Bi- and oligometallic early and late transition metal complexes based on alkynyl-titanocenes and related species spanned by carbon rich π-systems

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Abstract

The synthesis and reaction chemistry of bi- and oligometallic transition metal complexes containing Groups 4, 8, 10 as well as 11 metal atoms are presented. The respective metals are thereby linked by carbon rich π-conjugated organic units, mainly σ- and π-bonded alkynyls. The structural aspects and electrochemical properties of the corresponding complexes will be discussed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the early work of Creutz and Taube [1], there is a rapidly growing interest in the synthesis, chemical and physical properties of homo- and heterodinuclear species in which a π-conjugated organic ligand spans the two transition metal atoms [2–4].

Meanwhile, a series of redox-active model compounds have been synthesized, such as $(\eta^5\text{-}C_5Me_5)$-$(dppe)Fe\text{–}C\equiv C\text{–}C\equiv C\text{–}Fe(\eta^5\text{-}C_5Me_5)(dppe)$ [5] and $[(\eta^5\text{-}C_5Me_5)(NO)(Ph_3P)Re\text{–}C\equiv C\text{–}C\equiv C\text{–}C\equiv Mn(\eta^5\text{ - }C_5H_5)\text{-}(CO)_2]^+$ [6] in which a molecular wire consisting of an all-carbon C_4- or C_5-chain, bridges two metal centers giving rise to an electron coupling through five or six bonds.

Next to these late–late transition metal complexes, also a number of early–late species, e.g. $(\eta^5\text{-}C_5H_5)(Me_3P)_2Ru\text{–}C\equiv C\text{–}Zr(\eta^5\text{-}C_5H_5)_2(Cl)$ [7] are known [8].

Extending the idea of connecting early and late transition metal building blocks from all-carbon units to other carbon-rich π-conjugated organic groups enables the synthesis of molecules of type (Me_3SiCH_2)-$[Ti]\text{–}C\equiv C\text{–}C_6H_4\text{–}C\equiv N \rightarrow [Ru]\text{-}1,4$ $\{[Ti] = (\eta^5\text{-}C_5H_5)_2Ti, (\eta^5\text{-}C_5H_4SiMe_3)_2Ti, \ldots, [Ru] = RuCl_2[C_6H_3N(CH_2\text{-}NMe_2)_2\text{-}2,6]\}$ [9]. Beside linear organic bridges based on σ-bonded alkynyls, also organometallic π-tweezers of type $[Ti](C\equiv CR)_2$ (R = singly bonded organic or organometallic unit) allow the synthesis of early–late transition metal complexes in which the respective metal atoms are linked by σ- and π-bound alkynyl groups [10].

Thus, in this article we focus on the synthesis as well as the electrochemical behavior of early–late (Ti–M) and late–late (M–M′; M, M′ = Groups 8, 10 and/or 11 transition metal atoms of the periodic table of elements) complexes, since such species are well-suited to study electronic communication between the corresponding metal centers. Despite the many homo- and heterometallic redox active (model) complexes known [2–4,11,12] we focus here on species which are mainly based on titanium–alkynyl fragments.

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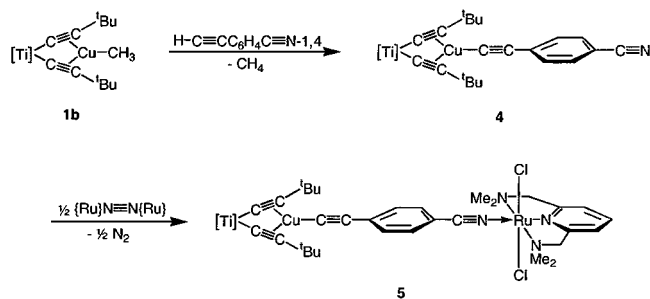
Scheme 1. Synthesis of 5 [14b].
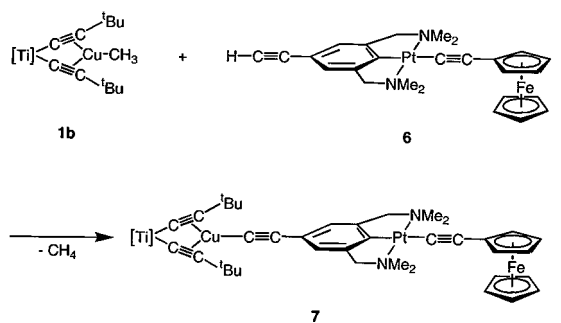
Scheme 2. Preparation of 7 [14b].

2. Results and discussion

2.1. Synthesis and reaction chemistry

The heterobimetallic tweezer molecules {[Ti]-(C≡CR)$_2$}MX {[Ti] = (η^5-C$_5$H$_5$)$_2$Ti, (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti, ...; M = Cu, Ag; R = SiMe$_3$, ^{t}Bu, Ph, Fc, ...; X = organic or inorganic ligand; Fc = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)} can be successfully used as suitable starting materials for the preparation of diverse hetero-oligonuclear transition metal complexes [10]. In this respect, {[Ti](C≡CR)$_2$}CuCH$_3$ (1) (1a, R = SiMe$_3$; 1b, R = ^{t}Bu) [13] affords on its reaction with acidic hydrogen-containing molecules such as H–C≡CFc (2) the trinuclear species {[Ti](C≡CR)$_2$}CuC≡CFc (3a, R = SiMe$_3$; 3b, R = ^{t}Bu) with concurrent loss of CH$_4$ [14–16]. In the latter complexes, an early (Ti) and two late (Cu, Fe) transition metals are linked via RC≡C and C≡CC$_5$H$_5$ groups.
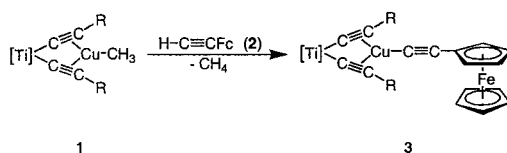
Other heterotrinuclear molecules like {[Ti]-(C≡C^{t}Bu)$_2$}CuC≡CC$_6$H$_4$–C≡N → {Ru}-1,4 (5) ({Ru} = RuCl$_2$[NC$_5$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]) are accessible by the reaction sequence shown in Scheme 1 [14b].

Even a heterotetranuclear complex can be obtained. Joining the tweezer molecule 1b with the preformed late–late platinum–iron species H–C≡C{Pt}C≡CFc [{Pt} = PtC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6] (6), Scheme 2] on subsequent loss of CH$_4$ produces 7 in very good yield [14a].

Complex 7 represents one of the rare examples of multinuclear metal complexes in which early and late transition metals are bridged via acetylide, phenyl and cyclopentadienyl groups, with the corresponding metal centers in different coordination modes: Ti (pseudo-tetrahedral), Cu (trigonal-planar), Pt (square-planar) and Fe (sandwich) [14a].

In addition, the Pt–Fe acetylide 6 (vide supra) allows the preparation of a wide variety of different heterometallic transition metal complexes. For example, the stepwise synthesis of the mixed metal acetylide (Ph$_3$P)AuC≡C{Pt}C≡CFc (13) is described in Scheme 3. The silyl-protected Pt–acetylide Me$_3$SiC≡C{Pt}Cl (8) produces by deprotection of the C≡C functionality H–C≡C{Pt}Cl (9) [17]. The latter complex affords on treatment with (Ph$_3$P)AuCl (10) in a 1:1 molar ratio in presence of CuCl as catalyst [18] the platinum–gold species (Ph$_3$P)AuC≡C{Pt}Cl (11) (Scheme 3) [19]. Reaction of 11 with Me$_3$SnC≡CFc (12) [20] gives upon formation of Me$_3$SnCl the linear heterotrimetallic rigid-rod shaped complex (Ph$_3$P)AuC≡C{Pt}C≡CFc (13) (Scheme 3) in which, again, the appropriate transition metals are span by acetylide, phenyl and cyclopentadienyl units [19].

In the latter molecules, only late metal centers are present. A series of related titanium–σ-acetylides of the type ([Ti](CH$_2$SiMe$_3$)(C≡CC$_5$H$_4$N → {Ru}-1,4) (15) and ([Ti](CH$_2$SiMe$_3$)(C≡CC$_6$H$_4$C≡N → {Ru}-1,4) (16) in which early and late transition metal centers are span by linear π-conjugated organic systems are accessible by
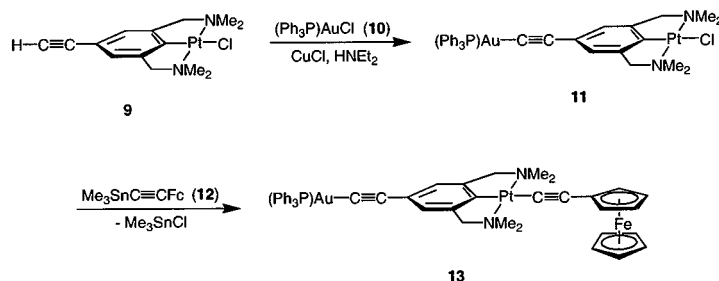

Scheme 3. Synthesis of the linear mixed metal complexes 11 and 13 [19].
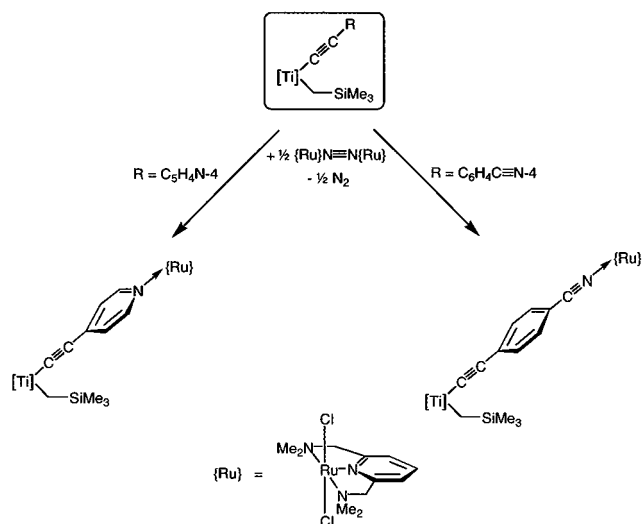
Scheme 4. Synthesis of early–late rigid-rod structured **15** and **16** [9].
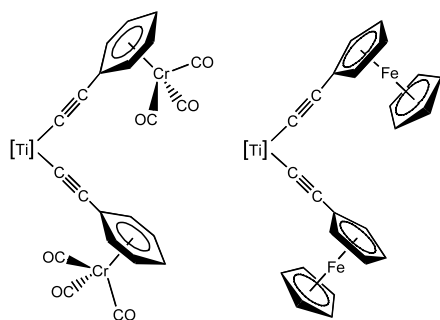
Fig. 1. Complexes **21** [21] (left) and **22** [8j] (right).

treatment of [Ti](CH$_2$SiMe$_3$)(C≡CR) (**14a**: R = C$_5$H$_4$N-4; **14b**: R = C$_6$H$_4$C≡N-4) with {Ru}N≡N{Ru} ({Ru} = RuCl$_2$[NC$_5$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]) in a 2:1 molar ratio (Scheme 4) [9]. Complexes **15** and **16** are thereby obtained in high yields [9].

Replacing the organic groups R (R = C$_5$H$_4$N, C$_6$H$_4$C≡N-4) in **14a** and **14b**, respectively, by an organometallic Fc unit leads to the early–late complex [Ti](CH$_2$SiMe$_3$)(C≡CFc) (**18**), which is a further example of a mixed transition metal species in which a reducible ([Ti]) and an oxidizable (Fc) group are connected via an C≡C(η^5-C$_5$H$_4$) unit; electronic communication between the two metal centers is reasonable [9]. Complex **18** can be synthesized by reacting [Ti](CH$_2$SiMe$_3$)(Cl) (**17**) with an equimolar amount of LiC≡CFc (for a detailed discussion of the electrochemical behavior of **18** see below) [9]. A similar reaction method also serves for the preparation of the homodinuclear Ti(IV) species (Me$_3$SiCH$_2$)[Ti]–C≡CC$_6$H$_4$C≡C–[Ti](CH$_2$SiMe$_3$)-1,4 (**19**) [9].

Likewise, LiC≡C[(η^6-C$_6$H$_5$)Cr(CO)$_3$] or LiC≡CFc can act as a starting material for the synthesis of the trimetallic π-tweezer molecules [Ti][C≡C(η^6-C$_6$H$_5$)Cr(CO)$_3$]$_2$ {**21**, [Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti} [21] or
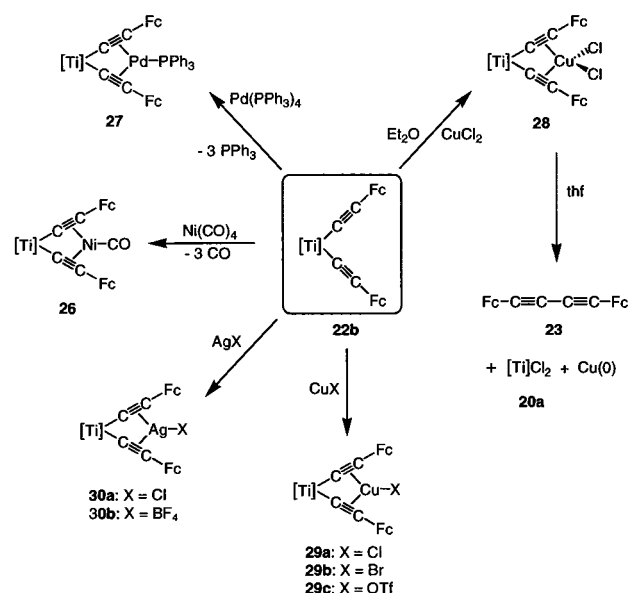
Scheme 5. Synthesis of complexes **26**–**30** [25].

[Ti](C≡CFc)$_2$ {**22a**, [Ti] = (η^5-C$_5$H$_5$)$_2$Ti; [8j] **22b**, [Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti [8j] (Fig. 1). Accordingly, **21** and **22** are formed when [Ti]Cl$_2$ {**20a**, [Ti] = (η^5-C$_5$H$_5$)$_2$Ti; **20b**, [Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti} is reacted with two equivalents of LiC≡C[(η^6-C$_6$H$_5$)Cr(CO)$_3$] or LiC≡CFc, respectively [8j,21].

Complexes **22a** and **22b** can electrochemically (for a detailed discussion see Section 2.2) or chemically (AgPF$_6$, NiCl$_2$) be oxidized to yield the 1,4-diferrocenyl substituted butadiyne **23** [8j].
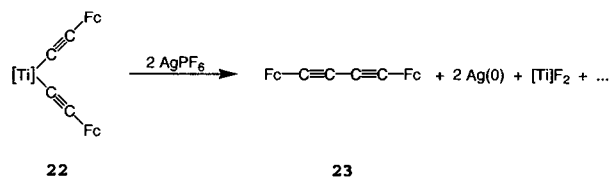
C$_4$-Bridged **23** can be considered as a coupling product of two FcC≡C units in which a C$_4$-chain links the two sandwich moieties (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$), thus acting as a molecular wire. This arrangement gives rise to an electron coupling through the cyclopentadienyl and C≡C connectivity [22].

The same electrochemically or chemically induced redox process is found for the tweezer molecules [Ti][(C≡C)$_2$Fc]$_2$ {**24a**, [Ti] = (η^5-C$_5$H$_5$)$_2$Ti; **24b**, [Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti} [8l,23] as well as [Hf](C≡CFc)$_2$ {[Hf] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Hf} (**25**) [8k].

To prove that the titanocene–ferrocenyl complexes **22** and **24** can act as organometallic chelating ligands (vide supra), they have been reacted with various transition metal complexes [23–25].

Depending on the ratio of the substrates used, different reaction products are formed. Thus, addition of one equivalent of Ni(CO)$_4$, Pd(PPh$_3$)$_4$, CuCl$_2$, CuX or AgX

(X = Cl, Br, OTf, BF$_4$) to **22b** results in the formation of the corresponding tetranuclear tweezer complexes **26–30** (Scheme 5) [25].

It is worth noting that the reaction of [Ti][(C≡CFc)$_2$] (**22b**) with CuCl$_2$ is strongly solvent dependent [25b]. Complex **28** is readily formed as main product when **22b** is reacted with CuCl$_2$ in diethyl ether as solvent. However, complexes **20a** and **23** along with elemental copper are produced when tetrahydrofuran instead of diethyl ether is used (Scheme 5) [25b].

The electrochemical properties of complexes **26–30** are presented in Section 2.2.

However, using a 2:1 molar ratio in the reaction of [Ti][(C≡C)$_n$Fc]$_2$ (**22**, n = 1; **24**, n = 2) or [Ti][(C≡CPh)$_2$] (**31a**) with Group 11 metal systems MX, produces the cationic complexes **32–34** in which the Group 11 metal atoms M act as the connecting points between two [Ti][(C≡C)$_n$R]$_2$ units (R = Fc, Ph; n = 1, 2) (Table 1) [23,26,27]. The appropriate ionic [{[Ti][(C≡C)$_n$R]}$_2$M]$^+$ X$^-$ complexes are obtained in very good yields [23,26,27].

22: R = Fc
24: R = C≡CFc
31a: R = Ph

32 - 34
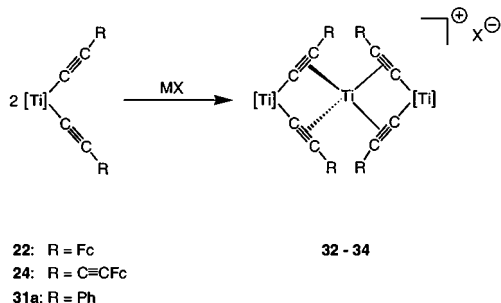
The cationic trinuclear complexes **34a–34c** along with the heptanuclear species **32a–32d**, **33a** and **33b**, represent the first examples of bis(titanium) tweezer-type chelate species with Cu(I) or Ag(I) centers, which are η^2-coordinated by the four C≡C triple bonds of the two titanocene moieties [Ti][(C≡CR)$_2$].

In **32–34** the cationic organometallic framework is built-up by two [Ti][(C≡C)$_n$R]$_2$ (R = Rc, Fc, Ph; n = 1,

2) tweezer units which are orientated almost perpendicular to each other with linear Ti–M–Ti arrangements [23,24,27].

While, the previously described early–late (Ti–Fe, Ti–Ru, Ti–Pt, Ti–Au) and late–late (Au–Pt, Pt–Fe, Au–Pt–Fe,...) transition metal complexes contain linear rigid-rod shaped sub-structures, it is apparent that the carbon rods in the cationic ({[Ti][(C≡C)$_n$R]$_2$}M)$^+$ units, as given in e.g. **32d** are curved in a s-shaped way by viewing along the Ti–M–Ti axis [23].

Similar compounds to **32–34** can be prepared when cis-bis(alkynyl) platinum complexes of type L$_2$Pt(C≡CR)$_2$ (e.g. L$_2$ = dppe, bipy′, bipy; L = PEt$_3$, PPh$_3$; R = Ph, ^{t}Bu) are reacted with a copper(I) or silver(I) salt MX (M = Cu, Ag; X = BF$_4$, ClO$_4$) in a 2:1 molar ratio [28–30].

Also, cationic as well as neutral heteroatomic complexes in which two {[Ti](C≡CSiMe$_3$)$_2$}M entities are connected by single halide or pseudohalide bridges could recently be synthesized [27,31]. Hereby, several approaches exist as outlined in Scheme 6.

The tetrametallic complexes of structural type [{[Ti](C≡CSiMe$_3$)$_2$}M$_a$–X–M$_b${(Me$_3$SiC≡C)$_2$[Ti]}]$^+$ClO$_4^-$ (**37–39**; M$_a$, M$_b$ = Cu, Ag; X = Cl, Br, I, CN, OCN, SCN, SeCN) (Table 3) can be obtained when {[Ti](C≡CSiMe$_3$)$_2$}M$_a$X ([Ti](C≡CSiMe$_3$)$_2$}M$_a$X (**35a**, X = Cl; **35b**, X = Br; **35c**, X = I; **35d**, X = CN; **35e**, X = SCN; M$_a$ = Ag: **36a**, X = Cl; **36b**, X = Br; **36c**, X = I; **36d**, X = CN; **36e**, X = OCN; **36f**, X = SCN; **36g**, X = SeCN) is reacted with {[Ti](C≡CSiMe$_3$)$_2$}M$_b$OClO$_3$ (**35f**, M$_b$ = Cu; **36h**, M$_b$ = Ag) in a 1:1 molar ratio [reaction (i), Scheme 6, Table 2]. The orange colored species **37–39** are obtained in almost quantitative yield [27]. A noticeable feature in the synthesis of **37–39** is the replacement of the Cu(I) or Ag(I) η^1-bound OClO$_3$ ligand in **35g** or **36h** by the ligands X in **35a–35e** or **36a–36g** (see above), leading to the formation of bent Ti–M$_a$–X–M$_b$–Ti arrays (**37–39**) with single halide or pseudohalide bridges. Within these substructures, the corresponding Group 11 metal atoms M$_a$ and M$_b$ main-

Table 1
Synthesis of complexes **32–34**

Compound	[Ti]	n	R	M′	X	References
32a	(η^5-C$_5$H$_4$)$_2$Ti	1	Fc ^{a}	Cu	BF$_4$	[26]
32b	(η^5-C$_5$H$_4$)$_2$Ti	1	Fc ^{a}	Ag	ClO$_4$	[26]
32c	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	1	Fc ^{a}	Ag	PF$_6$	[8l]
32d	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	1	Rc ^{b}	Ag	PF$_6$	[8l]
33a	(η^5-C$_5$H$_4$)$_2$Ti	2	Fc ^{a}	Ag	PF$_6$	[8l]
33b	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	2	Fc ^{a}	Ag	PF$_6$	[8l]
34a	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	1	Ph	Ag	ClO$_4$	[27]
34b	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	1	Ph	Ag	NO$_3$	[27]
34c	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	1	Ph	Cu	BF$_4$	[27]

^{a} Fc = Ferrocenyl, (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$).
^{b} Rc = Ruthenocyl, (η^5-C$_5$H$_4$)Ru(η^5-C$_5$H$_5$).
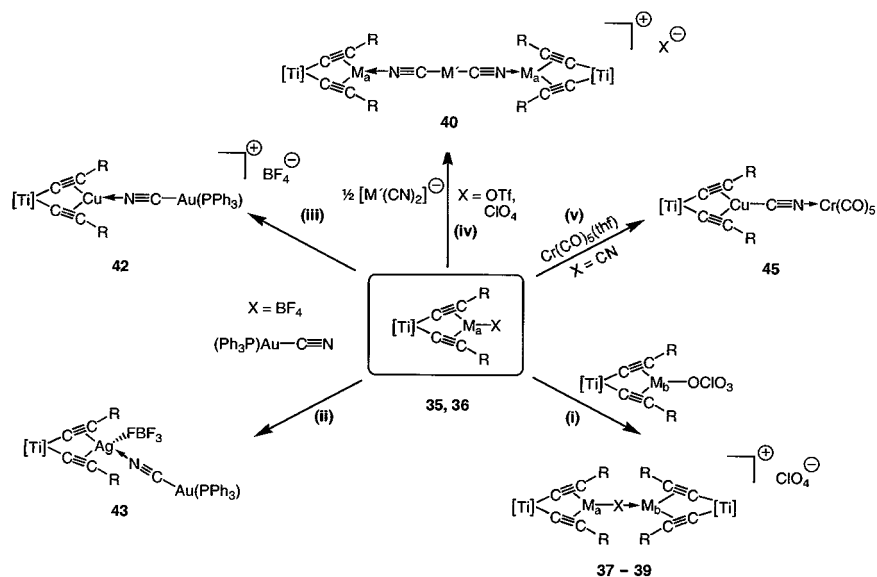
Scheme 6. Synthesis of complexes **37–40**, **42**, **43** and **45** (M_a, M_b = Cu, Ag; M' = Cu, Ag, Au; R = SiMe$_3$; X = Cl, Br, I, CN, SCN, SeCN, BF$_4$, OTf, ClO$_4$, ...) [27,31].

tain their trigonal-planar environment, as it could be shown by X-ray structure analysis [27].

In contrast, the pentametallic cationic transition metal complexes of type $\{[Ti](C\equiv CSiMe_3)_2\}M_a \leftarrow N\equiv C-M'-C\equiv N \rightarrow M_b\{(Me_3Si-C\equiv C)_2[Ti]\}^+$ (**40a–40d**) (Table 2) are easily accessible by treatment of **35g**, **35f** or **35h** with $[M'(C\equiv N)_2]^-$ (M' = Cu, Ag, Au) in a 2:1 molar ratio [reaction (iv), Scheme 6]. Complexes **40a–40d** possess a linear $Ti-M_a \leftarrow N\equiv C-M'-C\equiv N \rightarrow M_b-Ti$ array [27,31].

Even a cationic nonametallic complex can be synthesized by the reaction of four equivalents of $\{[Ti](C\equiv CSiMe_3)_2\}AgOClO_3$ (**36h**) with one equivalent of $K_3[Ag(C\equiv N)_4]$ [27,32]. Thereby, cross-shaped structured **46** can be isolated in excellent yield [27,32].
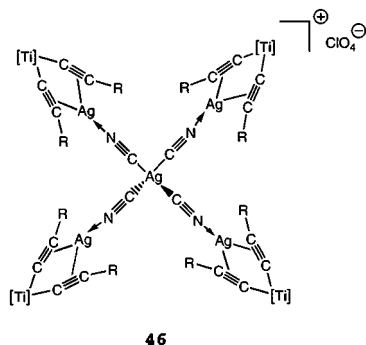
In **46** four cationic heterobimetallic tweezer moieties $[\{[Ti](C\equiv CSiMe_3)_2\}Ag]^+$ are linked by a $[Ag(C\equiv N)_4]^{3-}$ core in which each C≡N ligand is datively bonded to a silver(I) center of a individual tweezer fragment [14,19]. While, the inner silver atom possesses a tetrahedral surrounding, the outer silver(I) centers are trigonal-planar coordinated [27,32].

Formally, one tweezer unit in **37–40** can be replaced by other transition metal fragments such as $(Ph_3P)AuC\equiv N$ (**41**). As shown in reaction (iii) (Scheme 6) treatment of $[\{[Ti](C\equiv CSiMe_3)_2\}Cu(N\equiv CMe)]BF_4$ (**35f**) with one equivalent of **41** affords upon elimination of MeC≡N the Ti(IV)–Cu(I)–Au(I) species **42** (Scheme 6) in which the CuN≡CAu(PPh$_3$) building block is stabilized by the chelate effect of the tweezer entity [Ti](C≡CR)$_2$ [31].

To synthesize neutral oligometallic transition metal complexes, rather than cationic ones, stoichiometric

Table 2
Synthesis of complexes **37–40** [27]

Compound	M_a	M_b	X	M'
37a	Cu	Cu	Cl	–
37b	Cu	Cu	Br	–
37c	Cu	Cu	I	–
37d	Cu	Cu	CN	–
37e	Cu	Cu	SCN	–
38a	Cu	Ag	Cl	–
38b	Cu	Ag	Br	–
38c	Cu	Ag	I	–
38d	Cu	Ag	CN	–
38e	Cu	Ag	SCN	–
39a	Ag	Ag	Cl	–
39b	Ag	Ag	Br	–
39c	Ag	Ag	I	–
39d	Ag	Ag	CN	–
39e	Ag	Ag	OCN	–
39f	Ag	Ag	SCN	–
39g	Ag	Ag	SeCN	–
40a	Cu	Cu	–	Cu
40b	Cu	Cu	–	Ag
40c	Cu	Cu	–	Au
40d	Ag	Ag	–	Ag

Table 3
Synthesis of complexes [Ti](C≡CR^1)$_2$M^1–LL–M^2(R^{2}C≡C)$_2$[Ti] (47–49)

Compound	R^1	M^1	LL	M^2	R^2	References
47	^{t}C$_4$H$_9$	Cu	C≡CC≡N	Ag(OTf)	SiMe$_3$	[33b]
48a	^{t}C$_4$H$_9$	Cu	(O$_2$C)$_3$C$_6$H$_3$-1,3,5 [a]	Cu	^{t}C$_4$H$_9$	[14a,e]
48b	^{t}C$_4$H$_9$	Cu	(O$_2$C)$_2$C$_6$H$_3$-1,3-(CO$_2$H)-5	Cu	^{t}C$_4$H$_9$	[14a,e]
48c	^{t}C$_4$H$_9$	Cu	{O$_2$C(η^5-C$_5$H$_4$)}$_2$Fe	Cu	^{t}C$_4$H$_9$	[14a,e]
48d	^{t}C$_4$H$_9$	Cu	{O$_2$C(η^5-C$_5$H$_4$)}$_2$Fe	Cu	SiMe$_3$	[14a,e]
48e	^{t}C$_4$H$_9$	Cu	O$_2$CCH$_2$C(O)C(=CH$_2$)CO$_2$	Cu	SiMe$_3$	[14a,e]
48f	^{t}C$_4$H$_9$	Cu	O$_2$CC$_6$H$_4$CO$_2$-1,4	Cu	^{t}C$_4$H$_9$	[14a,e]
48g	^{t}C$_4$H$_9$	Cu	trans-O$_2$CCH=CHCO$_2$	Cu	^{t}C$_4$H$_9$	[14a,e]
48h	^{t}C$_4$H$_9$	Cu	cis-O$_2$CCH=CHCO$_2$	Cu	^{t}C$_4$H$_9$	[14a,e]
48i	^{t}C$_4$H$_9$	Cu	O$_2$C–CO$_2$	Cu	^{t}C$_4$H$_9$	[14a,e]
48j	^{t}C$_4$H$_9$	Cu	trans-O$_2$CCH=CHCO$_2$	Cu	SiMe$_3$	[14a,e]
48k	^{t}C$_4$H$_9$	Cu	O$_2$CC≡C	Cu	^{t}C$_4$H$_9$	[14a,e]
48l	^{t}C$_4$H$_9$	Cu	O$_2$CC≡CCO$_2$	Cu	^{t}C$_4$H$_9$	[14a,e]
48m	SiMe$_3$	Cu	O$_4$C$_6$H$_2$ [b]	Cu	SiMe$_3$	[14a,e]
48n	^{t}C$_4$H$_9$	Cu	O$_2$CFcCO$_2$H	–	–	
49a	SiMe$_3$	Ag	O$_2$CC$_6$H$_4$CO$_2$-1,4	Ag	SiMe$_3$	[27]
49b	SiMe$_3$	Ag	trans-O$_2$CCH=CHCO$_2$	Ag	SiMe$_3$	[27]
49c	Ph	Ag	O$_2$CCO$_2$	Ag	Ph	[27]
49d	SiMe$_3$	Ag	O$_4$C$_6$H$_2$ [b]	Ag	SiMe$_3$	[33b]
49e	SiMe$_3$	Ag [c]	C$_8$H$_6$N$_4$ [d]	Ag	SiMe$_3$	[33b]
49f	SiMe$_3$	Ag [e]	Pyrazine	Ag	SiMe$_3$	[27]
49g	SiMe$_3$	Ag [e]	4,4′-Bipyridine	Ag	SiMe$_3$	[27]

[a] Contains a additional third {[Ti](C≡C^{t}Bu)$_2$}Cu tweezer unit.
[b] O$_4$C$_6$H$_2$ = dianion of 2,5-dihydroxybenzoquinone.
[c] Contains two triflate (OTf) counter ions.
[d] C$_8$H$_6$N$_4$ = bipyrimidine.
[e] Contains two perchlorate counter ions.

amounts of {[Ti](C≡CSiMe$_3$)$_2$}AgBF$_4$ (36i) were reacted with 41 to yield {[Ti](C≡CSiMe$_3$)$_2$}Ag[← N≡CAu-(PPh$_3$)][FBF$_3$] (43) [reaction (ii), Scheme 6] [31]. While in cationic 42 a trigonal-planar copper(I) center is present, in neutral 43 the coordination sphere around silver(I) expands and an 18-valence electron fragment, with silver in a tetrahedral configuration is formed [31].

In contrast to 40 and 42, complex 43 displays a non-linear Ti–Ag ← N≡C sequence as required by the pseudotetrahedral geometry around silver. A similar structural motif has been observed in {[Ti]-(C≡CSiMe$_3$)$_2$}Ag(thf)(FBF$_3$) [33a]. The different coordination behavior of copper(I) and silver(I) towards Lewis bases (e.g. complexes 42 and 43) can be explained by the different sizes of the corresponding Group 11 metals (Cu: 1.28 Å; Ag: 1.45 Å) [34].

A modified approach to compounds, which feature linear heterometallic assemblies, is given by the reaction of 35d with Cr(CO)$_5$(thf) (44) [reaction (v), Scheme 6] [31]. However, the resulting complex {[Ti](C≡CSiMe$_3$)$_2$}CuC≡N → Cr(CO)$_5$ (45) could only be characterized spectroscopically, due to its high instability [31].

Multiple tweezer systems, as given in complexes 47–49, have also been linked together by functionalized organic or organometallic ligands, such as cyano-acetylide, bipyrimidine, pyrazine, 4,4′-bipyridine or the salts of bi- or tricarboxylic acids [27,33,35]. These species are summarized in Table 3.

As an example, the synthesis of 48d is described in Scheme 7. The alkyne stabilized copper(I) methyl complex 1b reacts even at low temperature with one equivalent of (η^5-C$_5$H$_4$CO$_2$H)$_2$Fe (50) with loss of CH$_4$ to produce orange-colored {[Ti](C≡C^{t}Bu)$_2$}CuO$_2$C(η^5-C$_5$H$_4$)$_2$Fe(η^5-C$_5$H$_4$CO$_2$H) (48n) in quantitative yield [36]. Further treatment of 48n with {[Ti](C≡CSiMe$_3$)$_2$}CuMe (1a) results in the formation of the asymmetric pentametallic complex 48d (Scheme 7) [36]. In 48d two different Ti–Cu complex fragments are connected via the ferrocenyl dicarboxylate entity (η^5-C$_5$H$_4$CO$_2$)$_2$Fe. It was found that in this reaction the yield of 48d is somewhat lowered when the reaction is carried out at higher temperature, due to concurrent decomposition of {[Ti](C≡CSiMe$_3$)$_2$}CuMe (1a) to form the tetrametallic Ti$_2$–Cu$_2$–acetylide {[Ti](C≡CSiMe$_3$)-(C≡CCu)}$_2$ [37].

Electrochemical studies have shown that only one pair of redox processes is observed for the copper(I) centers in 48c and 48f [36]. This indicates that electronic communication between the corresponding metal centers via the organometallic ferrocenyl dicarboxylate ligand is not favored (for a detailed discussion see Section 2.2). Moreover, it seems that the carboxylate units of the ferrocenyl connectivity act as an impedance rather than as a transmitter [36].

48d

48a

49e

49f
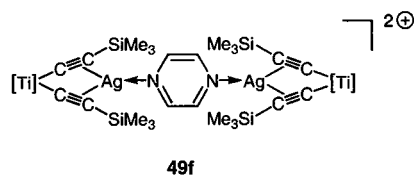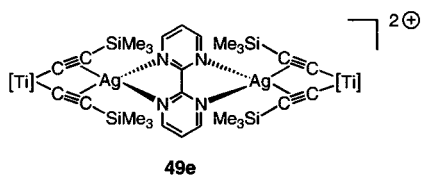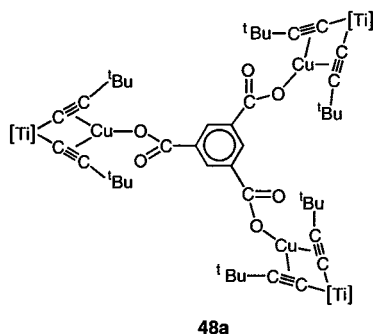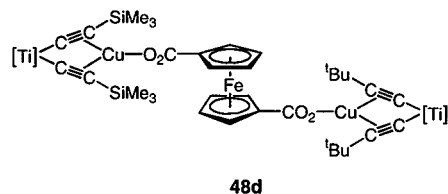
The main aspects of the structure and bonding properties of the (hetero)bi- and -oligonuclear complexes discussed, are based on IR and NMR (^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}) spectroscopic studies as well as X-ray structure analysis [10]. Significant observations with respect to the alkyne-to-M interactions are: (i) weakening of the C≡C triple bond of the Ti-bonded acetylide ligands,

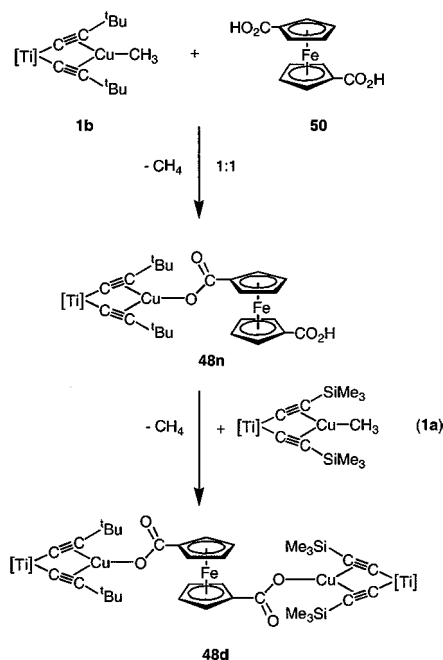Scheme 7. Synthesis of **48n** and **48d** [36].

(ii) *trans*-bending (with exception of the cationic trimetallic and pentametallic complexes **32**–**34**) of the Ti–C≡C–R units upon η^2-coordination to the appropriate M center and (iii) diminution of the angle C_α–Ti–$C_{\alpha'}$ (C_α = metal-bonded sp-hybridized carbon atoms, Ti–C_α≡C_β) [10].

Since, these main aspects have recently been reviewed [10] in the following we concentrate only on the electrochemical behavior of the above described complexes, because they are promising candidates to study intra- and/or intermolecular electronic communication between the appropriate transition metal centers.

2.2. Electrochemical studies

In this section cyclic voltammetric studies on selected titanium-containing mono- and bis(alkynyl) species (**1**, **3**–**5**, **7**, **26**–**30**, **42**, **43**, **45**, **48** and **49**) are discussed comparatively.

The objective of this work was to gain an insight into the influence of both, the nature of the organic groups and the effect of the proximity of a further metal atom on the Ti(IV)/Ti(III) redox potential, and indirectly, the effect of connecting early and late transition metal centers by inorganic and/or π-conjugated organic groups. Table 4 gives the relevant cyclic voltammetric data of representative mono-alkynyl functionalized examples and, for comparative purposes, the data of the parent compounds [Ti]Cl$_2$ and [Ti](Cl)(CH$_2$SiMe$_3$) (**17**) [8k,38]. The cyclic voltammogram of [Ti]Cl$_2$ (**20a**) in

Table 4
Comparison of electrochemical data of compounds **14–20** and **51**

Compound	Reduction		Oxidation		References
	E_0 (V)	ΔE (mV)	E_0 (V)	ΔE (mV)	
14a	−1.97	100			[9]
14c	−2.26	100			[9]
15	−2.15	60	−0.42	90	[9]
16	−1.98	80	−0.46	100	[9]
17	−1.85 [a]				[9]
18	−2.25	70	−0.08 [b]		[38]
19	−2.12	100			[9]
20a	−1.45	190			[38]
51			−0.32	70	[9]

The cyclic voltammograms have been recorded in tetrahydrofuran solutions ($c = 1 \times 10^{-3}$ M) in the presence of [$^nBu_4N$][PF_6] ($c = 0.1$ M) at 25 °C under N_2; scan rate 100 mV s^{-1}; potentials are referenced to the FcH/FcH$^+$ couple (internal standard).

[a] Irreversible process.
[b] Irreversible oxidative process and immediately appearance of a reversible wave at $E_0 = 0.01$ V ($\Delta E = 130$ mV).

tetrahydrofuran exhibits a quasi-reversible reduction process at $E_0 = -1.45$ V ($\Delta E = 190$ mV) which can be assigned to the Ti(III)/Ti(IV) redox couple [38]. This behavior contrasts with results obtained in acetonitrile solutions, where this process has been shown to be irreversible [8k]. Interestingly, when one reactive site is blocked with a σ-bonded Me_3SiCH_2 group, as in [Ti](Cl)(CH_2SiMe_3) (**17**), an irreversible reductive process is observed at $E_{red} = -1.85$ V [8k]. Nevertheless, compared with [Ti]Cl_2 (**20a**) the reduction of Ti(IV) to Ti(III) in **17** is shifted by ca. 0.4 V to a more negative potential. When the chloride ligand in **17** is substituted by an alkynyl ligand such as $Me_3SiC\equiv C$ {complex [Ti]($C\equiv CSiMe_3$)(CH_2SiMe_3), (**14c**)} [9] or $C\equiv CFc$ {complex [Ti]($C\equiv CFc$)(CH_2SiMe_3), (**18**)} [9], the cyclic voltammogram again reveals a reversible reduction wave for the Ti(IV)/Ti(III) couple [**18**: $E_0 = -2.25$ V ($\Delta E = 70$ mV), **14c**: $E_0 = -2.26$ V ($\Delta E = 100$ mV)], which is shifted by another ca. 0.4 V to a more negative potential (Table 4) [9].

In homo- or heterobimetallic (Me_3SiCH_2)[Ti]$C\equiv C$-$C_6H_4C\equiv C$-1,4-[Ti](CH_2SiMe_3) (**19**), (Me_3SiCH_2)[Ti]$C\equiv CC_5H_4N \rightarrow$ {Ru}-1,4 (**15**) and (Me_3SiCH_2)[Ti]$C\equiv C$-$C_6H_4C\equiv N \rightarrow$ {Ru}-1,4 (**16**) one could predict that the presence of two metal centers leads to the appearance of two distinct reduction waves. However, this is only found in complexes **15** and **16** [9].

As shown in Table 4, both titanocene fragments in **19** have the same reversible reduction potential, which manifests itself in a concerted two-electron process at $E_0 = -2.12$ V ($\Delta E = 100$ mV) [9]. This may be explained by the fact that the intermetallic distance imposed by the $C\equiv C$–C_6H_4–$C\equiv C$-1,4 array is either too large, or the overlap of the π-orbitals of this unit is disturbed, due to the rotation of the C_6H_4 ring around the $C\equiv C$–C_6H_4–$C\equiv C$ axis and thus, despite the presence

of a π-conjugated organic system, the two metals are electrochemically isolated from each other [39].

The Ti(VI)/Ti(III) redox potential of the mixed-metal complexes **15** [$E_0 = -2.15$ V ($\Delta E = 60$ mV)] and **16** [$E_0 = -1.98$ V ($\Delta E = 80$ mV)] indicates that the η^1-coordinated Ru(II) complex fragment {Ru} does not add electrochemically significant additional electron density to the Ti(IV) center. This fact has already been observed for **18** [9] and is corroborated by a comparison of the Ti(VI)/Ti(III) redox potentials of {[Ti](CH_2SiMe_3)$C\equiv CC_5H_4N$-4} (**14a**) and its {Ru}-adduct **15**. The electrochemical data of both complexes reveal that the relevant reversible Ti(IV)/Ti(III) redox couples remain virtually unaffected [9].

As expected, the mononuclear titanium complexes **14**, **17** and **20** do not exhibit metal centered oxidation processes, while for **15**, **16**, **18** and {Ru}$N\equiv CPh$ (**51**), e.g. an irreversible one-electron oxidation is observed at −0.1 V for **18** [9]. A second, reversible one-electron oxidation appears, which persists in multicyclic experiments and can be assigned to the Fe(II)/Fe(III)-couple in HC≡CFc, which is formed instantaneously under the conditions of the measurement [8j]. For the heterodinuclear ruthenium complexes **15** and **16**, a reversible oxidative process for the Ru(II)/Ru(III) redox couple is found as depicted in Fig. 2 (Table 4).

One can summarize that the presence of a titanocene entity in a position *para* to the ruthenium moiety, as in complexes **15** and **16**, influences the latter in such a way that the oxidation of Ru(II) to Ru(III) is facilitated, when compared with the benzonitrile–ruthenium complex {Ru}$N\equiv CPh$ (**51**) in which only one metal atom is present (Table 4) [9].

Cyclic voltammetric studies were also carried out on selected bi- and trimetallic gold-containing complexes [19]. For comparative purposes, the electrochemical

data of $(Ph_3P)AuCl$ (**10**) and $(Ph_3P)AuC\equiv CFc$ (**52**) are also given. Table 5 clearly shows that the reduction potential of Au(I)/Au(0) in $(Ph_3P)AuC\equiv C[C_6H_3-(CH_2NMe_2-2,6)PtCl-1,4]$ (**11**) and **52** is shifted to more negative values than in **10**, demonstrating that the gold centers in **11** and **52** are more difficult to reduce [19].

Similar observations were made for the oxidation of the platinum atoms in **11**, **13**, $Me_3SiC\equiv C\{Pt\}Cl$ (**53**) and $Me_3SiC\equiv C\{Pt\}C\equiv CFc$ (**54**) [19]. While, an irreversible two-electron oxidation is found at ca. $+0.8$ V for Pt(II)/Pt(IV) in **53**, in bi- or trimetallic **11**, **13** and **54** a shift to a more negative potential of the Pt(II)/Pt(IV) couple by ca. 0.4 V is typical [19]. The oxidation of the ferrocenyl moieties in complexes **13**, **52** and **54** is reversible and appears at ca. -0.1 V, which indicates that these species are more easily oxidized than FcH itself [19]. In general, it seems that the $C\equiv CC_6H_3-(CH_2NMe_2)_2-2,6$ building block, as well as the acetylide units in **11**, **13**, **52** and **54** support electronic communication between the appropriate transition metal atoms
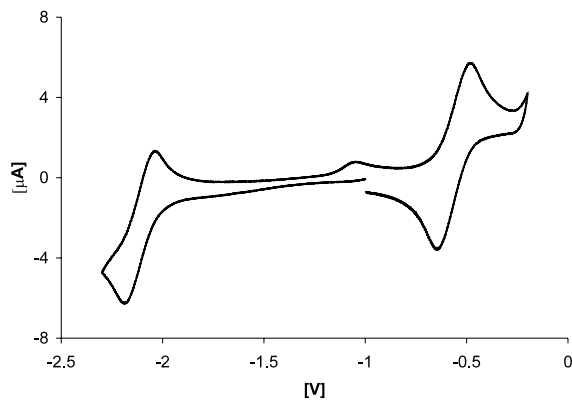

Fig. 2. Cyclic voltammogram of **15** in a tetrahydrofuran solution in the presence of $[^nBu_4N][PF_6]$ ($c = 0.1$ M) at 25 °C under N_2 at a scan rate of 100 mV s^{-1}. Potentials are referenced to the FcH/FcH$^+$ couple as an internal standard.

Table 5
Comparison of electrochemical data of **10**, **11**, **13** and **52–54** [19]

Compound	Reduction	Oxidation		
	Au(I)/Au(0)	Fe(II)/Fe(III)		Pt(II)/Pt(IV)
	E_{red} (V)	E_0 (V)	ΔE (mV)	E_{Ox} (V)
10	-2.70			
11	-2.91			0.53
13		-0.02	90	0.41
52	-3.12	-0.15	80	
53				0.76
54		-0.13	75	0.38

The cyclic voltammograms have been recorded in tetrahydrofuran solutions ($c = 1 \times 10^{-3}$ M) in the presence of $[^nBu_4N][PF_6]$ ($c = 0.1$ M) at 25 °C under N_2; scan rate 100 mV s^{-1}; potentials are referenced to the FcH/FcH$^+$ couple (internal standard).

platinum, gold and/or iron through the π-conjugated organic systems present [19].

In addition to the mono-alkynyl titanocene complexes described above, the bis(alkynyl) titanocene species **22**, **37–39** and **48** were also investigated by cyclic voltammetric methods. In carboxylate-bridged multinuclear systems, such as $[\{[Ti](C\equiv C'Bu)_2\}_2[CuO_2C(\eta^5-C_5H_4)]_2Fe]$ (**48c**) and $[\{[Ti](C\equiv C'Bu)_2\}[CuO_2C-(\eta^5-C_5H_4)Fe(\eta^5-C_5H_4)CO_2Cu]\{(Me_3SiC\equiv C)_2[Ti]\}]$ (**48d**) electrochemical studies showed that in these species the carboxylate units of the ferrocenyl connectivity act as an impedance rather than as a transmitter [36]. A similar behavior is observed in the tetranuclear halide-bridged bis(tweezer) complexes **37a–37c**, **38a–38c** and **39a–39c** (Table 2) [27]. In the pseudohalide-bridged tetranuclear complexes **37d–37e**, **38d–38e** and **39d–39g** (Table 2) a more detailed insight into the redox behavior of the corresponding metal centers could be obtained. For e.g., in the thiocyanato-bridged species **37e**, **38e** and **39f** it is found that first the easiest reducible metal center [M(I)] is irreversibly reduced to M(0) (M = Ag: **38e**, **39f**; M = Cu: **37e**), resulting, besides other undefined products, in the formation of heterobimetallic $\{[Ti](C\equiv CSiMe_3)_2\}M(SCN)$ [27]. If the reduction potential is further decreased to a more negative value, the M(I) center of the latter species undergo an irreversible reduction of the second M(I) center to produce elemental M, giving rise to the formation of the free bis(alkynyl) titanocene $[Ti](C\equiv CSiMe_3)_2$ (**31b**) [27]. Complex **31b** shows a reversible one-electron reduction at $E_0 = 1.94$ V ($\Delta E = 120$ mV) for the Ti(IV)/Ti(III) couple [27]. The described finding is identical for complexes **37e**, **38e** and **39f**, respectively [27].

Impressive examples of an electrochemical behavior are given by the tri- or tetrametallic bis(alkynyl) titanocene and hafnocene species $[M][(C\equiv C)_nFc]_2$ (M = Ti, Hf) as well as $\{[Ti][(C\equiv C)_nFc]_2\}M'X$ (M'X = Group 11 metal fragment; $n = 1, 2$) [8j-8l,23,25]. As an example, the cyclic voltammogram of $[Ti](C\equiv CFc)_2$ (**22b**) in $MeC\equiv N$ is shown in Fig. 3a [8j].

As typical for d^0-titanium centers, only one reversible reduction wave for the Ti(IV)/Ti(III) redox couple in **22b** is observed at ca. -1.3 V in $MeC\equiv N$ solution (Fig. 3a) [8j]. In addition to this reversible reduction, a total of three oxidation steps are found at $+0.37$, $+0.59$ and $+0.67$ V. By comparison with authentic $FcC\equiv C-C\equiv CFc$ (**23**) [40], the waves at $+0.59$ and $+0.67$ V can be assigned to the reversible Fe(II)/Fe(III) oxidative process of the coupling product **23** (Fig. 4), which was formed under the conditions of the measurement. The irreversible peak at $+0.37$ V corresponds to a two-electron oxidative process, indicating the electrochemical independence of the two ferrocenyl units present in **22b**. This assignment is in agreement with the total current, for which the Fe(II)/Fe(III) waves was about four times as large as for the one-electron reduc-
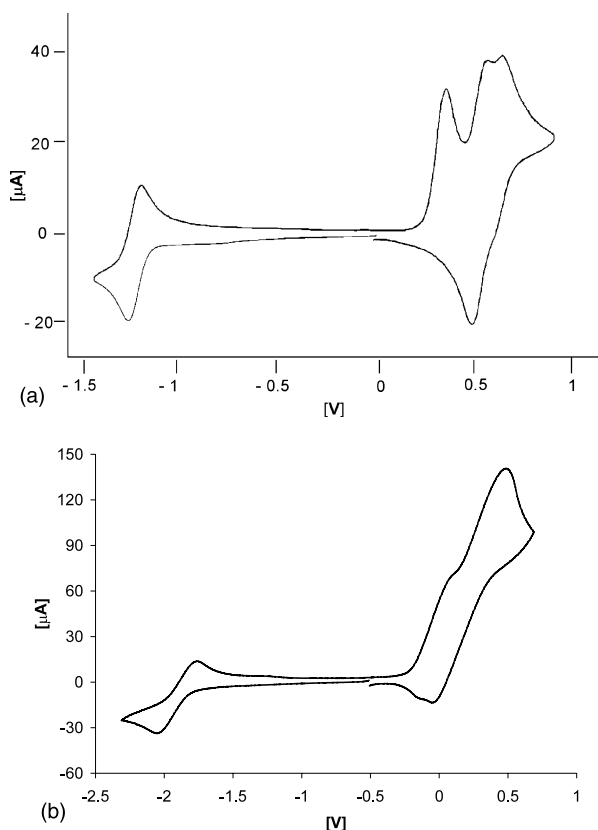
Fig. 3. Cyclic voltammogram of **22b** in a MeC≡N solution in the presence of [^{n}Bu$_4$N][PF$_6$] ($c = 0.1$ M) at 25 °C under N$_2$ at a scan rate of 200 mV s^{-1}. Potentials are referenced to the FcH/FcH$^+$ couple (internal standard). (b) Cyclic voltammogram of **22b** in a tetrahydrofuran solution in the presence of [^{n}Bu$_4$N][PF$_6$] ($c = 0.1$ M) at 25 °C under N$_2$ at a scan rate of 200 mV s^{-1}. Potential values are referenced to the FcH/FcH$^+$ couple (internal standard).
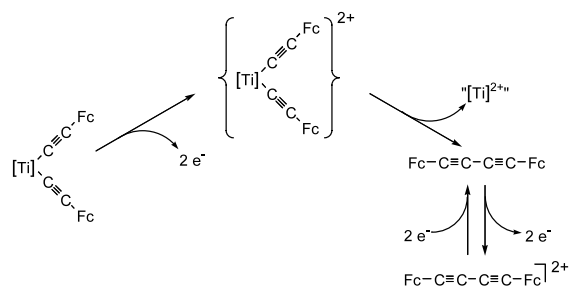

Fig. 4. Chemical behavior of **22** during cyclic voltammetric investigations [8j].

tion Ti(IV)/Ti(III). The disappearance of the oxidative wave at $+0.37$ V (**22b**) and the appearance of the two redox waves with $E_0 = +0.59$ and $+0.67$ V suggests that the oxidative coupling product **23** is formed instantaneously after oxidation of the two ferrocenyl entities in **22b** has taken place [8j].

However, the oxidatively induced coupling of the two FcC≡C moieties to produce FcC≡C–C≡CFc (**23**) is not even averted when both alkynyl ligands in [Ti](C≡CFc)$_2$ are η^2-coordinated to an additional transition metal

center as given in {[Ti](C≡CFc)$_2$}Ni(CO) (**55**) [8j]. Here, it is found that in addition to the redox wave at $E_0 = -1.83$V ($\Delta E = 84$ mV) during the oxidative scan three waves at $E = +0.22$, $+0.59$ and $+0.67$ V are found. While the first wave is irreversible, the last two are reversible and can be assigned to the oxidatively induced coupling product, compound **23** (see above) [8j]. Furthermore, the reduction potential of the Ti(IV)/Ti(III) couple is significantly shifted to a more negative value upon addition of the late transition metal center nickel (for comparison: [Ti](C≡CSiMe$_3$)$_2$ [41]: $E_0 = -1.17$ V, **22b** [8j]: $E_0 = -1.28$ V, **55** [8j]: $E_0 = -1.83$ V; MeC≡N solution) [42]. A similar behavior is found for {[Ti](C≡CFc)$_2$}Pd(PPh$_3$) (**56**) [25c]. In the region of -0.5 to 1.0 V the cyclic voltammogram of **56** displays synchronous irreversible one-electron oxidation for the two Fc entities at $E_{ox} = -0.06$ V (Fig. 5). Thus, the electrochemical response of the Fc units connected to Ti(IV) and Pd(0) via an organic π-system is shifted to a more negative potential compared to [Ti](C≡CFc)$_2$ (**22**) [25c]. This indicates a facilitation of the oxidation of Fe(II) to Fe(III). As in the case of **22**, Ti–C$_{C≡C}$ σ-bond cleavage and elimination of **23** takes place, immediately after oxidation of the Fc units [8j,k]. The reversible electrochemical response of the all-carbon bridged FcC≡C–C≡CFc molecule ($E_0 = +0.22$ V, $\Delta E = 210$ mV) can be observed at its reported potential in tetrahydrofuran solution (Fig. 3b) [25c,43].

In contrast to the reversible Ti(IV)/Ti(III) reductive wave observed for **22b** in tetrahydrofuran solution ($E_0 = -1.99$ V, $\Delta E = 150$ mV; Fig. 3b), the cyclic voltammogram of complex **56** exhibits an irreversible one-electron reduction at $E_{red} = -2.72$ V (Fig. 5) [25c]. The irreversibility of this wave has been demonstrated by multicyclic experiments between -1.5 and -3.0 V. In the course of these experiments, a new and subse-
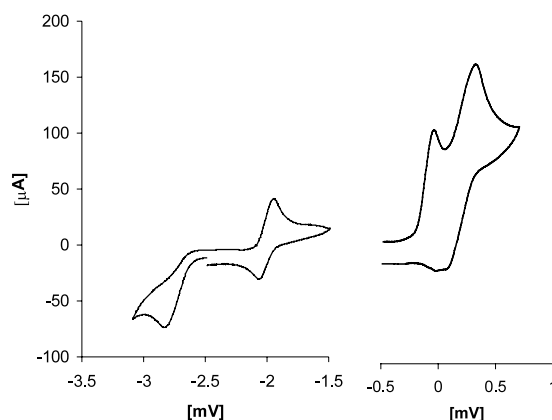

Fig. 5. Cyclic voltammogram in the reductive (left) and oxidative region (right) of {[Ti](C≡CFc)$_2$}Pd(PPh$_3$) (**56**) in a tetrahydrofuran solution in the presence of [^{n}Bu$_4$N][PF$_6$] ($c = 0.1$ M) at 25 °C under N$_2$ at a scan rate of 100 mV s^{-1}. Potentials are referenced to the FcH/FcH$^+$ couple (internal standard).

quently reversible wave at $E_0 = -1.99$ V ($\Delta E = 120$ mV) appears, which can be assigned to the Ti(IV)/Ti(III) redox couple of **22**. This indicates the loss of the 'Pd(PPh$_3$)' building block, initialized by the one-electron reduction of **56**, and subsequent formation of **22** [25c]. In order to gain a deeper insight into this finding, the heterobimetallic complex {[Ti](C≡CSiMe$_3$)$_2$}Pd-(PPh$_3$) (**57**) [44] in which the Fc units in **56** are replaced by SiMe$_3$ groups has been studied electrochemically. It revealed essentially an identical behavior, with an irreversible one-electron reduction process at $E_{red} = -2.71$ V and appearance of a reversible wave at $E_0 = -1.95$ V ($\Delta E = 120$ mV) [25c].

Upon changing the Ti(IV) center in [Ti](C≡CFc)$_2$ (**22b**) to Hf(IV) (complex **25**) a comparable electrochemical behavior is found [8k]. The cyclic voltammetric analysis in MeC≡N solutions of this species shows a reversible one-electron reduction at $E_0 = -1.99$ V ($\Delta E = 87$ mV), which can be assigned to the Hf(IV)/Hf(III) redox couple [8k]. From 0 to $+0.85$ V the cyclic voltammogram is dominated — as was described for the isostructural titanocene complex (vide supra) — by a total of three oxidative waves at $+0.42$, $+0.59$ and $+0.68$ V.

A comparison of the redox potentials of a series of related titanocene and hafnocene compounds shows that by changing from [Ti]Cl$_2$ (**20a**) to [Ti](C≡CSiMe$_3$)$_2$ (**31b**) or [Ti](C≡CFc)$_2$ (**22b**) the redox potentials in MeC≡N are shifted from $E_0 = -0.75$ V in **20a** to -1.17 V in **31b** or even -1.28 V in **22b** [8j,k]. This clearly demonstrates that the electron density of the Ti(IV) center is significantly increased by replacing the chlorides by acetylides. In contrast, the redox potentials of the hafnocene species remain virtually unchanged {[Hf]Cl$_2$: $E_0 = -1.89$ V, [Hf](C≡CPh)$_2$: $E_0 = -1.85$ V, [Hf](C≡CFc)$_2$: $E_0 = -1.99$ V} [8k]. However, changing from [Hf](C≡CPh)$_2$ to [Hf](C≡CFc)$_2$ as typical for the related titanium complex **22**, a shift of the Hf(IV)/Hf(III) potential to a more negative value is observed, indicating that the ferrocenyl entities in both, the titanocene and the hafnocene complexes, can be considered as weak electron-donating ligands through the C$_2$-entities [8k].

The oxidatively induced coupling of the FcC≡C moieties in **22** and **25** which produces the diyne **23** is not observed when the sandwich units Fc are replaced by the half-sandwich entities (η^6-C$_6$H$_5$)Cr(CO)$_3$ (complex **21**) [21].

Acknowledgements

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