Synthesis, electrochemistry and electronic spectra of tetranuclear bis(η^2-alkynyl) transition-metal complexes. The molecular structure of [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CFc)$_2$]CuBr

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Abstract

Tetrametallic complexes of type $\{[\text{Ti}](\text{C≡CFc})_2\}\text{MX}$ (M = Cu: **2a**, X = Cl; **2b**, X = Br; **2c**: X = OTf; M = Ag: **3a**, X = Cl; **3b**, X = BF$_4$; [Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti, Fc = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$), OTf = OSO$_2$CF$_3$) were synthesised by the reaction of trinuclear [Ti](C≡CFc)$_2$ (**1**) with one equivalent of [MX] (M = Cu, Ag; X = Cl, Br, OTf, BF$_4$). The solid-state structure of $\{[\text{Ti}](\text{C≡CFc})_2\}\text{CuBr}$ (**2b**) displays a three-coordinate Cu(I) centre with two η^2-coordinated C≡CFc units and a η^1-bound Br ligand. The Fc groups are both positioned on one side of the Ti(C≡C)$_2$Cu plane, while the Br ligand points towards the opposite side and is located 0.2566(57) Å out of this array. The electronic spectra of complexes **2b** (M = Cu) and **3a** (M = Ag) show a bathochromic shift of $\lambda_{\max}$ upon η^2-coordination of the FcC≡C units in **1** to the M(I) centre in **2b** or **3a**. Cyclic voltammetric studies reveal a behaviour dependent on M(I). In the case of Cu(I), the Ti σ-acetylide bonds are retained upon oxidation of the remote Fc units, while with Ag(I) immediate Ti–C$_{C≡C}$ σ-bond cleavage is observed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Titanocene; Ferrocenyl; Silver(I); Copper(I); Electrochemistry; X-ray; UV–vis

1. Introduction

The coordination chemistry of a number of mono(alkynyl) titanocenes of the type [(η^5-C$_5$H$_3$Si-Me$_3$)$_2$(SiMe$_2$)$_2$]TiCl(C≡CR′) and (η^5-C$_5$H$_4$SiMe$_3$)$_2$-TiCl(C≡CR′) or bis(alkynyl) titanocene species, such as (η^5-C$_5$H$_4$R)$_2$Ti(C≡CR′)$_2$ (R = H, SiMe$_3$; R′ = SiMe$_3$, ′Bu, Ph, SiMe$_2$C≡CSiMe$_3$, C≡CC$_6$H$_4$C≡CSiMe$_3$, C≡CSiMe$_3$ and C≡CEt) has been explored thoroughly in the recent years [1]. A great part of these studies has dealt with the synthesis and reaction behaviour of heterobimetallic complexes of the general type $\{[\eta^5\text{-}$C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CR′)$_2$]MX_n (M = transition metal of Groups 8–12 [1], main group metals of Groups 1 and 2 [2]; X = organic or inorganic ligand; n = 1, 2). All metal ions are either embedded into a trigonal–planar environment (e.g. Ni(0) [3], Pd(0) [4], Pt(0) [5], Cu(I) [6],

Ag(I) [7], Au(I) [8]) or are held in a tetrahedral sphere (e.g. Fe(II), Co(II), Ni(II) [9], Cu(II), Hg(II) [10], Mo(IV) [11]). Besides, transitions from the trigonal–planar to the tetrahedral coordination mode have been observed, e.g. in copper(I)- or silver(I)-containing complexes [12].

Recently, the synthesis and electrochemical behaviour of a new type of π-tweezer molecules, namely [Ti][(C≡C)$_n$Fc]$_2$ ([Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti, Fc = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$), n = 1 [13c,d], n = 2 [13a,b]) was reported. These molecules contain two redox-active ferrocenyl groups Fc which are connected to the Ti(IV) centre via the π-conjugated organic system (C≡C)$_n$ (n = 1, 2). Chemical and/or electrochemical oxidation of the two Fc units of the latter molecules leads to the formation of the all-carbon butadiyne FcC≡C–C≡CFc (n = 1) or octatetrayne FcC≡C–C≡C–C≡C–C≡CFc (n = 2) by means of an oxidatively induced cleavage of the Ti–C$_{C≡C}$ σ-bonds and coupling of the two C≡CFc or C≡C–C≡CFc fragments [13]. The oxidatively induced Ti–C$_{C≡C}$ σ-bond cleavage was not even averted when

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e.g. {[Ti](C≡CFc)$_2$}Pd(PPh$_3$) was oxidised electrochemically, although a strong electron-donating effect of the Pd(0) nucleus was observed [14].

In order to further investigate the stability and coordination behaviour of [Ti](C≡CFc)$_2$, we report here on the reaction of this complex with a number of different Cu(I) and Ag(I) compounds. Studies concerning the redox behaviour of tetranuclear {[Ti](C≡CFc)$_2$}MX (M = Cu, Ag; X = Cl, Br, OTf, BF$_4$; OTf = OSO$_2$CF$_3$) are reported.

2. Results and discussion

2.1. Synthesis and spectroscopy

Heterometallic [Ti](C≡CFc)$_2$ (1) {[Ti] = (η^5-C$_5$H$_4$Si-Me$_3$)$_2$Ti, Fc = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)} was reacted with equimolar amounts of [MX] (M = Cu, Ag; X = Cl, Br, OTf, BF$_4$) to produce tetrametallic complexes of the type {[Ti](C≡CFc)$_2$}MX (M = Cu: 2a, X = Cl; 2b, X = Br; 2c: X = OTf; M = Ag: 3a, X = Cl; 3b, X = BF$_4$) in good yields (Scheme 1). The progress of the reaction can be followed by a striking colour change from intense violet (characteristic of 1) [13c] to green (2a–2c)
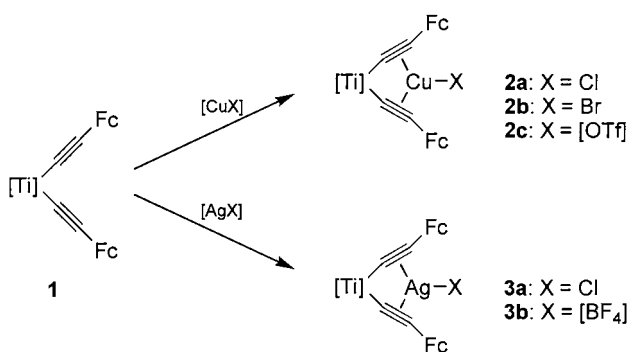
Scheme 1. Synthesis of complexes 2 and 3 by the reaction of 1 with [CuX] or [AgX] (X = Cl, Br,OTf, BF$_4$).
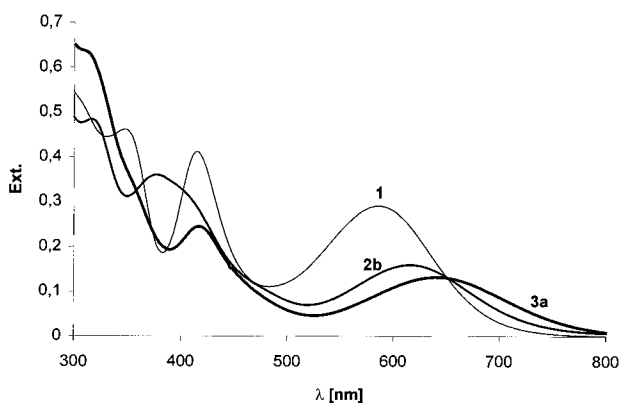
Fig. 1. UV–vis spectra of complexes 1, 2b and 3a, recorded in CH$_2$Cl$_2$ solutions ($c = 3.5 \times 10^{-5}$ mol l^{-1}).

or turquoise (3a, 3b). The Cu(I)-containing complexes 2a–2c are stable at ambient temperatures in a nitrogen atmosphere. In contrast, the respective Ag(I) complexes 3a and 3b decompose rapidly on exposure to light and at ambient temperature.

The course of the formation of complexes 2 and 3 was followed by IR spectroscopic studies. During the course of the corresponding reaction, the disappearance of the strong $v_{C≡C}$ absorption band at 2055 cm^{-1} (1) and the appearance of a new C≡C stretching vibration around 1975 cm^{-1} (2a–2c) or approximately 2005 cm^{-1} (3a, 3b), respectively, is characteristic and resembles the change from a free to a η^2-coordinated alkynyl unit [1,6,7].

The ^{1}H-NMR spectra of 2a–2c, 3a and 3b reveal that the resonance signals of the cyclopentadienyl-bonded SiMe$_3$ groups appear at virtually the same frequency as for 1 [13c]. The singlet at 4.25 ppm can be assigned to the resonance signal of the C$_5$H$_5$ protons of the Fc ligands. In addition, the region between 4 and 7 ppm exhibits a set of four pseudo triplets (complexes 2a–2c) or four broad singlets (complexes 3a and 3b) with the integral ratio of 1:1:1:1. The first two at around 4.3 ppm and 4.7 ppm can be attributed to the C$_5$H$_4$ group of Fc, while the latter two between 6 and 7 ppm are in a region typical for titanium-bonded C$_5$H$_4$ units [1,3,2,4–8]. Generally, after incorporation of a M(I) centre (M = Cu, Ag), as given in 2a–2c, 3a and 3b, the C$_5$H$_4$ protons of the Fc moieties exhibit their resonance signals at a lower field when compared to 1, while the respective signals of the titanocene units are shifted to higher field.

In the ^{13}C{^{1}H}-NMR spectra of the newly synthesised compounds the C$_\beta$ carbon signals of the Ti–C$_\alpha$≡C$_\beta$ entities are shifted by 10–15 ppm to lower field; the respective C$_\alpha$ resonance signals are shifted to higher field by around 10 ppm (2a–c) or 17 ppm (3a, 3b).

In the recorded UV–vis spectra, a bathochromic shift of λ_{max} from 585 nm (1) to 616 nm (2b) or 638 nm (3a) was observed (Fig. 1). The extinction coefficient ε ($\Delta\varepsilon$) diminishes from 8300 (200) cm^{-2} mol^{-1} (1) to 4400 (250) cm^{-2} mol^{-1} (2b) or 3900 (250) cm^{-2} mol^{-1} (3a), respectively. Suvorova and co-workers [15,16] assigned such absorptions to charge-transfer (CT) transitions between a Fe(II) and a Ti(IV) centre, since the Ti(IV) centre possesses a d^0 configuration and the extinction coefficient ε is too high for a spin-forbidden d–d transition [17]. It must be pointed out that the bis-η^2-coordination of the acetylenic moieties to a M(I) centre results in a bathochromic shift of the CT transition.

However, Mößbauer spectroscopy revealed that the IS and QS are unchanged when compared with the data obtained for neat FcH [18] and, therefore, the Fc units in compounds 1, 2b and 3a are not affected by the presence of the Ti(IV) centre or M(I) (M = Cu, Ag) ions on the Mößbauer time scale.
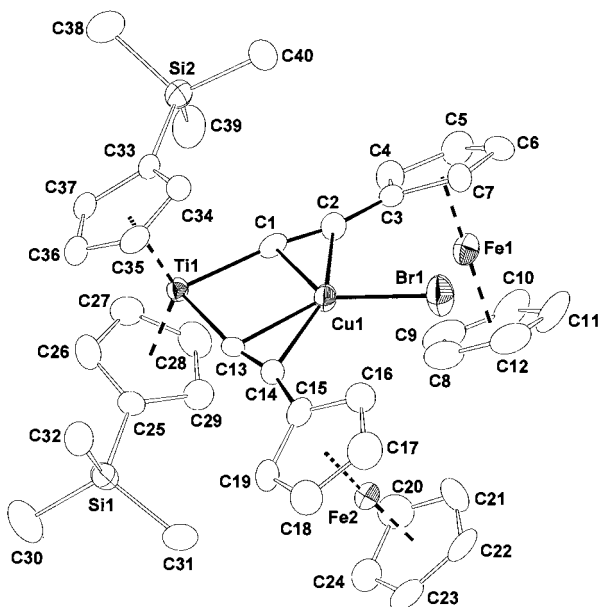
Fig. 2. ORTEP drawing (50% probability level) of **2b** with molecular geometry and atom numbering scheme.

Table 1
Important interatomic distances (Å) and angles (°) of complex **2b** [a]

Bond lengths

Ti(1)–C(1)	2.092(7)	Cu(1)–C(14)	2.236(7)
Ti(1)–C(13)	2.113(8)	Cu(1)–Br(1)	2.3201(12)
C(1)–C(2)	1.242(9)	Ti(1)–D(1) [b]	2.0522(11)
C(13)–C(14)	1.212(10)	Ti(1)–D(2) [b]	2.0452(12)
C(2)–C(3)	1.428(9)	Fe(1)–D(3) [b]	1.6405(11)
C(14)–C(15)	1.440(11)	Fe(1)–D(4) [b]	1.6501(11)
Cu(1)–C(1)	2.062(7)	Fe(2)–D(5) [b]	1.6377(11)
Cu(1)–C(2)	2.247(7)	Fe(2)–D(6) [b]	1.6461(11)
Cu(1)–C(13)	2.073(6)		

Bond angles

C(1)–Cu(1)–C(13)	90.9(3)	Ti(1)–C(13)–C(14)	170.1(6)
Br(1)–Cu(1)–Ti(1)	175.39(5)	C(13)–C(14)–C(15)	162.1(7)
C(1)–Ti(1)–C(13)	89.0(3)	D(1) [b]–Ti(1)–D(2) [b]	131.64(27)
Ti(1)–C(1)–C(2)	171.7(7)	D(3) [b]–Fe(1)–D(4) [b]	178.32(65)
C(1)–C(2)–C(3)	161.2(8)	D(5) [b]–Fe(2)–D(6) [b]	177.76(61)

[a] Standard deviation of the last significant figure in parentheses.
[b] D(1)–D(6), centroids of the cyclopentadienyl ligands.

2.2. X-ray crystal-structure determination

The solid-state structure of complex **2b** has been established by a single-crystal X-ray structure determination on suitable single crystals obtained by cooling a THF–CH$_2$Cl$_2$ solution of **2b** to −40°C (Fig. 2). Important structural details are listed in Table 1 and crystallographic data in Table 2.

Heterotrimetallic **2b** crystallises in the monoclinic space group $P2_1/n$ with four independent molecules per asymmetric unit cell and two molecules of THF per

formula unit. Both C≡CFc entities are η^2-coordinated to a monomeric CuBr moiety, thus, the low-valent Cu(I) centre is tricoordinate. The Ti(IV) and the Cu(I) centre as well as the alkynyl ligands are in one plane (maximum deviation from the Ti(1)–C(1)–C(13)–Cu(1)–C(2)–C(14)-containing plane: 0.0511(30) Å). The coordination sphere around Cu(1) is not trigonal–planar as in other cases [1,6], but the Br(1) atom is positioned by 0.2566(57) Å out of this plane. This deviation from the trigonal planarity can be assigned to the steric demand of the bulky Fc moieties. The Cu(1)–Br(1) distance at 2.3201(12) Å resembles other experimental values observed, e.g. for {[Ti](C≡CSiMe$_3$)(Cl)}-CuBr (2.296(2) Å) [19] or the Pt(II)–Cu(I) complex [(bipy)Pt(C≡CPh)$_2$]CuBr (2.3129(8) Å) [20]. However, it is slightly shorter than reported for a monomeric, Lewis base-stabilised Cu(I)-bromide as in [(NC$_5$H$_3$Me$_2$-2,6)-CuBr] (2.449(2) Å) [21a] or {[(C$_6$H$_4$Me-2)Ph$_2$P]$_2$CuBr} (2.346(2) Å) [21b]. The Ti–C$_{C≡C}$ σ-bond lengths (Ti(1)–C(1): 2.092(7) Å, Ti(1)–C(13): 2.113(8) Å) (Table 1) mirror typical separations from, e.g. the parent

Table 2
Crystal and intensity collection data for complex **2b**

Formula weight	C$_{48}$H$_{60}$BrCuFe$_2$O$_2$Si$_2$Ti
Molecular mass	1028.19
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	15.5853(2)
b (Å)	17.6956(2)
c (Å)	17.1659(3)
β (°)	100.636(1)
V (Å^3)	4652.87(11)
ρ_{calc} (g cm^{-3})	1.468
$F(000)$	2120
Z	4
Crystal dimensions (mm)	$0.4 \times 0.1 \times 0.01$
Diffractometer model	Bruker SMART CCD
Radiation (λ, Å)	Mo–K$_\alpha$ (0.71073)
Max. and min. transmission	0.990060 and 0.637813
Absorption coefficient (μ, mm^{-1})	2.175
Temperature (K)	173(2)
Scan mode	ω-Scan
Scan range (°)	$1.67 \leq \theta \leq 30.20$
Index ranges	$-21 \leq h \leq 15, -24 \leq k \leq 7,$ $-21 \leq l \leq 20$
Total reflections	21 725
Unique reflections	10 690
Observed reflections [$I \geq 2\sigma(I)$]	5236
Refined parameters	520
R_1 [a], wR_2 [a] [$I \geq 2\sigma(I)$]	0.0881, 0.1460
R_1 [a], wR_2 [a] (all data)	0.1919, 0.1863
S	1.054
Max., min. peak in final Fourier map (e Å^{-3})	0.606, −1.052

[a] $R_1 = [\Sigma(||F_o| - |F_c|)/\Sigma|F_o|)]$; $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 3.8794P]$ with $P = [F_o^2 + 2F_c^2]/3c)$ $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$; n is number of reflections, p is parameters used.
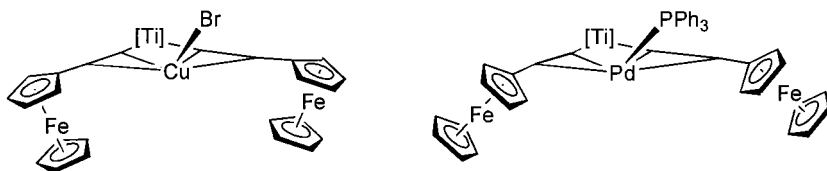
Fig. 3. Schematic representation of the differing Fc orientations in **2b** (left) and {[Ti] (C≡CFc)$_2$}Pd(PPh$_3$) (right) [14].

molecule **1** (2.088(13) Å, 2.104(10) Å) or other heterometallic tweezer-type molecules [1–8,13c]. The C≡C triple bond separations found for **2b** [C(1)–C(2): 1.242(9) Å; C(13)–C(14): 1.212(10) Å] are elongated when compared to the respective bond distances in **1** [13c]. This is a common feature of organometallic or organic alkynes upon their η^2-coordination to transition metal building blocks and is consistent with the observation of the shift of the $\nu_{C\equiv C}$ stretching frequency to lower wavenumbers in the IR spectrum of **2b** (vide supra) [1,22]. Due to the η^2-coordination of both C≡CFc units to the Cu(I) centre a typical *trans*-deformation of the Ti–C≡C–C$_{Fc}$ fragment is observed (Ti(1)–C(1)–C(2): 171.7(7)°, C(1)–C(2)–C(3): 161.2(8)°, Ti(1)–C(13)–C(14): 170.1(6)°, C(13)–C(14)–C(15): 162.1(7)°). At 175.39(5)° the angle Ti(1)–Cu(1)–Br(1) is only slightly deviated from linearity. Both Fc units are positioned on one side of the Ti(C≡C)$_2$Cu plane and are tilted towards each other, which is demonstrated by the angle between the best planes through C(3)–C(4)–C(5)–C(6)–C(7) and C(15)–C(16)–C(17)–C(18)–C(19) (31.68(42)°) (Fig. 3). This contrasts with the observation for {[Ti](C≡CFc)$_2$}Pd(PPh$_3$) where a tilting of the Fc entities in opposite direction was observed [14].

2.3. Electrochemical behaviour

The Ti(IV)–Fe(II) complex [Ti](C≡CFc)$_2$ (**1**) has been shown to stabilise monomeric Group 11 complex fragments [13,14]. Since the Ti–acetylide σ-bonds in **1** are cleaved upon electrochemical or chemical oxidation of the remote Fc units [13], it was of interest to test if the coordination of the TiC≡CFc building blocks to a M(I) centre leads to a stabilisation of the Ti–C$_{C\equiv C}$ σ-bonds and hence, to a retention of these σ-bonds. Exemplary complexes **2b** and **3a** were investigated by cyclic voltammetric studies. The cyclic voltammogram obtained for **2b** is depicted in Fig. 4.

In the cathodic region, the cyclic voltammogram of tetrametallic **2b** exhibits a reversible wave at $E_{1/2} = 0.01$ V ($\Delta E = 150$ mV) (Fig. 4). Compared to the oxidative behaviour of {[Ti](C≡CPh)$_2$}CuBr [23] and **1** [13c], this wave, which is in total a three-electron process, can be assigned to three different, but synchronous, redox steps, i.e. the reversible Cu(I)/Cu(II) and the Fe(II)/Fe(III) redox couples. Coincidentally, these appear at

virtually the same potential value. The reversibility of these processes has been demonstrated by multicyclic experiments. This indicates that the Ti–C$_{C\equiv C}$ σ-bonds in **2b** remain intact when the ferrocenyl units are oxidised. A contrasting behaviour has been observed for [Ti][(C≡C)$_n$Fc]$_2$ ($n = 1$, 2). There, an oxidatively induced bond cleavage takes place immediately after oxidation of the remote ferrocenyl units [13]. However, in the anodic region the cyclic voltammogram displays two 1-electron processes which lose intensity rapidly in multicyclic experiments (Fig. 4). While the irreversible wave at $E_{red} = -1.71$ V can be attributed to the Cu(I)/Cu(0) reduction, the wave at $E_{red} = -1.96$ V can be assigned to the irreversible Ti(IV)/Ti(III) reductive process.

In contrast, the Ti(IV)–Pd(0) complex {[Ti](C≡C-Fc)$_2$}Pd(PPh$_3$) [14] exhibits a strong shift to a more negative potential of the irreversible Ti(IV)/Ti(III) reduction to $E_{red} = -2.72$ V (**1**: $E_{1/2} = -1.99$ V) and the irreversible Fe(II) oxidation to $E_{ox} = -0.06$ V (**1**: $E_{ox} = 0.00$ V). Comparison of the anodic and cathodic processes observed for **2b** with those of {[Ti](C≡C-Fc)$_2$}Pd(PPh$_3$) [14] leads to the conclusion that an electron-donating effect of the d^{10}-fragment Cu(I) cannot be detected electrochemically, other than with the d^{10}-centre Pd(0).

The cyclic voltammetric studies for the corresponding AgCl complex **3a** resulted in an irreversible two-electron step at $E_{ox} = 0.06$ V followed by a reversible two-electron wave at $E_{1/2} = 0.22$ V ($\Delta E = 150$ mV) in the oxidative region and two irreversible one-electron

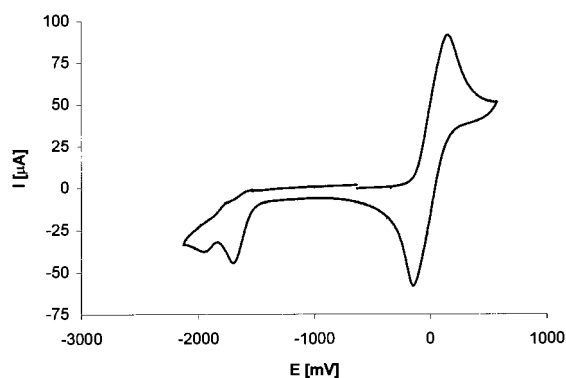Fig. 4. Cyclic voltammogram of compound **2b**; in THF solution in the presence of [n-Bu$_4$N][PF$_6$] ($c = 0.1$ mol dm^{-3}) at 25°C under N$_2$; scan rate 100 mV s^{-1}; potentials are referenced to FcH | FcH$^+$ as internal standard ($E_{1/2} = 0.00$ V).

processes. The one at $E_{red} = -1.31$ V can be assigned to the Ag(I)/Ag(0) reduction and the one at $E_{red} = -1.88$ V to the Ti(IV)/Ti(III) reduction.

The process at $E_{ox} = 0.06$ V can be ascribed to the oxidation of the two electrochemically independent Fc units of **3a**; the observed reversible wave at $E_{1/2} = 0.22$ V can be attributed to the bis-ferrocenyl butadiyne FcC≡C–C≡CFc [13c,14], which was formed under the conditions of the measurements. This oxidatively induced Ti–C$_{C≡C}$ σ-bond cleavage was observed earlier for the parent molecule **1** as well as for [Ti](C≡C–C≡CFc)$_2$ [13].

3. Conclusions

[Ti](C≡CFc)$_2$ (**1**) has been utilised successfully for the preparation of various tetranuclear compounds of the general type {[Ti](C≡CFc)$_2$}MX (M = Cu, Ag; X = Cl, Br, OTf, BF$_4$). The X-ray crystal structure analysis of **2b** clearly confirms the proposed structure of these complexes with a low-valent tricoordinate M(I) centre. The bathochromic shift of λ_{max} (**1**: 575 nm) upon η^2-coordination of the two C≡CFc moieties to a low-valent MX complex fragment (**2a**: 616 nm, **3a**: 638 nm) indicates a facilitation of the CT transitions observed. Cyclic voltammetric studies reveal that the coordination of CuBr in **2b** preserves the Ti–C$_{C≡C}$ σ-bond upon oxidation of the remote ferrocenyl units, while this is not the case for, e.g. the AgCl complex **3a**. However, an effect due to the introduction of late transition metals ions as Cu(I) or Ag(I) on the electrochemical responses of Ti(IV) or Fe(II) could not be observed.

4. Experimental

4.1. General methods

All reactions were carried out in an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were purified by distillation from sodium–benzophenone ketyl; n-pentane was purified by distillation from calcium hydride. Infrared spectra were recorded on 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. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal. UV–vis spectroscopy was conducted on a Perkin–Elmer Lambda 40 spectrometer. FD and FAB mass spectra were recorded on a Finnigan 8400 mass spectrometer operating in the positive-ion mode. Melting points were determined using sealed nitrogen purged

capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Organisch-Chemisches Institut der Universität Heidelberg. Electrochemical measurements were performed by cyclic voltammetry in a solution of [n-Bu$_4$N][PF$_6$] (0.1 mol dm^{-3}) in MeCN at 25°C, using a standard three-electrode cell on a Radiometer DEA 101 Electrochemical Analyser. All potentials were referenced to the ferrocene│ferrocenium couple [FcH│FcH$^+$: $E_{1/2} = 0.00$ V] as internal standard.

4.2. General remarks

Compound **1** [11] was prepared according to published procedures. All other chemicals were purchased by commercial providers and were used as received.

4.3. Synthesis of {[Ti](C≡CFc)$_2$}CuCl (**2a**)

To **1** (200 mg, 0.3 mmol) in THF (50 ml) CuCl (40 mg, 0.4 mmol) was added in one portion (25°C). In the course of the reaction the solution turned green. After 10 h stirring, all volatile materials were evaporated. The green residue was extracted with n-pentane and Et$_2$O and then filtered with THF through a pad of Celite. The THF filtrate was concentrated to 5 ml, 50 ml of n-pentane was added and the supernatant solution was decanted. The precipitate was dried under reduced pressure to yield **2a** as a green solid (190 mg, 75% based on **1**).

M.p.: (°C) 130 dec. IR (KBr): (cm^{-1}) 1975 (s) ($\nu_{C≡C}$). ^{1}H-NMR (CDCl$_3$): (δ) 0.36 (s, 18 H, SiMe$_3$), 4.26 (s, 5 H, C$_5$H$_5$), 4.31 (pt, $J_{HH} = 1.4$ Hz, 4 H, C$_5$H$_4$Fe), 4.76 (pt, $J_{HH} = 1.4$ Hz, 4 H, C$_5$H$_4$Fe), 6.13 (pt, $J_{HH} = 1.6$ Hz, 4 H, C$_5$H$_4$Ti), 6.21 (pt, $J_{HH} = 1.6$ Hz, 4 H, C$_5$H$_4$Ti). ^{13}C{^{1}H}-NMR (CDCl$_3$): (δ) 0.0 (SiMe$_3$), 67.7 (^iC/C$_5$H$_4$Fe), 69.0 (CH/C$_5$H$_4$Fe), 69.8 (C$_5$H$_5$), 71.6 (CH/C$_5$H$_4$Fe), 113.5 (CH/C$_5$H$_4$Ti), 116.8 (CH/C$_5$H$_4$Ti), 121.3 (^iC/C$_5$H$_4$Ti), 135.1 (TiC≡C), 142.5 (TiC≡C). FAB MS (m/z (rel. int.)): 838 (20) [M]$^+$, 803 (70) [M−Cl]$^+$, 322 (100) [C$_{16}$H$_{26}$Si$_2$Ti]$^+$. Anal. Calc. for C$_{40}$H$_{44}$ClCuFe$_2$Si$_2$Ti (839.53): C, 57.23; H, 5.28. Found: C, 56.97; H, 5.45%.

4.4. Synthesis of {[Ti](C≡CFc)$_2$}CuBr (**2b**)

Experimental procedures and work-up were the same as described for the synthesis of **2a**. Experimental details: 200 mg (0.3 mmol) **1**, 45 mg (0.3 mmol) CuBr, 50 ml THF. Yield: 200 mg, 80 % based on **1**.

M.p.: (°C) 135 (dec.). IR (KBr): (cm^{-1}) 1973 (s) ($\nu_{C≡C}$). ^{1}H-NMR (CDCl$_3$): (δ) 0.36 (s, 18 H, SiMe$_3$), 4.25 (s, 5 H, C$_5$H$_5$), 4.32 (pt, $J_{HH} = 1.4$ Hz, 4 H, C$_5$H$_4$Fe), 4.73 (pt, $J_{HH} = 1.4$ Hz, 4 H, C$_5$H$_4$Fe), 6.16 (pt, $J_{HH} = 2.1$ Hz, 4 H, C$_5$H$_4$Ti), 6.21 (pt, $J_{HH} = 2.1$ Hz, 4 H, C$_5$H$_4$Ti). ^{13}C{^{1}H}-NMR (CDCl$_3$): (δ) 0.0 (SiMe$_3$),

67.0 (^iC/C_5H_4), 69.3 (CH/C_5H_4Fe), 70.0 (C_5H_5), 72.0 (CH/C_5H_4Fe), 113.6 (CH/C_5H_4Ti), 116.9 (CH/C_5H_4Ti), 121.3 (^iC/C_5H_4Ti), 140.9 (TiC≡C), 143.1 (TiC≡C). UV–vis {λ_{max} ($\varepsilon(\Delta\varepsilon)$)}: (nm (cm^{-2}mol^{-1})) 615 (4400(250)). FD MS (m/z (rel. int.)): 884 (100) [M]$^+$. Anal. Calc. for $C_{40}H_{44}BrCuFe_2Si_2Ti$ (883.98): C, 54.35; H, 5.02. Found: C, 53.98; H, 5.09%.

4.5. X-ray structure determination of 2b

The structure of **2b** was determined from single-crystal X-ray diffraction, which were collected on a Bruker SMART CCD diffractometer using Mo–K$_\alpha$ radiation. Crystallographic data of **2b** are given in Table 2. The structure was solved by direct methods [24]. An empirical absorption correction was applied. The structure was refined by the least-squares method based on F^2 with all reflections. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were placed in calculated positions (see Section 5).

4.6. Synthesis of {[Ti](C≡CFc)₂}CuOTf (2c)

Experimental procedures and work-up were the same as described for the synthesis of **2a**. Experimental details: 210 mg (0.3 mmol) **1**, 70 mg (0.3 mmol) CuOTf, 50 ml THF. Yield: 190 mg, 70 % based on **1**.

M.p.: (°C) 120 dec. IR (KBr): (cm^{-1}) 1974 (s) ($\nu_{C≡C}$). ^{1}H-NMR (CDCl$_3$): (δ) 0.35 (s, 18 H, SiMe_3), 4.30 (s, 5 H, C_5H_5), 4.33 (pt, J_{HH} = 1.4 Hz, 4 H, C_5H_4Fe), 4.80 (pt, J_{HH} = 1.4 Hz, 4 H, C_5H_4Fe), 6.11 (pt, J_{HH} = 1.9 Hz, 4 H, C_5H_4Ti), 6.19 (pt, J_{HH} = 1.9 Hz, 4 H, C_5H_4Ti). ^{13}C{^{1}H}-NMR (CDCl$_3$): (δ) 0.0 (SiMe_3), 66.7 (^iC/C_5H_4Fe), 69.2 (CH/C_5H_4Fe), 69.9 (C_5H_5), 71.7 (CH/C_5H_4Fe), 113.5 (CH/C_5H_4Ti), 116.7 (CH/C_5H_4Ti), 121.3 (^iC/C_5H_4Ti), 140.1 (TiC≡C), 142.5 (TiC≡C). FAB MS [m/z (rel. int.)]: 955 (5) [M]$^+$, 883 (2) [M−CF$_3$]$^+$, 803 [M−OTf]$^+$, 322 (40) [C$_{16}$H$_{26}$Si$_2$Ti]$^+$. Anal. Calc. for $C_{41}H_{44}CuF_3Fe_2O_3SSi_2Ti$ (953.14): C, 51.67; H, 4.65. Found: C, 51.33; H, 4.94%.

4.7. Synthesis of {[Ti](C≡CFc)₂}AgCl (3a)

To a THF solution (50 ml) of **1** (85 mg, 0.1 mmol) was added AgCl (16 mg, 0.1 mmol) in one portion (25°C). After 5 h of stirring under the exclusion of light, the reaction mixture was evaporated to dryness. The residue was extracted with *n*-pentane and Et$_2$O and then filtered with THF through a pad of Celite. The THF filtrates were concentrated to 5 ml and then 30 ml of *n*-pentane were added. A turquoise precipitate formed and the supernatant solution was decanted. Drying under reduced pressure gave **3a** (yield: 60 mg, 60 % based on **1**).

M.p.: (°C) 87 (dec). IR (KBr): (cm^{-1}) 2002 (s) ($\nu_{C≡C}$). ^{1}H-NMR (CDCl$_3$): (δ) 0.33 (s, 18 H, SiMe_3), 4.26 (s, 5

H, C_5H_5), 4.27 (bs, 4 H, C_5H_4Fe), 4.71 (bs, 4 H, C_5H_4Fe), 6.34 (bs, 4 H, C_5H_4Ti), 6.39 (bs, 4 H, C_5H_4Ti). ^{13}C{^{1}H}-NMR (CDCl$_3$): (δ) − 0.1 (SiMe_3), 67.0 (^iC/C_5H_4Fe), 68.6 (CH/C_5H_4Fe), 69.7 (C_5H_5), 71.8 (CH/C_5H_4Fe), 115.5 (CH/C_5H_4Ti), 119.1 (CH/C_5H_4Ti), 123.5 (^iC/C_5H_4Ti), 145.7 (TiC≡C).[1] UV–vis (λ_{max} [$\varepsilon(\Delta\varepsilon)$]): (nm (cm^{-2}mol^{-1})) 638 (3900(250)). FD MS (m/z (rel. int.)): 884 (100) [M]$^+$. Anal. Calc. for $C_{40}H_{44}AgClFe_2Si_2Ti$ (884.4): C, 54.36; H, 5.02. Found: C, 54.32; H, 5.09%.

4.8. Synthesis of {[Ti](C≡CFc)₂}Ag[BF₄] (3b)

Experimental procedures and work-up were the same as described for the synthesis of **3a**. Experimental details: 250 mg (0.3 mmol) **1**, 70 mg (0.3 mmol) Ag[BF$_4$], 80 ml THF. Yield: 150 mg, 45% based on **1**.

M.p.: (°C) 75 (dec). IR (KBr): (cm^{-1}) 2005 (s) ($\nu_{C≡C}$). ^{1}H-NMR (CDCl$_3$): (δ) 0.33 (s, 18 H, SiMe_3), 4.28 (bs, 4 H, C_5H_4Fe), 4.42 (s, 5 H, C_5H_5), 4.42 (bs, 4 H, C_5H_4Fe), 6.49 (bs, 4 H, C_5H_4Ti), 6.58 (bs, 4 H, C_5H_4Ti). ^{13}C{^{1}H}-NMR (CDCl$_3$): (δ) − 1.1 (SiMe_3), 69.0 (CH/C_5H_4Fe), 69.9 (C_5H_5), 71.6 (^iC/C_5H_4Fe), 71.9 (CH/C_5H_4Fe), 114.5 (CH/C_5H_4Ti), 117.8 (CH/C_5H_4Ti), 123.5 (^iC/C_5H_4), 136.9 (TiC≡C), 140.5 (TiC≡C). FD MS [m/z (rel. int.)]: 936 (100) [M]$^+$. Anal. Calc. for $C_{40}H_{44}AgBF_4Fe_2Si_2Ti$ (935.21): C, 51.37; H, 4.74. Found: C, 50.92; H, 5.29%.

5. Supplementary material

Tables of crystal data and structure refinement, bond lengths, angles as well as anisotropic displacement factors have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 141209. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1223-336066; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[1] The resonance signal for TiC≡C could not be assigned unequivocally.

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