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First Example of Zinc(II) Monomeric Species Stabilized by η^2-Bonded Alkynes

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Monomeric ZnX_2 (X = Cl, Br) moieties have been stabilized by alkynes through the reaction of $[Ti](C{\equiv}CR)_2$ (R = $SiMe_3$ (**1**), Fc (**2**); Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$, [Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$) with the anhydrous Zn(II) salts ZnX_2 (X = Cl (**3**), Br (**4**)). The resulting heterodinuclear complexes of formula $\{[Ti](C{\equiv}CR)_2\}ZnX_2$ (R = $SiMe_3$, X = Cl (**5a**), Br (**5b**); R = Fc, X = Cl (**6a**), Br (**6b**)) could be obtained in high yield. The identities of all new complexes have been confirmed by analytical and spectroscopic (IR, ^1H and $^{13}C\{^1H\}$ NMR) data. Additionally, the structure of complex **6b** has been established by X-ray diffraction. Two different orientations within the molecule have been encountered (**6b$_1$** and **6b$_2$**). The solid-state structure of **6b** clearly demonstrates η^2 coordination of the $FcC{\equiv}C$ ligands to $ZnBr_2$, resulting in a pseudotetrahedral surrounding of the zinc(II) center, whereby the zinc atom is in-plane bonded with the $Ti(C{\equiv}C)_2$ moiety. Additionally, the electrochemical behavior of $\{[Ti](C{\equiv}CR)_2\}ZnBr_2$ (R = $SiMe_3$, Fc), in which early- and late-transition-metal atoms are linked via σ,π-coordinated alkyne ligands, is reported.

Introduction

The chemistry of organometallic zinc compounds has attracted much interest in the past few years as a consequence of the synthetic and physical applications of these species.[1−4]

However, zinc complexes, featuring σ- and/or π-bonded alkynyl moieties, are relatively unknown and the structural information available on them is very limited.[5−7] Homoleptic species of the type $Zn(C{\equiv}CR)_2$ (R = Et, Ph, C_6H_{13}, $(CH_2)_nNMe_2$) are believed to arrange as linear polymers via bridging acetylenic groups;[5] nevertheless, no crystal structures have been reported so far. More recently, anionic zinc acetylides with σ-bonded phenylethynyl ligands, such as $[Li(tmen)_2][Zn(C{\equiv}CPh)_4]$[6] (tmen = $Me_2NCH_2CH_2NMe_2$) and $[Na(12\text{-}crown\text{-}4)_2]_2[Zn(C{\equiv}CPh)_3(thf)]$,[7] have been structurally characterized.

We describe here the synthesis and characterization of the heterodinuclear early−late complexes $\{[Ti](C{\equiv}CR)_2\}ZnX_2$ ([Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; R = $SiMe_3$, Fc; X = Cl, Br; Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$), the first examples in organometallic chemistry in which monomeric $Zn^{II}X_2$ units are stabilized by the side-on coordination of two alkynyl ligands of the organometallic π-tweezer molecule $[Ti](C{\equiv}CR)_2$.

Results and Discussion

The reaction of $[Ti](C{\equiv}CR)_2$ (R = $SiMe_3$ (**1**),[8] Fc (**2**);[9] [Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$) with a slight excess of the anhydrous Zn(II) salts ZnX_2 (X = Cl (**3**), Br (**4**)) affords the novel alkyne-stabilized $Zn^{II}X_2$ complexes $\{[Ti](C{\equiv}CR)_2\}ZnX_2$ (R = $SiMe_3$, X = Cl (**5a**), Br (**5b**); R = Fc, X = Cl (**6a**), Br (**6b**)) in yields exceeding 80% (eq 1).

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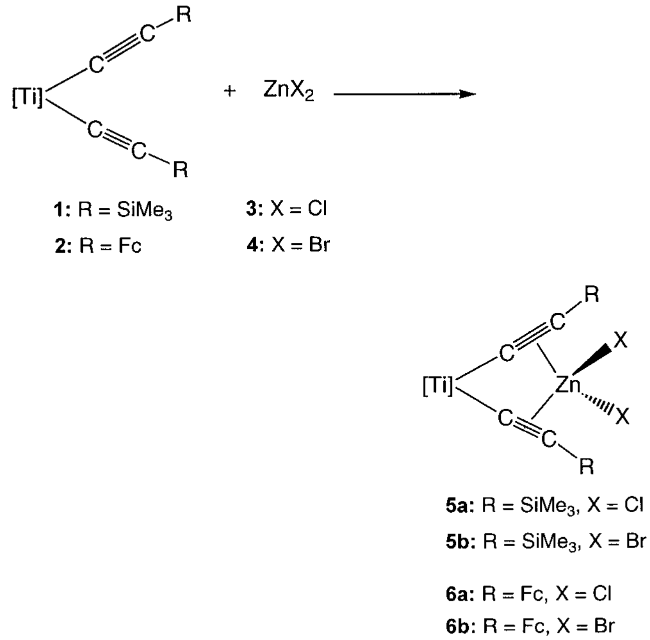

After appropriate workup the corresponding heterodinuclear complexes **5** and **6** can be isolated as deep red (**5a**,**b**) or deep green (**6a**,**b**) solids. All of them are nicely soluble in tetrahydrofuran and chlorinated solvents, such as dichloromethane, chloroform, and carbon tetrachloride, and only sparingly soluble in acetone.

Complexes **5a**,**b** are remarkably stable in the solid state as well as in chlorinated solvents. However, it must be noted that these species start to significantly decompose in tetrahydrofuran solutions on prolonged stirring. It was not possible to specify unequivocally the nature of such decomposition products. The same behavior is observed for complexes **6a**,**b**, although the temperature has proved to be an additional factor of instability. Complexes **6a**,**b** must be stored, even in the solid state, at temperatures below 0 °C.

In agreement with the formulation of complexes **5** and **6** as heterobimetallic titanium(IV)–zinc(II) complexes in which both alkynyl ligands of the bis(alkynyl)-titanocene fragment are η^2-coordinated to the corresponding ZnX_2 moiety is the observation of a distinct shifting of the C≡C stretching vibrations from 2005 cm^{-1} [8] and 2055 cm^{-1} [9] in the parent complexes **1** and **2** to 1989 cm^{-1} in **5a**, 1985 cm^{-1} in **5b**, 2010 cm^{-1} in **6a**, and 2006 cm^{-1} in **6b**. In the case of **5a**,**b** the extent of the appropriate bond weakening is similar to that reported for $[Ti](C{\equiv}CSiMe_3)_2$ systems π-bonded to other low-valent transition-metal moieties.[10] In contrast, the shifting in the $\nu_{C\equiv C}$ frequency for **6a**,**b** is significantly lower than is typical for other related complexes.[9,11]

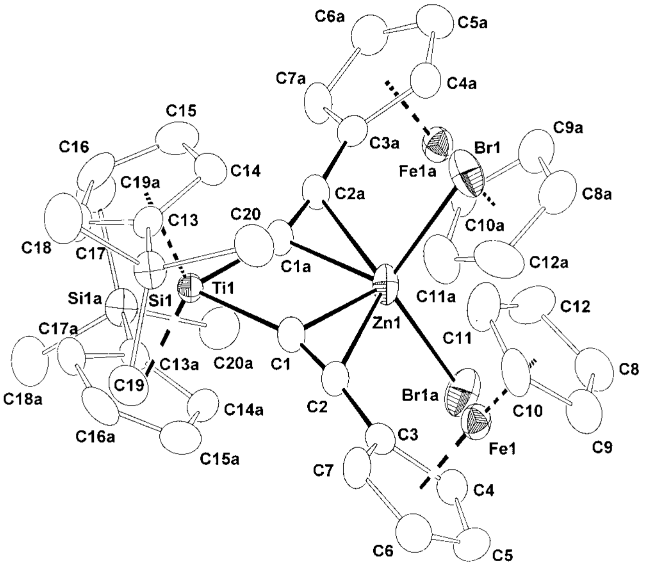

Figure 1. ZORTEP drawing[12] (drawn at the 50% probability level) of $\mathbf{6b_1}$ (with exclusion of the hydrogen atoms) with the atom-numbering scheme.

The formulation of complexes **5** and **6** as heterodinuclear tweezer-like molecules is further confirmed on the basis of ^1H and $^{13}C\{^1H\}$ spectroscopic studies. In all spectra, sharp and well-resolved signals according to the organic groups present are recorded. Most significant in the ^1H NMR spectra of complexes **5** and **6** is that the π-coordination of the alkynyl ligands to the $Zn^{II}X_2$ moieties causes a higher deshielding in the η^5-bonded C_5H_4 rings and consequently provokes a downfield shift for these protons, in comparison with the starting materials **1** and **2**. Thus, the signals at 6.71 and 6.20 ppm (**1**)[8] and 6.19 and 6.65 ppm (**2**)[9] in the starting materials are displaced to 7.18 and 6.65 ppm for **5a**, 7.16 and 6.62 ppm for **5b**, 6.99 and 6.62 ppm for **6a**, and 6.92 and 6.57 ppm for **6b**, respectively.

In the $^{13}C\{^1H\}$ NMR spectra of complexes **5** and **6** two resonance signals due to the acetylenic carbon atoms are found in the region of 130–140 (Ti-C≡*C*) and 160–170 ppm (Ti–*C*≡C). These signals are shifted to lower field in comparison to the respective resonances typical for complexes **1** and **2**[8,9] upon coordination of the C≡C triple bonds to the zinc(II) halide entities. This finding is in agreement with previously reported changes in the carbon resonance shifts from *non*coordinated to η^2-alkynyl-substituted titanocenes.[10]

To establish the solid-state structure of complexes **5** and **6**, an X-ray diffraction study was carried out on single crystals of **6b**. This complex crystallizes in the orthorhombic space group *Pbcn* with two independent molecules per asymmetric unit, each possessing an internal 2-fold axis; symmetry-generated atoms are indicated with the suffix a (molecule $\mathbf{6b_1}$) or b (molecule $\mathbf{6b_2}$). For these molecules two different orientations are found, $\mathbf{6b_1}$ and $\mathbf{6b_2}$, which are depicted in Figures 1 and 2, respectively. In $\mathbf{6b_1}$ one of the cyclopentadienyl ligands of the Fc units is disordered. Table 1 lists selected bond lengths and angles, and Table 2 contains the crystal and refinement data of $\mathbf{6b_1}$ and $\mathbf{6b_2}$.

In both orientations, $\mathbf{6b_1}$ and $\mathbf{6b_2}$, the zinc(II) center possesses a pseudotetrahedral environment, comprising η^2 coordination of the alkynyl groups and η^1 bonding of the bromo atom. Furthermore, in both molecules the side-on coordination of the alkynyl ligands to the group

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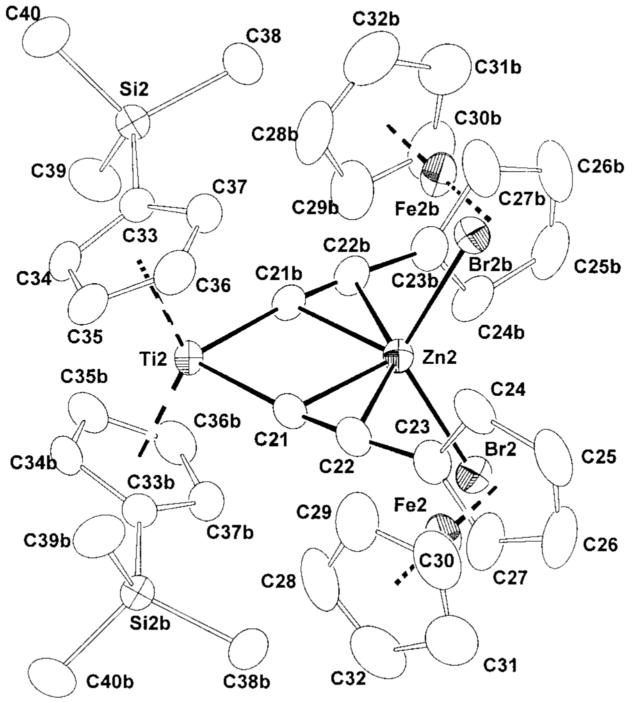

Figure 2. ZORTEP drawing[12] (drawn at the 50% probability level) of $\mathbf{6b_2}$ (with exclusion of the hydrogen atoms) with the atom-numbering scheme.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) and Torsion Angles (deg) of $\mathbf{6b_1}$ and $\mathbf{6b_2}$[a]

$\mathbf{6b_1}$		$\mathbf{6b_2}$	
	Distances		
Ti(1)−C(1)	2.120(5)	Ti(2)−C(21)	2.124(5)
C(1)−C(2)	1.229(7)	C(21)−C(22)	1.229(7)
C(2)−C(3)	1.435(7)	C(22)−C(23)	1.427(8)
Zn(1)−Br(1)	2.3655(7)	Zn(2)−Br(2)	2.3659(7)
Zn(1)−C(1)	2.181(5)	Zn(2)−C(21)	2.217(5)
Zn(1)−C(2)	2.703(5)	Zn(2)−C(22)	2.393(5)
Ti(1)−Zn(1)	3.1021(14)	Ti(2)−Zn(2)	3.1228(15)
	Angles		
Ti(1)−Zn(1)−Br(1)	122.02(2)	Ti(2)−Zn(2)−Br(2)	118.12(2)
Br(1)−Zn(1)−Br(1a)	115.97(5)	Br(2)−Zn(2)−Br(2b)	123.76(4)
C(1)−Ti(1)−C(1a)	89.3(3)	C(21)−Ti(2)−C(21b)	90.4(3)
C(1)−Zn(1)−C(1a)	86.2(3)	C(21)−Zn(2)−C(21b)	85.7(3)
C(2)−Zn(1)−C(2a)	138.6(2)	C(22)−Zn(2)−C(22b)	146.9(3)
Ti(1)−C(1)−C(2)	163.4(4)	Ti(2)−C(21)−C(22)	174.3(4)
C(1)−C(2)−C(3)	173.0(5)	C(21)−C(22)−C(23)	175.2(6)
	Torsion Angles		
Ti(1)−C(1)−C(2)−C(3)	−24(6)	Ti(2)−C(21)−C(22)−C(23)	−5(8)

[a] Standard deviations are given as the last significant figure in parentheses.

Table 2. Crystallographic Parameters for Complex 6b

empirical formula	$C_{40}H_{44}Br_2Fe_2Si_2TiZn$
fw	965.72
cryst syst	orthorhombic
space group	*Pbcn*
a, Å	21.1768(2)
b, Å	18.7144(2)
c, Å	20.1755(2)
V, Å^3	7995.77(14)
ρ_{calcd}, g cm^{-3}	1.604
Z	8
cryst size, mm	2.0 × 0.3 × 0.3
μ, mm^{-1}	3.583
radiation	Mo Kα
λ, Å	0.710 73
temp, K	173(2)
scan mode	ω-scan
2θ range, deg	1.45/30.27
index range	$-30 \leq h \leq 27$ $-26 \leq k \leq 17$ $-27 \leq l \leq 26$
no. of measd rflns	49 308
no. of unique rflns	10 975
no. of obsd rflns ($I \geq 2\sigma$(I))	6522
completeness to $\theta_{max} = 30.27°$, %	91.8
no. of ref params	462
min/max resid electron density, e Å^{-3}	−1.103/1.424
R1/wR2[a] ($I \geq 2\sigma(I)$)	0.0673/0.1356
R1/wR2[a] (all)	0.1289/0.1621
S (goodness of fit) on F^2 [b]	1.019

[a] $R1 = [\Sigma(||F_o| - |F_c|)/\Sigma|F_o|)]$. $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 3.8794P]$, with $P = [F_o^2 + 2F_c^2]/3c)$. [b] $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n - p))^{1/2}$; n = number of reflections, p = number of parameters used.

12 atom is accompanied by a decrease of the bite angles C_1−Ti−C_{1a} and C_{21}−Ti−C_{21b}, going from 98.8(4)° in **2** to 89.3(3) and 90.4(3)° in $\mathbf{6b_1}$ and $\mathbf{6b_2}$, respectively (Table 1). This result resembles the behavior already reported for other heterobimetallic tweezer-type molecules, featuring an early- and a late-transition-metal center connected via σ,π-bridging alkynyl groups.[10] On the other hand, it is found that the C≡C triple bonds of complex **6b** are not significantly elongated (C(1)−C(2), C(21)−C(22) 1.229(7) Å; Table 1), in comparison with the *non*coordinated starting material **2** (1.21(2), 1.227(13) Å).[9] This is in contrast to the experimental data found for other [Ti](C≡CR)$_2$-stabilized (R = SiMe$_3$, ^{t}Bu, Ph, Fc; Fc = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)) low-valent transition-metal fragments; e.g., typical values for {[Ti](C≡CFc)$_2$}Pd(PPh$_3$) are 1.260(6) and 1.259(6) Å.[11] The observed weak bond lengthening of the C≡C triple bonds upon η^2 coordination to the ZnBr$_2$ entity is in accordance with the shift of the ν(C≡C) vibration from 2015 cm^{-1} in **2**[8] to lower wavenumbers in **6** (2006 cm^{-1}) in the IR spectrum (vide supra).

The alkynyl carbon atoms C(1), C(2), C(1a), and C(2a) for $\mathbf{6b_1}$ or C(21), C(22), C(21a), and C(22b) for $\mathbf{6b_2}$ and the two metal centers Ti(1)/Ti(2) and Zn(1)/Zn(2) are arranged essentially in plane (root-mean-square deviation of fitted atoms: $\mathbf{6b_1}$, 0.0601 Å; for $\mathbf{6b_2}$, 0.0121 Å). Within this array, the positions of the alkynyl substituents of Fc in relation to the Ti(C≡C)Zn plane determine the structural differences encountered for $\mathbf{6b_1}$ and $\mathbf{6b_2}$ (Figure 3).

Figure 3 clearly shows that in $\mathbf{6b_1}$ the Fc groups are bent above and below the Ti(C≡C)$_2$Zn plane, while in $\mathbf{6b_2}$ both Fc groups are tilted to the same side of the plane. As a result, the Fc groups in $\mathbf{6b_1}$ are pointing away from the SiMe$_3$ substituents of the titanium-bonded cyclopentadienyl rings, and a Ti−C≡C$_{Fc}$ bending from 178.7(9) and 172.8(9)° in **2** to 163.4(4)° in $\mathbf{6b_1}$ is found. In contrast, in $\mathbf{6b_2}$ an almost linear arrangement of the Ti−C≡C$_{Fc}$ units is observed (Ti(2)−C(21)−C(22) = 174.3(4)°). The latter bending of the Ti−C≡C$_{Fc}$ units can be ascribed to the η^2 coordination of the alkynyl entities to the ZnBr$_2$ moiety, which is typical for many other heterobimetallic tweezer complexes of general composition {[Ti](C≡CR)$_2$}ML$_n$ (ML$_n$ = low-valent 10−14-valence-electron transition-metal fragment; R = singly bonded organic ligand).[10] However, the different *trans* bending behavior of molecules $\mathbf{6b_1}$ and

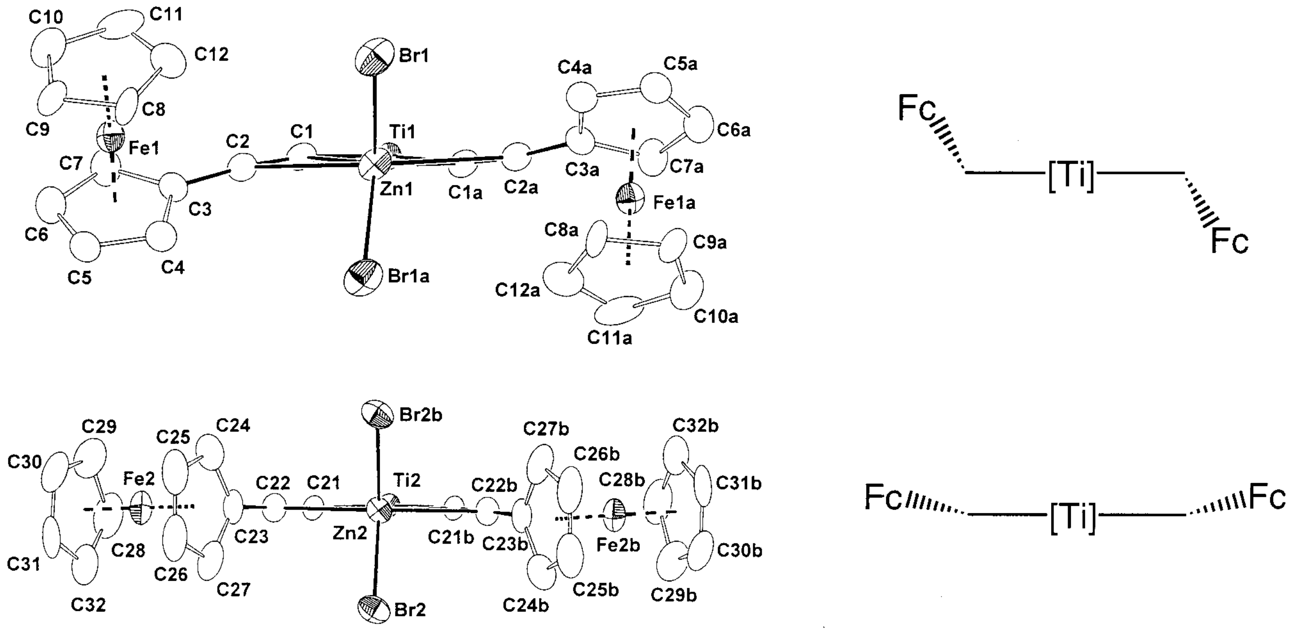

Figure 3. View of $\mathbf{6b_1}$ (top) and $\mathbf{6b_2}$ (bottom) along the Ti–Zn vector, showing displacement of the alkynyl substituents of Fc from the Ti(C≡C)$_2$Zn plane: (a) ferrocenyl groups bent above and below the plane; (b) ferrocenyl groups bent apart within the plane Ti(C≡C)$_2$Zn.

$\mathbf{6b_2}$ which is typical for complexed tweezer molecules, a result[10] of geometrical constraints, can be explained on the basis of the impossibility for the Fc units to bend any further in $\mathbf{6b_2}$ due to the proximity of the SiMe$_3$ groups; consequently, the two acetylide ligands cannot open up.

In accord with all these facts, the following additional features are encountered: (i) there is a smaller Ti–Zn bond distance in $\mathbf{6b_1}$ than in $\mathbf{6b_2}$ ($\mathbf{6b_1}$, Ti(1)–Zn(1) = 3.1021(14) Å; $\mathbf{6b_2}$, Ti(2)–Zn(2) = 3.1228(15) Å), the deformation of the Ti–C≡C–Fc unit in $\mathbf{6b_1}$ allowing the ZnBr$_2$ fragment to move closer to the Ti(IV) center; (ii) the iron-bound cyclopentadienyl rings C(8)–C(12) and C(8a)–C(12a) in $\mathbf{6b_1}$ are disordered and have been refined in two positions. The higher flexibility of $\mathbf{6b_1}$ with regard to the free rotation of the cyclopentadienyl rings C(8)–C(12) and C(8a)–C(12a) seem to be responsible for this effect.

In heterobimetallic **5a**,**b** as well as heterotetrametallic **6a**,**b**, the corresponding early–late metal centers are linked via σ,π-conjugated organic acetylide ligands (**5a**,**b**) or σ,π-coordinated as well as η^5-bonded cyclopentadienyl groups (**6a**,**b**); thus, electronic communication between the transition-metal centers should be possible. For this reason, cyclic voltammetry measurements have been carried out for selected complexes, **5a** and **6a**, to examine the redox behavior of the reducible group [Ti] and the oxidatable group Fc present in the molecules.

Characteristic for titanium(IV) centers with a d^0 configuration, as is typical in bis(alkynyl)titanocenes, is the observation of only one reversible wave in the cyclic voltamogram (**1**, $E_{1/2} = -1.79$ V, $\Delta E = 190$ mV;[13] **2**, $E_{1/2} = -1.99$ V, $\Delta E = 150$ mV[9]), which can be assigned to the Ti(IV)/Ti(III) redox couple. In contrast, upon

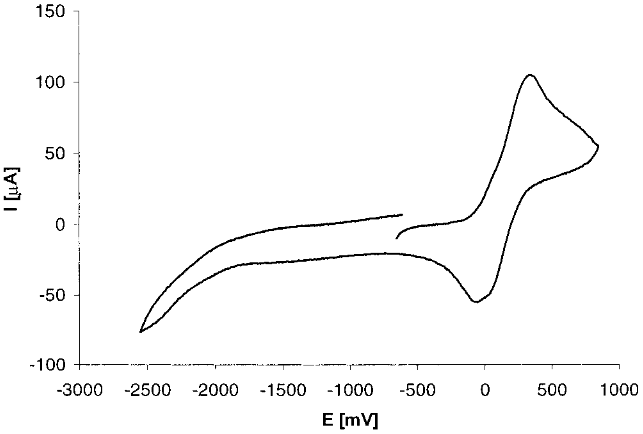

Figure 4. Cyclic voltammogram of **6a** in dichloromethane in the presence of [n-Bu$_4$N][PF$_6$] ($c = 0.1$ mol dm^{-3}) at 25 °C under N$_2$ (scan rate 100 mV s^{-1}). Potentials are referenced to the FcH/FcH$^+$ couple as internal standard ($E_{1/2} = 0.00$ V).

π-coordination of the alkynyl ligands of the organometallic π-tweezers [Ti](C≡CR)$_2$ (R = SiMe$_3$, Fc) to ZnCl$_2$ moieties, the cyclic voltammograms of **5a** and **6a** exhibit only an irreversible one-electron reduction (**5a**, $E_{\text{red}} = -1.19$ V; **6a**, $E_{\text{red}} = -2.3$ V) (Figure 4). The irreversibility of these waves has been demonstrated by multicyclic experiments from -1.3 to -3.0 V. A similar behavior has been reported for heterometallic {[Ti](C≡CFc)$_2$}Pd(PPh$_3$).[11]

For **6a**, where two Fc groups are present, the wave corresponding to the Fe(II)/Fe(III) redox couple (Figure 4) appears in the region of -0.5 to 1.0 V. The voltammogram of **6a** displays a reversible one-electron oxidation of the two Fc entities at $E_{1/2} = 0.18$ mV ($\Delta E = 120$ mV). Thus, the electrochemical response of the Fc units connected to Ti(IV) and Zn(II) shows a significant variation in comparison to that of the *non*coordinated bis(alkynyl) titanocene **2** ($E_{1/2} = 0.22$ mV, $\Delta E = 260$ mV).[9] This result points out that the η^2 coordination of

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the $[\mathrm{Ti}](\mathrm{C{\equiv}CFc})_2$ building block to a $\mathrm{ZnCl_2}$ moiety facilitates the oxidation of the Fc groups.

Experimental Section

General Methods. All reactions were performed under an atmosphere of purified nitrogen ($\mathrm{O_2}$ traces, CuO catalyst, BASF AG, Ludwigshafen, Germany; $\mathrm{H_2O}$ traces, molecular sieves, 4 Å) using standard Schlenk techniques. Solvents were dried and distilled prior to use; tetrahydrofuran and *n*-pentane were refluxed with sodium/benzophenone ketyl and dichloromethane with calcium hydride. IR spectra were obtained with a Perkin-Elmer FT-IR 1000 spectrometer as a film between NaCl plates. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance 250 spectrometer. ^{1}H NMR spectra were recorded at 250.130 MHz (internal standard relative to $\mathrm{CDCl_3}$, δ 7.27 ppm); ^{13}C{^{1}H} NMR spectra were recorded at 67.890 MHz (internal standard, relative to $\mathrm{CDCl_3}$, δ 77.0 ppm). Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane (δ 0 ppm). The C, H microanalyses were performed by the Organic Department, Technical University of Chemnitz, using a Foss Heraeus Vario EL Analysator. Cyclic voltammetry was carried out in dichloromethane solutions in the presence of $[n\text{-}\mathrm{Bu_4N}][\mathrm{PF_6}]$ (0.1 mol dm^{-3}) at 25 °C, using a Radiometer DEA 101 digital electrochemical analyzer, with a standard three-electrode cell arrangement (Pt, Pt, SCE) and were referenced to the ferrocene/ferrocenium couple FcH/FcH$^+$ ($E_{1/2}$ = 0.00 V) as internal standard.

General Remarks. $[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2$ (**1**)[8] and $[\mathrm{Ti}](\mathrm{C{\equiv}CFc})_2$ (**2**)[9] were prepared according to published procedures. The anhydrous $\mathrm{ZnX_2}$ (X = Cl, Br) salts were commercially purchased and used without further purification.

Synthesis of {[Ti](C≡CSiMe$_3$)$_2$}ZnX$_2$ (X = Cl (5a), Br (5b)). $[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2$ (**1**; 250 mg, 0.48 mmmol) was dissolved in tetrahydrofuran (30 mL), and then anhydrous $\mathrm{ZnCl_2}$ (**3**; 85 mg, 0.62 mmmol) was added in one portion at 25 °C. After the mixture was stirred for 2 h, all volatiles were evaporated in vacuo. Subsequently, the residue was extracted with 3 × 10 mL portions of dichloromethane and the extract was filtered through a pad of Celite. The filtrate was then concentrated to ca. 10 mL, and another 5 mL of *n*-pentane was added. Cooling to −30 °C afforded red needles of complex **5a** (260 mg, 0.40 mmol, 83% yield based on **1**).

Complex **5b** (red needles, 430 mg, 0.58 mmol, 93% yield based on **1**) was obtained in an analogous way, starting from $[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2$ (320 mg, 0.62 mmol) and anhydrous $\mathrm{ZnBr_2}$ (**4**; 180 mg, 0.80 mmol).

Complex 5a. Mp: 112 °C dec. IR (NaCl): 1989 cm^{-1} (C≡C). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.21 (s, 18H, SiMe$_3$), 0.34 (s, 18H, SiMe$_3$), 6.6 (m, 4H, C$_5$H$_4$), 7.2 (m, 4H, C$_5$H$_4$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 0.05 (SiMe$_3$), 0.16 (SiMe$_3$), 121.6 (C$_5$H$_4$), 123.6 (C$_5$H$_4$), 127.7 (C$_{\mathrm{ipso}}$, C$_5$H$_4$), 131.5 (TiC≡*C*), 160.0 (Ti*C*≡C). Anal. Calcd for $\mathrm{C_{26}H_{44}Cl_2Si_4TiZn}$ (653.23): C, 47.80; H, 6.80. Found: C, 47.75; H, 6.93.

Complex 5b. Mp: 129 °C dec. IR (NaCl): 1985 cm^{-1} (C≡C). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.19 (s, 18H, SiMe$_3$), 0.32 (s, 18H, SiMe$_3$), 6.62 (pt, 4H, C$_5$H$_4$, J_{HH} = 2.3 Hz), 7.15 (pt, 4H, C$_5$H$_4$, J_{HH} = 2.3 Hz). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −0.2 (m, SiMe$_3$), 121.2 (C$_5$H$_4$), 123.2 (C$_5$H$_4$), 130.7 (C$_{\mathrm{ipso}}$, C$_5$H$_4$), 134.1 (TiC≡*C*), 161.5 (Ti*C*≡C). Anal. Calcd for $\mathrm{C_{26}H_{44}Br_2Si_4TiZn}$ (742.13): C, 42.08; H, 5.99. Found: C, 41.82; H, 5.61.

Synthesis of {[Ti](C≡CFc)$_2$}ZnX$_2$ (X = Cl (6a), Br (6b)). $[\mathrm{Ti}](\mathrm{C{\equiv}CFc})_2$ (**2**; 250 mg, 0.33 mmmol) was dissolved in 30 mL of tetrahydrofuran at 25 °C, and then anhydrous $\mathrm{ZnCl_2}$ (60 mg, 0.43 mmol) was added in one portion. After the reaction mixture was stirred for 1 h at 25 °C, all volatiles were removed in vacuo, affording a bright green residue. Extraction with dichloromethane in 2 × 15 mL portions, followed by filtration of the extracts through a pad of Celite, produced after removal of all volatiles in vacuo heterometallic **6a** as a dark green solid (245 mg, 0.28 mmol, 85% yield based on **2**). Suitable crystals for X-ray diffraction studies could be obtained by slow diffusion of *n*-pentane into a tetrahydrofuran solution containing **6b** at 0 °C.

The same procedure described for the preparation of **6a** was applied to the synthesis of **6b**. With $[\mathrm{Ti}](\mathrm{C{\equiv}CFc})_2$ (**2**; 200 mg, 0.27 mmmol) and $\mathrm{ZnBr_2}$ (79 mg, 0.35 mmol) as starting materials, complex **6b** could be obtained (230 mg, 0.23 mmol, 88% yield based on **2**).

Complex 6a. Mp: 48 °C dec. IR (NaCl): 2010 cm^{-1} (C≡C). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.25 (s, 18H, Si*Me*$_3$), 4.49 (s, 10H, C$_5$*H*$_5$), 4.51 (pt, 4H, FcC$_5$*H*$_4$, J_{HH} = 1.7 Hz), 4.70 (pt, 4H, FcC$_5$*H*$_4$, J_{HH} = 1.7 Hz), 6.62 (pt, 4H, C$_5$*H*$_4$SiMe$_3$, J_{HH} = 2.3 Hz), 6.99 (pt, 4H, C$_5$*H*$_4$SiMe$_3$, J_{HH} = 2.3 Hz). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −0.16 (SiMe$_3$), 68.5 (Fc*C*$_5$H$_4$), 68.6 (C$_{\mathrm{ipso}}$, Fc*C*$_5$H$_4$), 69.9 (Fc*C*$_5$H$_4$), 70.6 (*C*$_5$H$_5$), 119.6 (C$_5$H$_4$SiMe$_3$), 121.8 (C$_5$H$_4$SiMe$_3$), 126.3(C$_{\mathrm{ipso}}$, C$_5$H$_4$SiMe$_3$), 134.2 (TiC≡*C*), 161.2 (Ti*C*≡C). Anal. Calcd for $\mathrm{C_{40}H_{44}Cl_2Fe_2Si_2TiZn}$ (876.89): C, 54.78; H, 5.07. Found: C, 54.55; H, 4.87.

Complex 6b. Mp: 56 °C dec. IR (NaCl): 2006 cm^{-1} (C≡C). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.21 (s, 18H, Si*Me*$_3$), 4.47 (pt, 4H, FcC$_5$*H*$_4$, J_{HH} = 1.7 Hz), 4.48 (s, 10H, C$_5$*H*$_5$), 4.66 (pt, 4H, FcC$_5$*H*$_4$, J_{HH} = 1.7 Hz), 6.57 (pt, 4H, C$_5$*H*$_4$SiMe$_3$, J_{HH} = 2.3 Hz), 6.92 (pt, 4H, C$_5$*H*$_4$SiMe$_3$, J_{HH} = 2.3 Hz). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): −4.55 (SiMe$_3$), 66.2 (*C*$_5$H$_5$), 67.0 (Fc*C*$_5$H$_4$), 67.3 (C$_{\mathrm{ipso}}$, Fc*C*$_5$H$_4$), 68.6 (Fc*C*$_5$H$_4$), 115.2 (C$_5$H$_4$SiMe$_3$), 117.5 (C$_5$H$_4$SiMe$_3$), 121.1(C$_{\mathrm{ipso}}$, C$_5$H$_4$SiMe$_3$), 132.1 (TiC≡*C*), 157.4 (Ti*C*≡C). Anal. Calcd for $\mathrm{C_{40}H_{44}Br_2Fe_2Si_2TiZn}$ (965.79): C, 49.74; H, 4.60. Found: C, 49.82; H, 4.52.

X-ray Structure Determination of 6b. The solid-state structure of **6b** was determined from single-crystal X-ray diffraction. Data collection was performed on a Bruker SMART CCD area detector using Mo Kα radiation. Crystallographic data of **6b** are given in Table 2. The structure was solved by direct methods (SHELX 97; G. M. Sheldrick, University of Göttingen, Göttingen, Germany, 1997). 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.

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Supporting Information Available: Figures giving additional views and tables giving crystallographic data for **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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