Titanocene-based group-11 metal ions; solid-state structure of $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CPh)_2]_2Ag\}NO_3$

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Abstract

The reaction of $[Ti](C\equiv CR)_2$ $\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti; \mathbf{1a}, R = Fc, Fc = (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5); \mathbf{1b}, R = Ph\}$ with MX $\{\mathbf{2a}, MX = [Cu(N\equiv CCH_3)_4]BF_4; M = Ag; \mathbf{2b}, X = ClO_4; \mathbf{2c}, X = NO_3\}$ in a 2:1 molar ratio produces the trinuclear heterobimetallic (Ti_2M) or heptanuclear heterotrimetallic (Ti_2MFe_4) complexes $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CR)_2\}_2M]X$ ($R = Fc$: $\mathbf{3a}$, $M = Cu$, $X = BF_4$; $\mathbf{3b}$, $M = Ag$, $X = ClO_4$. $R = Ph$: $\mathbf{3c}$, $M = Cu$, $X = BF_4$; $\mathbf{3d}$, $M = Ag$, $X = ClO_4$; $\mathbf{3e}$, $M = Ag$, $X = NO_3$) in high yield. Complexes $\mathbf{3c}$–$\mathbf{3e}$ are also accessible, when $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CPh)_2\}MX$ ($M = Cu$: $\mathbf{4a}$, $X = FBF_3$; $M = Ag$: $\mathbf{4b}$, $X = OClO_3$; $\mathbf{4c}$, $X = ONO_2$) is reacted with one equivalent of $\mathbf{1b}$. Transferring this reaction scheme to $[Ti](C\equiv CSiMe_3)_2$ ($\mathbf{1c}$) only the formation of the heterobimetallic tweezer complex $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}MX$ $\{\mathbf{4d}, MX = [Cu(N\equiv CCH_3)]BF_4; \mathbf{4e}, MX = AgOClO_3\}$ is observed which is attributed to the bulkiness of the acetylide-bound Me_3Si group. The solid-state structure of $\mathbf{3e}$ is reported. In $\mathbf{3e}$, two $[Ti](C\equiv CPh)_2$ tweezer moieties are chelate-bound by their carbon–carbon triple bonds to a silver(I) ion, resulting in a pseudo-tetrahedral environment at the group-11 metal. NO_3^- is acting as counter-ion to cationic $[\{[Ti](C\equiv CPh)_2\}_2Ag]^+$.

Additionally, the result of cyclic voltammetric studies on $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CPh)_2\}_2Cu]BF_4$ ($\mathbf{3c}$) is reported.
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1. Introduction

Bis(alkynyl) titanocenes $[Ti](C\equiv CR)_2$ $\{[Ti] = (\eta^5\text{-}C_5H_5)_2Ti, (\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4SiMe_3)Ti, (\eta^5\text{-}C_5H_4SiMe_3)_2Ti,\ldots; R = $ singly bound organic or organometallic group$\}$ can be used as organometallic π-tweezers to stabilise a high variety of low-valent group-11 metal species MX (M = group-11 metal atom, X = singly or chelate-bound inorganic or organic fragment) in their monomeric state [1]. The respective MX entities are thereby chelate-bound by the alkynyl groups of the or-

ganometallic π-tweezer $[Ti](C\equiv CR)_2$ [1]. In the so assembled $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CR)_2\}$ MX species, an early (Ti) and a late (M) transition metal atom are spanned by the σ- and π-bound alkynyl groups $RC\equiv C$ [1].

Next to such heterobimetallic early-late tweezer systems, also oligometallic complexes can be synthesised [1–9] in which $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CR)_2\}M$ units (M = Cu, Ag) are spanned by halides [2–4], pseudohalides [2], bi- or oligocarboxylates [2,5,6] or even di- and tetracyano-argentates or -cuprates [2,7,8]. The latter species are of interest as model compounds to study intramolecular electron-transfer [9], since the corresponding inorganic, organic or organometallic linking groups allow to set-up π-conjugated bridges between the respective transition metal atoms. Synergistic and co-operative effects between the respective metals are typical [1,9].

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The title complexes in which two titanium-tweezer fragments are connected via a group-11 transition metal ion, have recently been reported with sterically less demanding groups at the alkynyl ligands, for example, $\{[(\eta^5\text{-}C_5H_4R')_2Ti(C\equiv C\text{-}C\equiv CFc)_2]_2Ag\}PF_6$ [R′ = H, SiMe$_3$; Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$] [10]. Similar compounds are accessible, when the bis(alkynyl) titanocene units are replaced by bis(alkynyl) platinum entities [11–13].

In this paper, we focus on the synthesis, reaction chemistry, structure and bonding of complexes of structural type $[\{[Ti](\mu\text{-}\sigma, \pi\text{-}C\equiv CR)_2\}_2M]^+X^-$ (M = Cu, Ag). The electro-chemical behaviour of such systems is also reported, since it is expected that the group-11 connectivity allows electronic communication between the remote transition metal ions Ti(IV) and M(I) (M = Cu, Ag) via the σ-, π-bound acetylides RC≡C.

2. Results and discussion

2.1. Synthesis and reaction chemistry of [{[Ti](μ-σ,π-CCR)₂}₂M]X

Treatment of $[Ti](C\equiv CR)_2$ {[Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2$-Ti; **1a**, R = Fc, Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ [14]; **1b**, R = Ph[15]} with MX {MX = [Cu(N≡CMe)₄]BF₄ **2a**; M = Ag: **2b**, X = ClO₄; **2c**, X = NO₃} in a 2:1 molar ratio results in the formation of the title complexes [{[Ti](μ-σ, π-C≡CR)₂}₂M]X (R = Fc: **3a**, M = Cu, X = BF₄; **3b**, M = Ag, X = ClO₄. R = Ph: **3c**, M = Cu, X = BF₄; **3d**, M = Ag, X = ClO₄; **3e**, M = Ag, X = NO₃). After appropriate work-up **3a**–**3e** can be isolated in yields between 80% and 95% (Scheme 1 and Table 1). The respective reactions are accompanied by a distinct colour change from green (**1a**) to turquoise (**3a** and **3b**) from red (**1b**) to orange (**3d** and **3e**) or yellow (**3c**). A further possibility to prepare **3c**–**3e** is given on treatment of the heterobimetallic π-tweezer complexes {[Ti](μ-σ,π-C≡CPh)₂}MX with [Ti](C≡CR)₂, as it could be shown, for example,

Table 1
Synthesis of **3a**–**3e**[a]

Compound	M	X	R	Yield[b] (%)
3a	Cu	BF₄	Fc[c]	90
3b	Ag	ClO₄	Fc[c]	80
3c	Cu	BF₄	Ph	88
3d	Ag	ClO₄	Ph	92
3e	Ag	NO₃	Ph	95

[a] Reaction of **1** with **2** in a 1:2 molar ratio (Scheme 1).
[b] Based on **1a** or **1b**, respectively.
[c] Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$.

in the reaction of {[Ti](μ-σ,π-C≡CPh)₂}MX (**4a**: M = Cu, X = FBF₃; **4b**: M = Ag, X = OClO₃; **4c**: M = Ag, X = ONO₂) with equimolar amounts of [Ti](C≡CPh)₂ (**1b**) (Scheme 1). In this reaction, the free tweezer molecule **1b** adds to the respective group-11 transition metal atom in **4** upon replacement of X. Complexes **3c**–**3e** are thereby formed in quantitative yield.

Furthermore, it was found that the reaction of **4a**–**4c** with **1b** is reversible. On treatment of **3c**–**3e** with the copper(I) or silver(I) salts [MX] (**2**) in the ratio of 1:1 gives the respective heterobimetallic Ti–Cu (**4a**) or Ti–Ag species (**4b** and **4c**) in quantitative yield (Scheme 1). This reaction demonstrates that the two tweezer entities [Ti](C≡CR)₂ are only weakly bound to the tetrahedral coordinated copper(I) or silver(I) ions M in **3**. The driving force of the latter reaction is probably attributed to the fact that in organometallic π-tweezer chemistry the most common, and apparently most stable coordination number at M is 3 [1–9]. In **4a**–**4c**, M possesses a trigonal–planar environment and the [(η²-C≡CPh)₂M]⁺ units follow a 16-valence electron count.

The reaction of **1** with **2** strongly depends on the group R at the alkynyl ligands in the starting materials **1a** and **1b**, respectively. If R (**1a**, R = Fc; **1b**, R = Ph) is replaced by a sterically more demanding group, such as Me₃Si {**1c**, [Ti](C≡CSiMe₃)₂} [15] only the heterobimetallic tweezer complexes {[Ti](μ-σ,π-C≡CSiMe₃)₂}MX [**4d**: M = Cu(N≡CCH₃), X = BF₄; **4e**: M = Ag, X = ClO₄
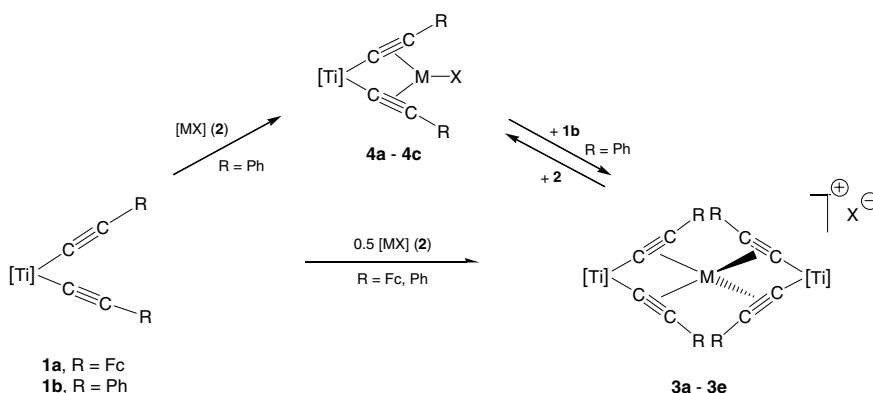
Scheme 1. Synthesis of **3a**–**3e** (M = Cu, Ag; R = Fc, Ph; X = ClO₄, BF₄, NO₃).

[2,16]] are formed. Neither prolonged stirring, nor heating the reaction mixture, or even using an excess of **1c**, did succeed in the formation of complexes similar to **3**. Obviously, the bulkiness of the Me_3Si groups in **1c**, as compared to Ph or Fc, prevents the formation of the corresponding metal-bridged bis(tweezer) complexes **3**.

A further interesting observation of our studies is that the heterobimetallic complexes **4a**–**4e** do not react with other chelating bis(alkynyl) transition metals, for example, cis-[Pt]($C\equiv CPh)_2$ {[Pt]=(bipy)Pt (**5a**), bipy = 2,2′-bipyridine; (bipy′)Pt (**5b**), bipy′ = 4,4′-dimethyl-2,2′-bipyridine} [11] to give bis-tweezer complexes of the general composition [{[Ti](μ-σ, π-$C\equiv CPh)_2$}M{[Pt](μ-σ,π-$C\equiv CPh)_2$}]X (**6**) (Eq. 1).

4a - 4c   **5a, 5b**   **6**

R = Ph
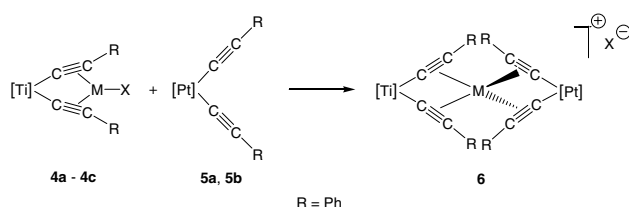
This is astonishing, since complexes of structural type [{[Ti](μ-σ, π-$C\equiv CR)_2$}$_2$M]X (vide supra) and [{[Pt](μ-σ,π-$C\equiv CR)_2$}$_2$M]X are known [11]. Presumably, not only sterical arguments, but also electronic effects may be playing a diminishing role. The titanocene tweezer [Ti]($C\equiv CPh)_2$ part binds more strongly to the respective MX entities than the respective bis(alkynyl) platinum entities [1,9].

2.2. Spectroscopy

All new complexes **3a**–**3e** were fully characterised by IR and NMR spectroscopy.

The IR spectra of **3a**–**3e** exhibit characteristic $C\equiv C$ stretching vibrations at 1986 (**3a**), 2015 (**3b**), 2002 cm^{-1} (**3c**) and 2036 (**3d, 3e**), while the starting materials **1a** and **1b** show their respective absorptions at 2054 [14] or 2068 cm^{-1} [15]. This is attributed to the η^2-coordination of the alkyne units to the metal ions M^+ (M = Cu, Ag), and corresponds to a bond weakening of the $C\equiv C$ triple bonds. However, this effect is less pronounced in **3** as in heterobimetallic π-tweezer complexes {[Ti](μ-σ,π-$C\equiv CR)_2$}MX [1], and can be explained by the presence of four competing (π-bound) alkyne units in **3**.

The counter-ions X^- [X = ClO_4 (**3d**), NO_3 (**3e**) and BF_4 (**3c**)] possess only one distinguished stretching vibration in the IR spectra at 1092 (ν_{ClO}, **3d**), 1383 (ν_{NO}, **3e**) or 1051 cm^{-1} (ν_{BF}, **3c**) which is typical for non-coordinated anions [17–19].

In addition, the side-on coordination of the alkynyl groups to M (M = Cu, Ag) is nicely reflected by the

chemical shifts of the C_α and the C_β carbon atoms (Ti–$C_\alpha\equiv C_\beta$). In the $^{13}C\{^1H\}$ NMR spectrum of **1a** the C_α carbon atoms appear at 153.7 ppm and the C_β atoms at 129.8 ppm [14], while in **3b** these signals are observed at 152.1 (C_α) and 182.3 ppm (C_β). However, in **3c**–**3e** the C_α and the C_β carbon atoms are shifted to higher field with respect to **1b** (C_α: **1b**, 152.3 [15]; **3d**, 141.8; **3e**, 142.0; **3c**, 142.4 ppm; C_β: **1b**, 132.4 [15]; **3d**, 130.6; **3e**, 130.4; **3c**, 128.3 ppm). This differs from heterobimetallic bis(alkynyl) titanocene tweezer chemistry, where the C_α atoms are shifted to lower field and the C_β carbon to higher field, when compared with non-coordinated [Ti]($C\equiv CR)_2$ [1].

All other organic groups in **3a**–**3e** appear as expected in the $^{13}C\{^1H\}$ NMR spectra.

The ^1H NMR spectra of all newly synthesised complexes (Scheme 1 and Table 1) exhibit well-resolved resonance signals for each of the organic groups present and show no conspicuous behaviour. For the different resonance sets of the cyclopentadienyl ring protons (**3a** and **3b**) a total of five signals are found of which the resonance signals for the ferrocene moieties [**3a**: 4.23 (s), 4.35 (pt), 4.45 (pt) ppm; **3b**: 4.33 (s), 4.57 (pt), 4.67 (pt) ppm] are shifted by ca. 1.8 ppm to higher field compared with the titanocene signals [**3a**: 6.2 (bs); **3b**: 6.01 (pt), 6.19 (pt) ppm]. In comparison with **1a**, the cyclopentadienyl protons of the Fc groups are somewhat shifted to lower field, while the C_5H_4 protons of the [Ti] entities are observed at higher field [14]. The signal pattern of the respective groups remains unaffected. This behaviour corresponds to observations made in systems of type {[Ti](μ-σ,π-$C\equiv CFc)_2$}MX [10,14,20].

In the same manner, the resonance signals of the C_5H_4 entities in **3c**–**3e** are high-field shifted in comparison to **1b** [15]. In **3d** and **3c**, as in **1b**, two sets are found at 6.06 and 6.27 ppm (**3d**) or 6.20 and 6.30 ppm (**3c**), while **3e** shows only one broad signal at 6.40 ppm (for comparison **1b**: 6.41 and 6.86 ppm) [1,15].

FAB-MS spectrometry of complexes **3a** and **3b** show for **3b** the M^+ peak at m/z = 1588, while for **3a** $M^+ - X$ (m/z = 1632) as peak with the highest m/z value is typical. For both complexes $(C_5H_4SiMe_3)_2Ti^+$ is found as base peak.

2.3. X-ray diffraction study

Single crystals of **3e** could be obtained by slow evaporation of a concentrated tetrahydrofuran solution containing **3e** at 20 °C. The solid-state structure of **3e** is depicted in Fig. 1 (the NO_3^- counter-ion is omitted for clarity). Selected interatomic distances and angles are listed in Table 2 and the crystallographic data are given in Table 3.

Complex **3e** crystallises in the monoclinic space group P2(1)/n with the cation, the anion and two non-coordinated Thf molecules in the asymmetric unit. Complex
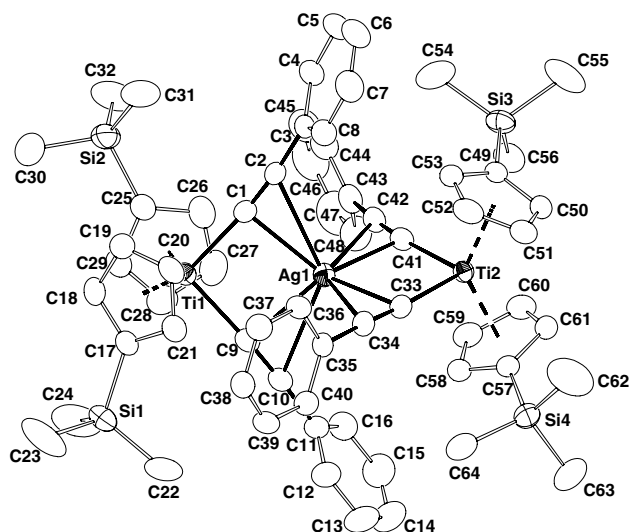
Fig. 1. Molecular structure and atom numbering scheme of the cationic part of **3e** (ZORTEP-PLOT with 50% probability level); the NO_3^- counter-ion is omitted for clarity.

Table 2
Interatomic distances (Å) and angles (°) of **3e**[a]

Interatomic distances			
Ti(1)–C(1)	2.132(3)	C(1)–C(2)	1.226(4)
Ti(1)–C(9)	2.118(3)	C(9)–C(10)	1.222(4)
Ti(2)–C(41)	2.127(3)	C(33)–C(34)	1.226(4)
Ti(2)–C(33)	2.121(3)	C(41)–C(42)	1.219(4)
Ti(1)–Ag(1)	3.2551(5)	Ti(2)–Ag(1)	3.2600(5)
Ag(1)–C(1)	2.386(3)	Ag(1)–C(2)	2.752(3)
Ag(1)–C(9)	2.399(3)	Ag(1)–C(10)	2.738(3)
Ag(1)–C(33)	2.409(3)	Ag(1)–C(34)	2.638(3)
Ag(1)–C(41)	2.353(3)	Ag(1)–C(42)	2.784(3)
Angles			
Ti(1)–C(1)–C(2)		173.4(2)	
Ti(1)–C(9)–C(10)		172.1(3)	
C(1)–C(2)–C(3)		173.2(3)	
C(9)–C(10)–C(11)		176.4(3)	
Ti(2)–C(33)–C(34)		176.4(2)	
Ti(2)–C(41)–C(42)		168.9(2)	
C(33)–C(34)–C(35)		176.1(3)	
C(41)–C(42)–C(43)		170.2(3)	
Ti(1)–Ag(1)–Ti(2)		176.50(1)	
C(1)–Ti(1)–Ti(9)		94.2(1)	
C(33)–Ti(2)–C(41)		93.7(1)	

[a] The estimated standard deviations of the last significant digit(s) are shown in parantheses.

3e features two [Ti](C≡CPh)$_2$ moieties, which are, via their alkynyl ligands PhC≡C, side-on bound to a silver(I) ion, thus resulting in a pseudo-tetrahedral coordination sphere around Ag(1) (Fig. 1). The two tweezer entities [Ti](C≡CPh)$_2$ are thereby positioned almost orthogonally to each other [80.63 (0.05)°]. While Ag(1) is placed in the plane spanned by the tweezer entity Ti(2), C(33), C(34), C(41) and C(42), it is located 0.230(3) Å outside of the plane spanned by Ti(1), C(1), C(2), C(9) and C(10).

Table 3
Crystal and intensity collection data for **3e**

Formula	$C_{72}H_{88}AgNO_5Si_4Ti_2$
Molecular mass	1363.46
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	15.4592(2)
b (Å)	27.29760(10)
c (Å)	16.9041(2)
V (Å^3)	7067.87(13)
β (°)	97.7790(10)
D_{calc} (g cm^{-3})	1.281
$F(000)$	2856
Z	4
Crystal dimensions (mm)	0.5×0.45×0.25
Diffractometer model	Bruker Smart CCD
Radiation (λ, Å)	0.71073
Maximum and minimum transmission	0.834979 and 0.672147
Absorption coefficient (μ, mm^{-1})	0.610
Temperature (K)	173(2)
Scan mode	ω-scan
Scan range (°)	1.43⩽θ⩽30.48
Total reflections	51,738
Unique reflections	19,264
Observed reflections [$I \geqslant 2\sigma(I)$]	12,048
Refined parameters	1043
R_1[a], wR_2[a] [$I \geqslant 2\sigma(I)$]	0.0474, 0.1031[b]
R_1[a], wR_2[a] (all data)	0.0970, 0.1246[b]
R_{int}, S	0.0480, 1.008[b]
Maximum and Minimum peak in final Fourier map (e Å^{-3})	0.864, −0.716

[a] $R_1 = [\sum(||F_o| - |F_c|) / \sum |F_o|]; wR_2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum(wF_o^4)]^{1/2};$ $p = [F_o^2 + 2F_c^2]/3c; S = [\sum w(F_o^2 - F_c^2)^2]/(n-p)^{1/2};$ $n =$ number of reflections, $p =$ parameters used.
[b] $w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 3.7035P]$.

Through the side-on coordination of the C≡C triple bonds to a tetra-coordinated silver(I) ion the bite angles C_α–Ti–C'_a in **3e** show, as typical for tweezer-type molecules [1], a reduction from 96.1(2)° in **1b** [1,20,21] to 94.2(1)° and 93.7(1)° in **3e** [1,21].

In this context, however, the interatomic bond distances of the alkynyl units C(1)–C(2) [1.226(4) Å], C(9)–C(10) [1.222(4) Å], C(33)–C(34) [1.226(4) Å] and C(41)–C(42) [1.219(4) Å] (Fig. 1) (Table 2) are almost not affected, when compared to [Ti](C≡CPh)$_2$ (**1b**) [1,21]. This differs from systems reported so far in organometallic π-tweezer chemistry, where elongations between 0.1 and 0.2 Å are typical [1].

A very remarkable feature of **3e** is the *cis*-deviation of the Ti–C_α≡C_β–C_{Ph} entities from linearity [Ti(1)–C(1)–C(2), 173.4(2)°; C(1)–C(2)–C(3), 173.2(3)°; Ti(1)–C(9)–C(10), 172.1(3)°; C(9)–C(10)–C(11), 176.4(3)°; Ti(2)–C(33)–C(34), 176.4(2)°; C(33)–C(34)–C(35), 176.1(3)°; Ti(2)–C(41)–C(42), 168.9(2)° and C(41)–C(42)–C(43), 170.2(3)°] (Table 2), which is typical for this type of molecules. However, this differs significantly from the geometrical behaviour characteristic for heterobimetallic early-late complexes of the type {[Ti](μ-σ,π-C≡CR)$_2$}MX {[Ti] = (η^5-C$_5$H$_5$)$_2$Ti, (η^5-C$_5$H$_4$SiMe$_3$)$_2$-Ti,...; R = SiMe$_3$, ^{t}Bu, Ph, Fc,...; MX = 10 to 12

valence electron complex fragment}, where a *trans*-deviation of the respective Ti–C≡C–C$_R$ units is observed. This is attributed to the tweezer effect of such species [1]. The unusual structural property of **3e** is probably based on the steric demands of the [Ti](C≡CR)$_2$ building blocks. As a result thereof, the distances Ag(1)–C$_\alpha$ [Ag(1)–C(1), 2.386(3); Ag(1)–C(9), 2.399(3); Ag(1)–C(33), 2.409(3); Ag(1)–C(41), 2.353(3) Å] are shorter than the Ag(1)–C$_\beta$ distances [Ag(1)–C(2), 2.752(3); Ag(1)–C(10), 2.738(3); Ag(1)–C(34), 2.638(3); Ag(1)–C(42), 2.784(3) Å] (Ti–C$_\alpha$–C$_\beta$) (Table 2). This points to an asymmetric η^2-coordination of the Ti–C≡C–Ph units to Ag(1). The Ag–C$_\beta$ distances resemble the upper limit of known silver–carbon interactions [22].

2.4. Electrochemical studies on 3c

In order to gain a closer insight into the electrochemical behaviour of the described complexes (vide supra), [{[Ti](µ-σ,π-C≡CPh)$_2$}$_2$Ag]BF$_4$ (**3c**) has been representatively subjected to cyclic voltammetric studies. The appropriate experiment was carried out in a tetrahydrofuran solution in the presence of [*n*-Bu$_4$N][PF$_6$] ($c = 0.1$ mol dm^{-3}) at 25 °C under N$_2$ with a scan rate of 200 mV s^{-1}. The potentials are referenced to the FcH/FcH$^+$ couple as internal standard.

Complex **3c** shows a wave at $E_0 = 0.10$ V ($\Delta E = 130$ mV), which can be assigned to the redox-couple Cu(I)/Cu(II). This observation is remarkable, since copper(II) complexes based on **1b**, where a singly bound organic group is present at the alkynyl ligands, could not be synthesised so far. Attempts to prepare such complexes failed, due to redox processes involved [1,23]. Up to now, only complexes, which feature the alkynyl σ-bound Fc ligand, as given in **1a**, could successfully be applied as organometallic chelating ligands to stabilise copper(II) salts such as CuCl$_2$ [24]. The latter species undergo in solution, as it is obtained for other systems (vide supra), a redox process to afford [Ti]Cl$_2$, FcC≡C–C≡CFc along with elemental copper [1,24].

The Cu(I)/Cu(0) reduction proves to be irreversible with E_{red} being −1.64 V, which is typical for titanium(IV)–copper(I) tweezer systems [2,9]. This finding is supported by the precipitation of elemental copper during the measurement. Going to even more negative values, another irreversible reduction at $E_{red} = -2.26$ V is observed. This can be assigned to the Ti(IV)/Ti(III) reduction. In comparison to **1b** [Ti(IV)/Ti(III): $E_0 = -1.76$ V ($\Delta E = 150$ mV)] [21] this reduction is significantly shifted to a more negative value. Similar data were found for {[Ti](µ-σ,π-C≡CPh)$_2$}Ni(CO), where the Ti(VI)/Ti(III) redox couple appears at $E_0 = -2.45$ V ($\Delta E = 150$ mV) [21]. Thus, the nature of the chemical species, which is formed after the Cu(I)/Cu(0) reduction process in **3c** can hardly be determined by means of cyclic voltammetric investigations.

3. Experimental section

All reactions were carried out in an atmosphere of purified nitrogen (O$_2$ traces: CuO catalyst, BASF AG/Ludwigshafen; H$_2$O: molecular sieve 4 Å) using standard Schlenk techniques. The light sensitive silver salts were handled in the dark, using flasks covered with aluminum foil. Solvents were purified by distillation; *n*-pentane, diethylether and tetrahydrofuran: sodium/benzophenone ketyl. FT-IR spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer as KBr pellets, as film between NaCl plates or as solution between CaF$_2$ plates. NMR spectra were recorded with a Bruker Avance 250 spectrometer; ^{1}H NMR spectra: 250.130 MHz (internal standard CDCl$_3$, $\delta = 7.27$); ^{13}C{^{1}H} NMR spectra: 67.890 MHz (internal standard CDCl$_3$, $\delta = 77.0$). Chemical shifts are reported in δ units (ppm) downfield from SiMe$_4$ with the solvent signal as reference ($\delta = 0$ ppm). Melting points were determined using analytically pure samples, sealed off in nitrogen purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. FAB-MS spectra were obtained with a Finnigan (Varian) MAT, model 8400. Electrochemical measurements were performed in tetrahydrofuran solutions containing (N^nBu$_4$)PF$_6$ (0.1 mol dm^{-3}) at 298 K, using a Radiometer system (type VoltaLab 31) with a glassy carbon working electrode, a platinum auxiliary electrode and a Ag/AgNO$_3$ reference electrode. The potentials are referenced to the ferrocene/ferrocenium couple. Microanalyses were performed by the Organic Department of Chemnitz, the Technical University and the Institute of Organic Chemistry at the University of Heidelberg.

3.1. General remarks

Complexes [Cu(N≡CCMe)$_4$]BF$_4$ (**2a**) [25], [Ti](C≡CFc)$_2$ (**1a**) [12], [Ti](C≡CPh)$_2$ (**1b**) [15], {[Ti](µ-σ,π-C≡CPh)$_2$}CuFBF$_3$ (**4a**) [1,2], {[Ti](µ-σ,π-C≡CPh)$_2$}AgOClO$_3$ (**4b**) [1,2] and {[Ti](µ-σ,π-C≡CPh)$_2$}AgONO$_2$ (**4c**) [1,2] were prepared according to the literature procedures. All other chemicals were purchased from commercial providers and used as received.

3.2. Synthesis of 3a

To 200 mg (0.24 mmol) of **1a**, dissolved in 40 mL of tetrahydrofuran, 38 mg (0.12 mmol) of [Cu(N≡C-CMe)$_4$]BF$_4$ (**2a**) is added in one portion at 25 °C. After 3 h of stirring at this temperature all volatile materials are evaporated in oil-pump vacuum. The residue is extracted with *n*-pentane (2×10 mL), dissolved in 30 mL of dichloromethane and then filtered through a pad of Celite. The filtrate is evaporated and dried in oil-pump vacuum to give 175 mg (0.11 mmol, 90% based on **1a**) of green coloured **3a**.

Anal. Calc. for $C_{80}H_{88}BCuF_4Fe_4O_4Si_4Ti_2$ (1631.63): C, 58.89; H, 5.43. Found: C, 58.89; H, 5.59%; m.p. [°C]: 117 (decomp.). IR (KBr) [ν_{max}/cm^{-1}]: 1986 [$\nu_{C\equiv C}$]. ^{1}H NMR (CDCl$_3$): [δ] 0.31 (s, 36H, SiMe$_3$), 4.23 (s, 20H, C$_5$H$_5$), 4.35 (pt, J_{HH} = 1.4 Hz, 8H, C$_5$H$_4$Fe), 4.45 (pt, J_{HH} = 1.4 Hz, 8H, C$_5$H$_4$Fe), 6.2 (bs, 16H, C$_5$H$_4$Ti). ^{13}C{^{1}H} NMR (CDCl$_3$): [δ] 0.3 (SiMe$_3$), 68.7 (^iC/C$_5$H$_4$), 69.8 (C$_5$H$_5$), 70.1 (CH/C$_5$H$_4$), 71.7 (CH/C$_5$H$_4$), 114.3 (CH/C$_5$H$_4$), 117.1 (CH/C$_5$H$_4$), 119.2 (^iC/C$_5$H$_4$); the signals of the C≡C units could not be detected. FAB-MS [m/z(rel. int.)]: 1632 (20) [M]$^+$, 803 (90) [C$_{40}$H$_{44}$CuFe$_2$Si$_2$Ti]$^+$, 322 (100) [C$_{16}$H$_{26}$Si$_2$Ti]$^+$.

3.3. Synthesis of 3b

Complex **3b** is prepared in an analogous manner to **3a** (Section 3.1). Starting materials: 200 mg (0.24 mmol) of **1a** and 25 mg (0.12 mmol) of [AgClO$_4$] (**2b**). Yield: 160 mg (0.096 mmol, 80% based on **1a**) of turquoise coloured **3b**.

Anal. Calc. for $C_{80}H_{88}AgClFe_4O_4Si_4Ti_2$ (1688.30): C, 56.91; H, 5.27. Found: C, 57.13; H, 5.05%; m.p. [°C]: 98 (decomp.). IR (KBr) [ν_{max}/cm^{-1}]: 2015 [$\nu_{C\equiv C}$]. ^{1}H NMR (CDCl$_3$): [δ] 0.32 (s, 36H, SiMe$_3$), 4.33 (s, 20H, C$_5$H$_5$), 4.57 (pt, J_{HH} = 1.8 Hz, 8H, C$_5$H$_4$Fe), 4.67 (pt, J_{HH} = 1.8 Hz, 8H, C$_5$H$_4$Fe), 6.01 (pt, J_{HH} = 1.2 Hz, 8H, C$_5$H$_4$Ti), 6.19 (pt, J_{HH} = 1.2 Hz, 8H, C$_5$H$_4$Ti). ^{13}C{^{1}H} NMR (CDCl$_3$): [δ] 0.3 (SiMe$_3$), 68.1 (^iC/C$_5$H$_4$), 68.8 (CH/C$_5$H$_4$), 70.0 (C$_5$H$_5$), 71.6 (CH/C$_5$H$_4$), 114.3 (CH/C$_5$H$_4$), 117.8 (CH/C$_5$H$_4$), 123.2 (^iC/C$_5$H$_4$), 152.1 (TiC≡C), 182.3 (TiC≡C). FAB-MS [m/z(rel. int.)]: 1588 (10) [M − ClO$_4$]$^+$, 849 (70) [C$_{40}$H$_{44}$AgFe$_2$Si$_2$-Ti]$^+$, 322 (100) [C$_{16}$H$_{26}$Si$_2$Ti]$^+$.

3.4. Synthesis of 3c

To 200 mg (0.38 mmol) of **1b**, dissolved in 80 mL of diethylether, 60 mg (0.19 mmol) of [Cu(N≡CMe)$_4$]BF$_4$ (**2a**) are added in one portion. The reaction mixture is stirred for 12 h at 25 °C. Afterwards all volatiles are removed in oil-pump vacuum. The residue is extracted with *n*-pentane (2×15 mL), redissolved in 40 mL of tetrahydrofuran and filtered through a pad of Celite. The filtrate is evaporated and dried in oil-pump vacuum to yield 220 mg (0.16 mmol, 88% based on **1b**) of yellow **3c**.

Anal. Calc. $C_{64}H_{72}BCuF_4Si_4Ti_2$ (1199.73): C, 64.07; H, 6.05. Found: C, 64.46; H, 5.99%; m.p. [°C]: 110 (decomp.). IR (KBr) [ν_{max}/cm^{-1}]: 2002 [$\nu_{C\equiv C}$], 1051 [ν_{B-F}]. ^{1}H NMR (CDCl$_3$): [δ] 0.23 (s, 36H, SiMe$_3$), 6.20 (pt, J_{HH} = 2.2 Hz, 8H, C$_5$H$_4$), 6.30 (pt, J_{HH} = 2.2 Hz, 8H, C$_5$H$_4$), 7.3–7.4 (m, 12H, C$_6$H$_5$), 7.6–7.7 (m, 8H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$): [δ] 0.0 (SiMe$_3$), 114.1 (CH/C$_5$H$_4$), 117.2 (CH/C$_5$H$_4$), 123.5 (^iC/C$_5$H$_4$), 127.2 (^iC/C$_6$H$_5$), 128.2 (CH/C$_6$H$_5$), 128.3 (TiC≡C), 131.8 (CH/C$_6$H$_5$), 132.1 (CH/C$_6$H$_5$), 142.4 (TiC≡C).

3.5. Synthesis of 3d

Complex **3d** is prepared in an analogous manner to **3c** (Section 3.4). Starting materials: 500 mg (0.95 mmol) of **1b** and 100 mg (0.48 mmol) of [AgClO$_4$] (**2b**). Yield: 555 mg (0.44 mmol, 92% based on **1b**) of red **3d**.

Anal. Calc. for $C_{64}H_{72}AgClO_4Si_4Ti_2$ (1256.69): C, 61.16; H, 5.77. Found: C, 61.26; H, 5.71%; m.p. [°C]: 122 (decomp.). IR (KBr) [ν_{max}/cm^{-1}]: 2036 [$\nu_{C\equiv C}$], 1092 [ν_{Cl-O}]. ^{1}H NMR (CDCl$_3$): [δ] 0.24 (s, 36H, SiMe$_3$), 6.06 (bs, 8H, C$_5$H$_4$), 6.27 (bs, 8H, C$_5$H$_4$), 7.5–7.7 (m, 20H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$): [δ] −0.2 (SiMe$_3$), 118.0 (CH/C$_5$H$_4$), 120.9 (CH/C$_5$H$_4$), 123.4 (^iC/C$_5$H$_4$), 125.2 (^iC/C$_6$H$_5$), 128.5 (CH/C$_6$H$_5$), 129.3 (CH/C$_6$H$_5$), 130.6 (TiC≡C), 132.5 (CH/C$_6$H$_5$), 141.8 (TiC≡C).

3.6. Synthesis of 3e

Complex **3e** is prepared in an analogous manner to **3c** (Section 3.4). Starting materials: 500 mg (0.95 mmol) of **1b** and 90 mg (0.48 mmol) of AgNO$_3$ (**2c**). Yield 500 mg (0.41 mmol, 95% based on **1b**); red solid.

Anal. Calc. for $C_{64}H_{72}AgNO_3Si_4Ti_2$ (1219.25): C, 63.05; H, 5.95; N, 1.15. Found: C, 63.53; H, 6.01; N, 1.16%; m.p. [°C]: 106 (decomp.). IR (KBr) [ν_{max}/cm^{-1}]: 2036 [$\nu_{C\equiv C}$], 1383 [ν_{N-O}]. ^{1}H NMR (CDCl$_3$): [δ] 0.22 (s, 36H, SiMe$_3$), 6.42 (bs, 16H, C$_5$H$_4$), 7.3–7.6 (m, 20H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$): [δ] −0.3 (SiMe$_3$), 117.8 (CH/C$_5$H$_4$), 120.6 (CH/C$_5$H$_4$), 123.8 (^iC/C$_5$H$_4$), 124.9 (^iC/C$_6$H$_5$), 128.5 (CH/C$_6$H$_5$), 129.2 (CH/C$_6$H$_5$), 130.4 (TiC≡C), 132.7 (CH/C$_6$H$_5$), 142.0 (TiC≡C).

3.7. Single crystal structure analysis of 3e

For data collection a Bruker Smart 1k CCD diffraktometer with graphite monochromatised Mo Kα radiation (λ = 0.71073 Å) was used. Data collection was done at 173(2) K. For protection against oxygen and moisture, the preparation of single crystals was performed in perfluoro alkyl ether (ABCR GmbH & Co KG; viscosity 1600 cSt). Data collection and cell determination has been done with the program SMART [26]. For data integration and refinement of the unit cell the program SAINT was used [26]. The space group was determined using the programs XPREP [26] and the absorption has been corrected empirically with SADABS [27]. The structure was solved by direct methods with the program SHELX97 and structure refinement was based on least-square methods based on F^2 using SHELX97 [28]. The plots of the molecular structures were visualised using ZORTEP.

All *non*-hydrogen atoms were fully refined anisotropically in their located positions. The hydrogen atom positions have been refined with a riding model.

4. Supplementary material

The crystallographic data for compound **3e** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-234 393. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1ET, UK. [fax: +44-1223-336033, E-mail: depsoit@ccdc.cam.ac.uk].

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