the reverse reactions does not occur.



7 **6** (4)

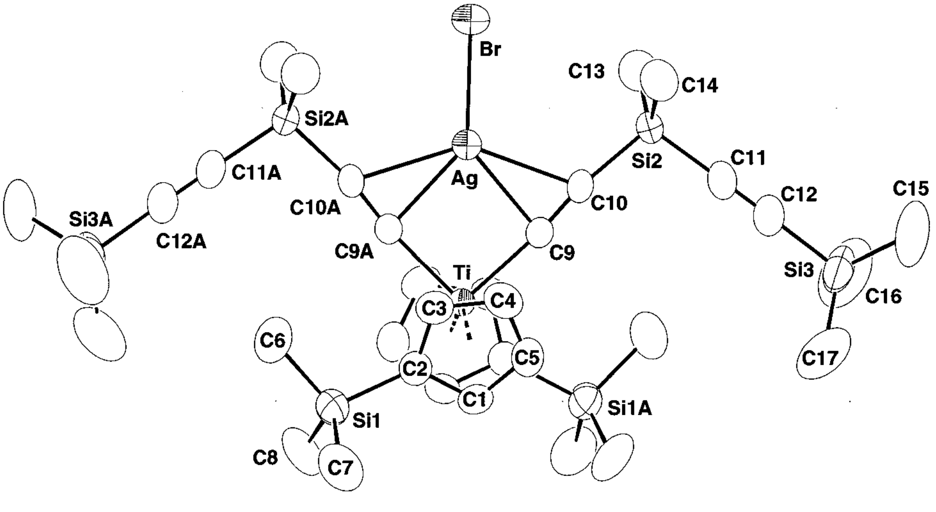


Fig. 1. Molecular geometry and atomic numbering scheme for **7b**. Selected bond distances (Å) and angles (°) are as follows: Ag–Ti 3.1711(14), Ag–Br 2.5172(10), Ag–C9 2.324(4), Ag–C10 2.484(4), Ti–C9 2.120(4), C9–C10 1.245(6), C10–Si2 1.844(5), Si2–C11 1.848(5), C11–C12 1.212(6); Ti–Ag–Br 180.0*, C9–Ti–C9A 94.2(2), Ti–C9–C10 173.2(3), C9–C10–Si2 171.3(4), Si2–C11–C12 178.0(5), C11–C12–Si3 177.4(5), D1–Ti–D2 135.5(1) (D1, D2 = centroids of the cyclopentadienyl ligands); *C_2-axis through Ti–Ag–Br.

The organometallic π-tweezer complexes $\{[Ti](C\equiv C{-}SiMe_2{-}C\equiv CSiMe_3)_2\}CuX$ (**6a** X = Cl, **6b** X = Br) are produced in quantitative yields (Eq. (4)). This experimental observation verifies the conclusion that the η^2-alkyne–copper bonding is stronger than the η^2-alkyne–silver one [3b,6a]. In this respect, metal exchange reactions are also typical for complexes of type $\{[Ti](C\equiv CR)_2\}ML_n$ ($ML_n = FeCl_2$, $CoCl_2$, $NiCl_2$) [2,17].

2.3. Structure and bonding

Compounds **6** and **7** are monomeric in solution as it could be shown by cryoscopy in benzene. FD- as well as FAB-MS studies are in agreement with this finding. For all new synthesized compounds the M^+ ion is observed. As further characteristic fragments M^+–X (X = Cl, Br) (**6**, **7**) and M^+–AgCl (**7a**) are found of which M^+–X represents in each case the basis peak.

The molecular structure in the solid state of **7b** was established by X-ray diffraction analysis [18]. Selected geometrical details are listed in the appendix of Fig. 1. Crystallographic parameters as well as atomic coordinates and equivalent isotropic displacement parameters are summerized in Table 1 and Table 2.

The monoclinic cell (space group $C2/c$) contains one discrete molecule of **7b** in which the titanium atom, the Group 11 metal silver and the σ-bonded bromine lie on a two-fold rotation axis. The coordination sphere around the silver atom is trigonal planar, involving η^2-coordinated $TiC\equiv CSi$ units and a η^1-bonded bromine atom. The symmetry requirements make the Ag and Br atoms as well as the two alkynyl units (centroides of the $TiC\equiv CSi$ triple bonds) strictly coplanar. The sum of the angles around silver is 360°. It is noteable that in **7b** the η^2-coordination of the $TiC\equiv CSi$ units results in a lengthening of the C≡C triple bonds as it can be nicely concluded by an internal comparison of the coordinated and non-coordinated C≡C units of the $Me_3SiC\equiv C{-}SiMe_2{-}C\equiv C$ units [C9–C10 1.245(6), C11–C12 1.212(6) Å] (Fig. 1). In addition, a *trans*-bending of

Table 1

Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($Å^2 \times 10^{-3}$) of **7b**[a]

Atom	x/a	y/b	z/c	U_{eq}
Ag	0	569(1)	2500	52(1)
Br	0	2792(1)	2500	80(1)
Ti	0	−2230(1)	2500	39(1)
Si(1)	−1364(1)	−4050(1)	703(1)	63(1)
Si(2)	879(1)	948(1)	4833(1)	48(1)
Si(3)	1957(1)	−1513(2)	7345(1)	76(1)
C(1)	−569(2)	−3869(4)	2559(3)	48(1)
C(2)	−953(2)	−3327(4)	1757(3)	51(1)
C(3)	−1112(2)	−2202(4)	1921(3)	54(1)
C(4)	−815(2)	−2041(4)	2787(3)	60(1)
C(5)	−479(2)	−3074(4)	3171(3)	59(1)
C(6)	−1745(3)	−2862(6)	−104(4)	113(2)
C(7)	−1963(3)	−5032(6)	679(4)	100(2)
C(8)	−840(3)	−4946(6)	490(4)	95(2)
C(9)	355(2)	−957(3)	3465(2)	46(1)
C(10)	544(2)	−119(4)	3966(3)	51(1)
C(11)	1262(2)	38(4)	5788(3)	62(1)
C(12)	1525(3)	−573(5)	6407(3)	67(1)
C(13)	1488(2)	1855(5)	4820(3)	71(1)
C(14)	257(2)	1874(5)	4778(3)	72(2)
C(15)	1915(4)	−796(7)	8182(4)	144(4)
C(16)	2771(4)	−1683(8)	7615(5)	144(4)
C(17)	1548(5)	−2968(7)	7104(5)	152(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2
Anisotropic displacement parameters ($Å^2 \times 10^3$)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag	74(1)	38(1)	39(1)	0	27(1)	0
Br	125(1)	40(1)	65(1)	0	45(1)	0
Ti	54(1)	32(1)	34(1)	0	25(1)	0
Si(1)	74(1)	58(1)	49(1)	−7(1)	28(1)	−15(1)
Si(2)	63(1)	43(1)	34(1)	−4(1)	24(1)	0(1)
Si(3)	95(1)	91(1)	49(1)	22(1)	43(1)	31(1)
C(1)	59(3)	39(2)	59(3)	4(2)	39(2)	0(2)
C(2)	53(3)	51(2)	49(2)	0(2)	28(2)	−3(2)
C(3)	53(3)	48(3)	63(3)	3(2)	32(2)	4(2)
C(4)	76(4)	54(3)	75(3)	−10(2)	56(3)	0(2)
C(5)	73(3)	67(3)	52(3)	−2(2)	42(3)	−11(3)
C(6)	146(6)	94(5)	57(4)	12(3)	26(4)	−6(4)
C(7)	108(5)	99(5)	93(5)	−31(4)	55(4)	−47(4)
C(8)	117(5)	96(4)	79(4)	−44(4)	57(4)	−26(4)
C(9)	61(3)	40(2)	35(2)	2(2)	24(2)	4(2)
C(10)	70(3)	46(2)	32(2)	4(2)	24(2)	4(2)
C(11)	78(3)	62(3)	40(3)	−6(2)	27(2)	−2(3)
C(12)	84(4)	71(3)	45(3)	−1(2)	33(3)	4(3)
C(13)	72(4)	72(3)	65(3)	−2(3)	34(3)	−4(3)
C(14)	84(4)	72(3)	67(3)	−6(3)	45(3)	9(3)
C(15)	204(9)	173(8)	63(4)	29(4)	77(5)	86(7)
C(16)	111(6)	204(10)	127(7)	66(6)	71(5)	62(6)
C(17)	201(9)	118(6)	129(7)	53(5)	83(7)	3(6)

[a] The anisotropic displacement factor exponent takes the form: $-2\ \mathrm{pi}^2\ [h^2\ a^{*2}\ U_{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U_{12}]$.

the TiC≡CSi entities is observed as result of the η^2-coordination to AgBr [Ti–C9–C10 173.2(3), C9–C10–Si2 171.3(4)°] (Fig. 1). However, this bending is not as significant as it is typically for $\{[Ti](C{\equiv}CR)_2\}AgX$ complexes (X = singly bonded organic or inorganic ligand) [1,2,5,6]. Through this deformation different silver–carbon bond lengths are found (Ag–C9 2.324(4), Ag–C10 2.484(4) Å) (Fig. 1). The Ag–Br interatomic distance of 2.5172(10) Å in **7a** is almost as long as experimentally observed in $[P(C_6H_4CH_2NMe_2\text{-}2)_3]AgBr$ (2.481(7) Å) [19], but significantly shorter as found in e.g. $\{[P(C_6H_5)_3]_2AgBr\}_2 \cdot CHCl_3$ (2.739 Å) [20a], $\{[P(C_6H_5)_3]_2AgBr\}_4$ (2.800 Å) [20a], $[P(C_2H_5)_3AgBr]_4$ (2.73 Å) [20b], or other phosphane–silver(I) species [20c–e].

A further characteristic feature of the $\{Ti(\eta^2\text{-}C{\equiv}CSi)_2\}AgBr$ building block is that the bite angle C9–Ti–C9a with 94.2(2)° is reduced in size when compared with non-coordinated bis(alkynyl) or bis(diynyl) titanocene species [1,2,3a,c]. The D1–Ti1–D2 angle (D1, D2 = centroids of the cyclopentadienyl ligands) is thereby not influenced (Fig. 1).

Additionally, it must be noted that the two SiC≡CSi entities are orientated away from each other (Fig. 1), which is different from the behavior of this compound in solution, where these two units are directed to each other in such a way that the silver atom is η^2-coordinated by a total of four C_2-building blocks (two TiC≡CSi and two SiC≡CSi moieties) (for a detailed discussion see below).

While in the solid-state only the TiC≡CSi moieties are η^2-coordinated to a low-valant monomeric MX unit, it is found that in solution all four C≡C building blocks are bonded in a η^2-fashion to the appropriate Group 11 metal center M (M = Cu, Ag; Fig. 2) as it could be clearly concluded by IR spectroscopy. For compounds **6** and **7** two distinct C≡C stretching vibrations for the TiC≡CSi units as well as for the SiC≡CSi entities are found (Fig. 2).

Through the η^2-coordination of the C≡C building blocks to the metal centers M in **6** and **7**, the ν(C≡C) vibrations are shifted from 2070 (SiC≡CSi) or 2019 cm^{-1} (TiC≡CSi) in the parent compound **3** to lower wavenumbers, indicating a bond weakening of the C≡C triple bonds. This shifting is similar to that generally observed for π-bonding of alkynes or diynes to copper(I) or silver(I) moieties in which the C≡C units are acting as two-electron donor entities [1,2,20]. A similar

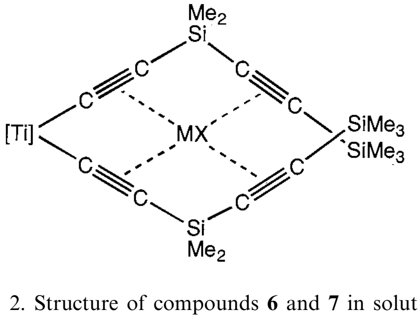


Fig. 2. Structure of compounds **6** and **7** in solution.

behavior of the C≡C moieties is found for oligomeric **8** in which the TiC≡CSi as well as the SiC≡CSi entities are complexed by the transition metal fragment CuBr, respectively. Since in the latter compound the SiC≡CSi building blocks are each η^2-coordinated to one CuBr fragment, the C≡C stretching vibration appears at a higher frequency as compared with compound **6b**. This points to the fact—as expected—that in **8** a stronger alkyne-to-copper bonding is observed for the (η^2-SiC≡CSi)CuBr fragments than for **6b** in solution, where (η^2-SiC≡CSi)$_2$CuBr entities are typical.

By comparing the ν(TiC≡CSi) stretching vibrations of the isostructural copper(I) and silver(I) halides **6** and **7** (**6a**: 1916, **6b**: 1914 cm^{-1}; **7a**: 1947, **7b**: 1946 cm^{-1}) it is obvious that these data show that in the alkyne-to-metal interaction the C≡C triple bond is weakened more in the case of copper(I) than for silver(I). In this respect, the back-donation of filled metal orbitals into empty alkyne π^*-orbitals is stronger in the series copper > silver [2–6].

The ^{1}H- and ^{13}C{^{1}H}-NMR spectra of all new synthesized compounds **3**, **6** and **7** in CDCl$_3$ consist of sharp and well resolved signals for each of the organic groupings present; i.e. two singlets for the TMS protons of the C$_5$H$_4$ and C≡C units, one singlet for the protons of the SiMe$_2$ link as well as two pseudo-triplets for the cyclopentadienyl protons with $J_{HH} = 1.6–2.3$ Hz.

Noteworthy in the ^{1}H-NMR spectra of compounds **6** and **7** is the shifting of the cyclopentadienyl protons from 5.7 and 6.4 in **3** to 5.9–6.3 in **6** and **7**. While the AA′XX′ resonance patterns in **3** are nicely separated ($\Delta\delta = 0.7$ ppm), it is observed that in heterobimetallic **6** the difference of the two AA′XX′ patterns is 0.2 ppm and in **7** only 0.03 ppm, resulting in almost magnetical equivalent groupings in the latter molecules. This behavior is specific for (η^2-alkyne)$_2$AgX compounds (X = inorganic and organic singly bonded ligands) [2,5a].

Due to the η^2-coordination of the TiC$_\alpha$≡C$_\beta$Si units to the appropriate MX units in **6** (M = Cu) or **7** (M = Ag) the ^{13}C-NMR signals of the C$_\alpha$ atoms at 171.9 ppm in **3**, shift downfield (**6a**: 169.5, **6b**: 170.0, **7a**: 155.4, **7b**: 156.1 ppm), while the C$_\beta$ atoms, at 131.1 ppm in **3**, are shifted to higher field in **6** (**6a**: 130.7, **6b**: 130.7 ppm) and to lower field in **7** (**7a**: 135.5, **7b**: 135.6 ppm), a phenomena typical for this type of compound [1–8].

In contrast to (η^2-alkyne)$_2$AgR molecules (R = single bonded organic ligand) no coupling constant $J^{107,109}$Ag^{13}C of the silver atom with the C$_\alpha$ and C$_\beta$ carbon atoms of the TiC$_\alpha$≡C$_\beta$Si entities is found.

Upon the η^2-coordination of the TiC≡CSi building blocks to MX the SiC≡CSi units are thereby not significally influenced, when the chemical shift of the alkynyl carbon atoms of **6** and **7** are compared with **3**.

3. Experimental section

3.1. General comments

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Diethyl ether, THF and toluene were purified by distillation from sodium/benzophenone ketyl; *n*-pentane was purified by distillation from calcium hydride. IR spectra were obtained with a Perkin-Elmer 983G spectrometer. ^{1}H-NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200.132 MHz in the Fourier transform mode; ^{13}C{^{1}H}-NMR spectra were recorded at 50.323 MHz and ^{29}Si{^{1}H}-NMR spectra at 39.763 MHz. Chemical shifts are reported in δ units (ppm) downfield from TMS with the solvent as the reference signal. FD and FAB MS were recorded on a Finnigan 8400 mass spectrometer operating in the positive-ion mode. Melting points were determined using analytically pure samples sealed off in nitrogen-purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. C, H, N-Microanalyses were performed by the Organisch-Chemisches Institut, University of Heidelberg.

3.2. Synthesis of [Ti](C≡C–SiMe$_2$–C≡CSiMe$_3$) (3)

To 1.0 g (2.54 mmol) of [Ti]Cl$_2$ (**1**) [14] in 150 ml of diethyl ether was added two equivalents of LiC≡C–SiMe$_2$–C≡CSiMe$_3$ [15] (**2**) at −50°C. After the reaction mixture was warmed to 25°C stirring was continued for 3 h. All volatiles were then evaporated in vacuo. The resulting dark red residue was extracted with 50 ml of a *n*-pentane/diethyl ether mixture (1:1) and filtrated through a pad of Celite. Removal of the solvents afforded orange oily **3** in 1.5 g (2.20 mmol, 87% based on **1**).

IR (KBr): 2070 (s) $\nu_{SiC≡CSi}$, 2019 (vs) $\nu_{TiC≡CSi}$ cm^{-1}. ^{1}H-NMR (C$_6$D$_6$) δ 0.17 (s, SiMe$_3$, 18 H), 0.37 (s, SiMe$_2$, 12 H), 0.44 (s, SiMe$_3$, 18 H), 5.8 (m, C$_5$H$_4$, 4 H), 6.4 (m, C$_5$H$_4$, 4 H). ^{13}C{^{1}H}-NMR (C$_6$D$_6$) δ −1.0 (SiMe$_3$), −0.2 (SiMe$_3$), −0.1 (SiMe$_2$), 111.1 (C≡C), 112.5 (C$_5$H$_4$), 122.6 (C$_5$H$_4$), 124.8 (C≡C), 125.2 (^{i}C/C$_5$H$_4$), 131.1 (TiC≡*C*), 171.9 (Ti*C*≡C). ^{29}Si{^{1}H} DEPT NMR (45°, 10 Hz) (C$_6$D$_6$) δ −46.7 (SiMe$_2$), −19.1 (SiMe$_3$), −5.9 (SiMe$_3$). MS-FAB [*m*/*z* (rel. int.)] 681(28) M$^+$, 502 (38) M$^+$–C$_4$Si$_2$Me$_5$, 323 (100) M$^+$–C$_4$Si$_2$Me$_5$. Anal. Calc. for C$_{34}$H$_{56}$Si$_6$Ti (681.23): C, 59.94; H, 8.29. Found: C, 59.70; H, 8.47.

3.3. Synthesis of {[Ti](C≡C–SiMe$_2$–C≡CSiMe$_3$)$_2$}CuX (6a X = Cl, 6b X = Br)

3.3.1. Reaction of 3 with 4

In total 650 mg (0.95 mmol) of [Ti](C≡C–SiMe$_2$–C≡CSiMe$_3$)$_2$ (**3**) were dissolved in 80 ml of toluene. In one portion one equivalent of [CuX] [21] (X = Cl, Br) was added. After the reaction mixture was stirred for 2 h at 25°C the dark red solution was filtered through a pad of Silicagel. All volatile materials were removed in vacuo and the corresponding yellow to orange residues were extracted twice each with 50 ml of *n*-pentane.

Compound **6a**: Yield: 630 mg (0.8 mmol, 84% based on **3**). M.p. 132°C (Decomp.). IR (KBr): 1944 (s) $\nu_{SiC\equiv CSi}$, 1916 (vs) $\nu_{TiC\equiv CSi}$ cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.27 (s, $SiMe_3$, 18 H), 0.28 (s, $SiMe_3$, 18 H), 0.53 (s, $SiMe_2$, 12 H), 5.96 (dd, $J_{HH} = 2.1$ Hz, C_5H_4, 4 H), 6.17 (dd, $J_{HH} = 2.1$ Hz, C_5H_4, 4 H). $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ -0.1 ($SiMe_3$), 0.2 ($SiMe_3$), 0.3 ($SiMe_2$), 112.2 ($C\equiv C$), 114.0 ($C\equiv C$), 114.5 (C_5H_4), 116.6 (C_5H_4), 123.6 ($^iC/C_5H_4$), 130.7 ($TiC\equiv \mathit{C}$), 169.5 ($Ti\mathit{C}\equiv C$). MS-FD [*m*/*z* (rel. int.)] 780(97) M^+, 743(100) M^+-Cl. Anal. Calc. for $C_{34}H_{56}ClCuSi_6Ti$ (780.23): C, 52.34; H, 7.23. Found: C, 52.12; H, 6.98.

Compound **6b**: 580 mg (0.7 mmol, 85% based on **3**). M.p. 149°C (decomp.). IR (KBr): 1942 (s) $\nu_{SiC\equiv CSi}$, 1914 (vs) $\nu_{TiC\equiv CSi}$ cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.17 (s, $SiMe_3$, 18 H), 0.26 (s, $SiMe_3$, 18 H), 0.53 (s, $SiMe_2$, 12 H), 6.00 (dd, $J_{HH} = 2.3$ Hz, C_5H_4, 4 H), 6.19 (dd, $J_{HH} = 2.3$ Hz, C_5H_4, 4 H). $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ -0.1 ($SiMe_3$), 0.3 ($SiMe_3$), 0.7 ($SiMe_2$), 112.2 ($C\equiv C$), 113.8 ($C\equiv C$), 114.3 (C_5H_4), 116.7 (C_5H_4), 123.9 ($^iC/C_5H_4$), 130.7 ($TiC\equiv \mathit{C}$), 170.0 ($Ti\mathit{C}\equiv C$). MS-FD [*m*/*z* (rel. int.)] 826(100) M^+, 745(24) M^+-Br. Anal. Calc. for $C_{34}H_{56}BrSi_6Ti$ (824.68): C, 49.51; H, 6.85. Found: C, 49.00; H, 6.54.

3.3.2. Reaction of **7** with **4**

In total 100 mg of **7a** (0.12 mmol) or **7b** (Synthesis Section 3.4) were dissolved in 50 ml of toluene and one equivalent of CuX [21] (**4a** X = Cl, **4b** X = Br) were added in one portion. After 2 h of stirring at 25°C the reaction mixture was worked-up as described in Section 3.3.1. The yield of **6a** and **6b** was quantitative. The spectroscopic and analytical data of **6a** and **6b** are listed in Section 3.3.1.

3.4. Synthesis of compounds $\{[Ti](C\equiv C-SiMe_2-C\equiv CSiMe_3)_2\}AgX$ (**7a** X = Cl, **7b** X = Br)

3.4.1. Reaction of **3** with **5**

In total 500 mg (0.73 mmol) of $[Ti](C\equiv C-SiMe_2-C\equiv CSiMe_3)_2$ (**3**) were dissolved in 100 ml of toluene. To this solution equimolar amounts of [AgX] (**5a** X = Cl, **5b** X = Br) were added in one portion. Stirring was continued for 5 h in the dark. The reaction mixture was then filtered through a pad of Celite. The solvent was evaporated in vacuo and the red residue obtained was crystallized from diethyl ether/*n*-pentane (1:1) at −30°C.

Compound **7a**: Yield: 540 mg (0.66 mmol, 90% based on **3**). M.p. 181°C (decomp.). IR (KBr): 1947 (vs) $\nu_{TiC\equiv CSi}$ cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.16 (s, $SiMe_3$, 18 H), 0.26 (s, $SiMe_3$, 18 H), 0.50 (s, $SiMe_2$, 12 H), 6.26 (dd, $J_{HH} = 2.2$ Hz, C_5H_4, 4 H), 6.30 (dd, $J_{HH} = 2.2$ Hz, C_5H_4, 4 H). $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ -0.1 ($SiMe_3$), 0.2 ($SiMe_3$), 0.6 ($SiMe_2$), 111.0 ($C\equiv C$), 114.7 ($C\equiv C$), 116.4 (C_5H_4), 118.8 (C_5H_4), 126.1 ($^iC/C_5H_4$), 135.5 ($TiC\equiv \mathit{C}$), 155.4 ($Ti\mathit{C}\equiv C$). MS-FAB [*m*/*z* (rel. int.)] 787(55) M^+-Cl, 680(100) M^+-AgCl. Anal. Calc. for $C_{34}H_{56}AgClSi_6Ti$ (824.55): C, 49.53; H, 6.85. Found: C, 48.84; H, 6.66.

Compound **7b**: Yield: 580 mg (0.67 mmol, 90% based on **3**). M.p. 175°C (decomp.). IR (KBr): 1946 (vs) $\nu_{TiC\equiv CSi}$ cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.16 (s, $SiMe_3$, 18 H), 0.27 (s, $SiMe_3$, 18 H), 0.52 (s, $SiMe_2$, 12 H), 6.29 (dd, $J_{HH} = 1.6$ Hz, C_5H_4, 4 H), 6.31 (dd, $J_{HH} = 1.6$ Hz, C_5H_4, 4 H). $^{13}C\{^1H\}$-NMR ($CDCl_3$) δ -0.2 ($SiMe_3$), 0.1 ($SiMe_3$), 0.8 ($SiMe_2$), 110.9 ($C\equiv C$), 115.0 ($C\equiv C$), 116.4 (C_5H_4), 118.9 (C_5H_4), 126.2 ($^iC/C_5H_4$), 135.6 ($TiC\equiv \mathit{C}$), 156.1 ($Ti\mathit{C}\equiv C$). MS-FD [*m*/*z* (rel. int.)] 789 M^+-Br. Anal. Calc. for $C_{34}H_{56}AgBrSi_6Ti$ (869.00): C, 46.99; H, 6.50. Found: C, 46.54; H, 6.04.

3.5. X-ray structure determinations of **7b**

The structure of heterobimetallic **7b** was determined from single crystal X-ray diffraction data, which were collected using a Siemens R3m/V (Nicolet Syntex) diffractometer. Single crystals were obtained by cooling a concentrated solution of **7b** in methylenchloride/*n*-pentan to −30°C. Crystal data and numerical details of the structure determination are as fellows: empirical formula $C_{34}H_{56}AgBrSi_6Ti$, molecular weight 869; crystal dimension $0.40 \times 0.30 \times 0.20$ mm^3. Crystal system: monoclinic with space group $C2/c$ with unit cell dimensions $a = 25.097(8)$, $b = 11.327(3)$, $c = 19.014(6)$ Å; $\beta = 122.36(3)°$; $V = 4566(2)$ Å^3, $Z = 4$ and $D_{calc.} = 1.264$ g cm^{-3}.

Accurate unit cell parameters and orientation matrices were derived from the setting angles of 25 well-centered reflections in the range $1.92 \leq \theta \leq 25.5°$. All data were collected at 293(2) K, scan mode $\omega/2\theta$ (2θ limits: $3.8 \leq 2\theta \leq 51°$) using Mo–$K_\alpha$ radiation ($\lambda = 0.71069$ Å, graphite monochromator). A total of 5021 reflections were measured of which 4227 independent reflections were used for refinement (2830 observed reflections $[I \leq 2\sigma(I)]$). Parameters refined: 251. Final R-values $[I \geq 2\sigma(I)]$: $R_1 = 0.0467$ and $wR_2 = 0.1063$. Absorption coefficient: 1.656 mm^{-1}. Residual electron density: 0.577 and -0.981 e Å^{-3}. $F(000)$: 1792. Goodness-of-fit on F^2: 0.999.

The structure of **7b** was solved by direct methods (SHELXS 86, G.M. Sheldrick, Program for Crystal Structure Solution, University of Göttingen, 1986) and subsequent difference Fourier techniques. An empirical absorption correction was applied. The structure was refined by the least-squares method based on F^2 with all measured reflections (SHELXL 93; G.M. Sheldrick, Program for Crystal Structure Refinement, University of Göttingen, 1993). Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters.

3.6. Synthesis of $\{[Ti](C{\equiv}C{-}SiMe_2{-}C{\equiv}CSiMe_3)_2\}$-$(Cu_3Br_3)$ (**8**)

3.6.1. Reaction of **3** with **4b**

As already described for the preparation of **6b** 500 mg (0.73 mmol) of **3** were treated with three equivalents of [CuBr] (**4b**) in 80 ml of toluene at 25°C. Appropriate work-up afforded **8b** in 790 mg (0.71 mmol, 97% based on **3**) yield.

Mp. 126°C. IR (KBr): 1936 (s) $\nu_{SiC\equiv CSi}$, 1916 (vs) $\nu_{TiC\equiv CSi}$ cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.0–0.2 (m, $SiMe_3$, 36 H), 0.9 (m, $SiMe_2$, 12 H), 6.0–6.5 (m, C_5H_4, 8 H). Anal. Calc. for $C_{34}H_{56}Br_3Cu_3Si_6Ti$ (1111.59): C, 36.72; H, 5.10. Found: C, 36.90; H, 4.94.

3.6.2. Reaction of **6b** with **4b**

In a similar manner as described above 100 mg (0.12 mmol) of **6b** are reacted with two equivalents of **4b** in 40 ml of toluene. The analytical and spectroscopic data of **6b** are listed in Section 3.6.1. Yield: 125 mg (0.11 mmol, 95% based on **6b**).

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