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Electron transfer reactions of $(C_5R_5)_2(CO)_2Ti$ ($R = H$ or Me) with TCNE or TCNQ

Spectroelectrochemical assignment of metal and ligand oxidation states in $[(C_5Me_5)_2(CO)Ti(TCNX)]^{2-|q|+}$

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Abstract

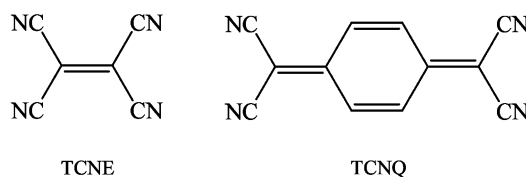
The TCNX ligands TCNE (tetracyanoethene) and TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) react instantaneously with $(C_5R_5)_2(CO)_2Ti$, $R = H$ or Me , to yield highly air-sensitive mononuclear complexes $(C_5R_5)_2(CO)Ti(TCNX)$ of which the soluble species ($R = Me$) were characterized also in the oxidized and reduced forms through cyclic voltammetry, EPR, IR and UV–vis spectroelectrochemistry. While oxidation at rather low potentials yields labile carbonyltitanium(IV) species of the $TCNX^{\bullet-}$ ligands, the reduction occurs stepwise at unusually negative potentials, first on the ligand (to yield coordinated $TCNX^{2-}$) and then on the metal (to form Ti^{II}). For the neutral complexes $(C_5R_5)_2(CO)Ti^{2+q}(TCNX^{-q})$ the results support a rather large amount of charge transfer $1 < q < 2$ from the metal to the acceptors TCNX. Evidence for the previously formulated $\{(\mu-TcNE^{2-})[(C_5H_5)_2Ti^{IV}(CO)]_2\}(TCNE^{2-})$ could not be found. The complexes $(C_5R_5)_2(CO)Ti(TCNE)$ are compared with related compounds $(C_5R_5)_2BrV(TCNE)$, $(C_6R_6)(CO)_2Cr(TCNE)$ and $(C_5R_5)(CO)_2Mn(TCNE)$.

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Keywords: Electron transfer; Spectroelectrochemistry; TCNE; TCNQ; Titanium compounds

1. Introduction

The TCNE and TCNQ molecules are among the least ‘innocent’ ligands in coordination chemistry [1] due to their very low-lying π^* orbitals. Typically, these easily reducible compounds ($E_{1/2}$ ca. -0.25 V vs. $[(C_5H_5)_2Fe]^{+/0}$) form radical ions $TCNX^{\bullet-}$ or even dianions $TCNX^{2-}$ in their reactions with metal complexes, leading to mono-, di-, tri- or tetranuclear nitrile-bonded σ complexes, to π complexes with side-on coordination, or to corresponding ion pair compounds $(TCNX^{\bullet-})(^+ML_n)$ without direct coordination [1].



The combination of radicals $TCNX^{\bullet-}$ in conjunction with paramagnetic metal centers has produced some of the most remarkable molecular magnetic materials [2,3] such as ferromagnetic $(TCNE^{\bullet-})[Fe(C_5Me_5)_2]$ [4], or $(TCNE^{\bullet-})_2V \cdot 2CH_2Cl_2$, an organometallic ferrimagnet active beyond room temperature (T_c ca. 400 K) [5].

Despite the neighborhood of V and Ti in the periodic table and the resulting chemical similarity there have not been many reports on complexes between organotitanium compounds and the TCNX ligands. In one communication [6] it was postulated that the reaction of TCNE with $(C_5H_5)_2(CO)_2Ti$ in benzene produces insoluble diamagnetic $\{(\mu-$

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TCNE) $\{[(C_5H_5)_2Ti(CO)]_2\}$ (TCNE) with titanium(IV) centers and TCNE²⁻ dianions, one free and one bridging. This interpretation was based on the occurrence of several $\nu(CN)$ bands in the infrared spectra [6]. Other reports have appeared on compounds between bis(dicyclopentadienyltitanium(IV)) species and TCNE^{•-} [7] or TCNQ (CT complex) [8]. Herein we demonstrate through elemental analysis, cyclic voltammetry, EPR, IR and UV–vis spectroelectrochemistry the formation of mononuclear complexes $(C_5R_5)_2(CO)Ti(TCNX)$, taking largely advantage of the better soluble pentamethylcyclopentadienide systems (R = Me).

2. Results and discussion

2.1. Formation, composition and properties

Both TCNE and TCNQ react spontaneously with one molar equivalent of red $(C_5R_5)_2(CO)_2Ti$, R = H or Me, in THF to yield complexes which analyze as $(C_5R_5)_2(CO)Ti(TCNX)$. The green complexes with R = H were either insoluble or unstable in common organic solvents, we thus report only their IR spectra (cf. Fig. 1) in connection with those of the better soluble but highly air-sensitive species $(C_5Me_5)_2(CO)Ti(TCNE) = \mathbf{1}$ (blood-red) and $(C_5Me_5)_2(CO)Ti(TCNQ) = \mathbf{2}$ (dark blue). We assume that the green insoluble complexes $(C_5H_5)_2(CO)Ti(TCNX)$ are intermolecularly associated, possibly through π/π interactions [1], whereas the soluble and differently colored $\mathbf{1}$ and $\mathbf{2}$ exist as monomeric molecules in solution. Reactions of the TCNX ligands with four equivalents of $(C_5Me_5)_2(CO)_2Ti$ gave only $\mathbf{1}$ and $\mathbf{2}$ as isolable material.

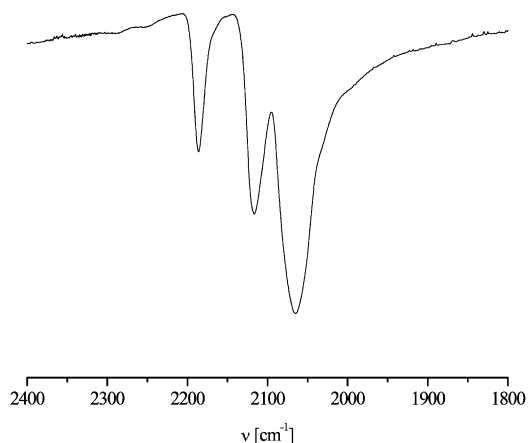
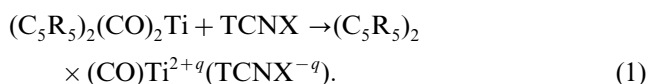


Fig. 1. Infrared spectrum of $(C_5H_5)_2(CO)Ti(TCNQ)$ in nujol.

2.2. IR vibrational spectra

Infrared spectra of the complexes $(C_5R_5)_2(CO)Ti(TCNX)$ in nujol show three main bands in the region of the cyanide and carbonyl stretching vibrations (Fig. 1, Table 1).

These bands situated between 2039 and 2193 cm^{-1} are shifted to lower energies relative to $\nu(CN) > 2216 cm^{-1}$ of the free TCNX ligands [1,9] but to higher energies relative to $\nu(CO) < 1977 cm^{-1}$ of the Ti^{II} precursors (Table 1). Like the instantaneous formation (which can be attributed to electron transfer catalysis [1,10]) these spectroscopic results point to an oxidation of the carbonyltitanium fragments and to a corresponding reduction of the TCNX ligands on coordination (Eq. (1)).



Although the identification of $\nu(CN)$ or $\nu(CO)$ is not straightforward, IR spectroelectrochemistry (see below) helped to confirm the assignments made in Table 1. For a singly nitrile-N coordinated $TCNX^{n-}$ ligand (the situation assumed here) the expected number of $\nu(CN)$ bands is four [1,11], however, some of these bands may not be observed due to weak intensity or overlap [12]. Complexes with TCNE coordinated in π fashion through the central C–C bond (metallacyclopropane situation) typically exhibit only one strong $\nu(CN)$ band [1,12,13].

Compared with related data for the structurally characterized complexes $(C_5H_5)_2BrV(\eta^1-TCNE)$ [11] and $(C_5H_5)(CO)_2Mn(\eta^1-TCNE)$ [14], both effectively containing the antiferromagnetically coupled TCNE^{•-} ligand (q ca. 1), the titanium compounds $(C_5R_5)_2(CO)Ti(TCNE)$ exhibit higher $\nu(CO)$ and lower $\nu(CN)$ values (Table 1), suggesting already a higher degree $q > 1$ of electron exchange between the TCNX ligands and the precursors which contain the rather low-valent Ti^{II} . On the other hand, the high $\nu(CN)$ values of 2195 and 2181 cm^{-1} reported for what was formulated as $\{(\mu-TCNE^{-II})[(C_5H_5)_2Ti^{IV}(CO)]_2\}(TCNE^{2-})$ [6] are not compatible with the presence of free or coordinated TCNE²⁻ (cf. Table 1), leaving an intermediate value of $1 < q < 2$ for Eq. (1).

A dinuclear vanadium compound formulated as $[(C_5Me_5)_2BrV^{IV}]_2(\mu-TCNE^{2-})$ has been reported [15] with $\nu(CN) = 2172$ and 2099 cm^{-1} .

2.3. UV–vis absorption spectra

The absorption spectrum of $\mathbf{1}$ is shown in Fig. 2, Table 2 summarizes data relevant for the discussion.

In agreement with Eq. (1) and q ca. 1 the two long-wavelength absorption bands of $\mathbf{1}$ can be attributed to

Table 1
Infrared stretching frequencies of ligands and complexes

Compound	ν (cm ⁻¹)		Reference
	$\nu(\text{CN})$	$\nu(\text{CO})$	
(C ₅ H ₅) ₂ (CO)Ti(TCNE) ^b	2193m, 2178m, 2103s	2039s	This work
(C ₅ Me ₅) ₂ (CO)Ti(TCNE) ^b (1)	2179w, 2097s	2078s	This work
TCNE ^a	2255, 2216	-	[9a]
TCNE ^{•- a}	2253, 2198, 2178, 2171 ^d	-	[9a]
TCNE ^{2- a}	2160, 2095	-	[9a]
{[(C ₅ H ₅) ₂ (CO)Ti] ₂ (μ-TCNE)}(TCNE) ^b	2195sh, 2181, 2145sh, 2104	2055	[6]
(C ₅ Me ₅) ₂ BrV(TCNE) ^{a,b}	2204w, 2189s, 2174s, 2110m	-	[15]
(C ₅ Me ₅)(CO) ₂ Mn(TCNE) ^c	2230vw, 2205s, 2125m	1985vs, 1950s	[12]
(C ₆ Me ₆)(CO) ₂ Cr(TCNE) ^c	2210w, 2190s	1960, 1895s	[12]
(C ₅ H ₅) ₂ (CO)Ti(TCNQ) ^b	2186m, 2117ms	2066s	This work
(C ₅ Me ₅) ₂ (CO)Ti(TCNQ) ^b (2)	2182m, 2102ms	2050s	This work
TCNQ ^a	2228	-	[9b]
TCNQ ^{•- a}	2197, 2166	-	[9b]
TCNQ ^{2- a}	2164, 2096	-	[9b]
(C ₅ H ₅) ₂ (CO) ₂ Ti ^c	-	1977s, 1899s	This work
(C ₅ Me ₅) ₂ (CO) ₂ Ti ^c	-	1940s, 1858s	This work

^a KBr.

^b Nujol.

^c *n*-Hexane.

^d Ion pair with Li⁺.

^e THF.

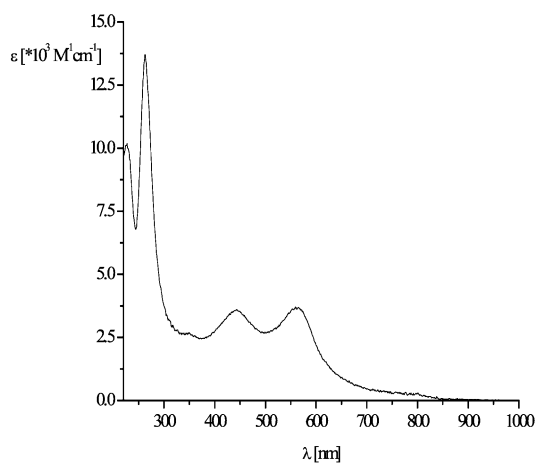


Fig. 2. Absorption spectrum of **1** in CH₂Cl₂.

an intra-ligand transition of TCNE^{•-} at 439 nm ($\lambda_{\text{max}} = 428$ nm in 'free' TCNE^{•-} [1,16]) and to a charge transfer transition at 559 nm. That transition can involve either a metal-to-ligand charge transfer (MLCT), $d(\text{Ti}^{\text{III}}) \rightarrow \pi^*(\text{TCNE}^{\bullet-})$ Eq. (2), or a ligand-to-metal charge transfer (LMCT), $\pi^*(\text{TCNE}^{\bullet-}) \rightarrow d(\text{Ti}^{\text{III}})$ Eq. (3).



Similarly, **2** exhibits the typical long-wavelength absorption features of the TCNQ radical anion around

800 and 400 nm [1,10a,17], in addition to an MLCT shoulder at about 700 nm (cf. Fig. 4 and Table 2).

In comparison to (C₅R₅)₂BrV(TCNE) and (C₅H₅)(CO)₂Mn(TCNE) [10a,15], both with structural evidence for an antiferromagnetically coupled TCNE^{•-} ligand [11,14], the titanium complex **1** exhibits the highest energy of the charge transfer band (Table 2), confirming a high *q* value $q > 1$ in Eq. (1) and thus a predominantly LMCT character (Eq. (3)) of the corresponding transition.

2.4. Cyclic voltammetry

Both soluble compounds **1** and **2** are reversibly reduced in two steps, however, oxidation appears as a reversible process only for the TCNQ complex (Fig. 3). Table 3 summarizes the electrochemical potentials.

Again in agreement with a large amount *q* of charge transferred according to (Eq. (1)) the reduction potentials are very negative, in particular for **1**. TCNE itself is much easier reduced, by more than 1 V, than the corresponding complex **1**. Even in comparison with the compounds (C₅R₅)₂BrV(TCNE) (-0.93 V [15]) and (C₅R₅)(CO)₂Mn(TCNE) (-0.63 V [10a]) with their structural evidence for a TCNE^{•-} ligand [11,14], the titanium complex **1** exhibits a much more cathodically shifted first reduction at -1.41 V versus [(C₅H₅)₂Fe]^{+ / 0}. Charge uptake by the coordinated TCNX ligands in **1** or **2** is also evident from strongly changed potential differences $\Delta E = E_{\text{red1}} - E_{\text{red2}}$ or the correspondingly calculated (Eq. (4)) comproporciona-

Table 2
Absorption maxima of ligands and complexes

Compound	Solvent	λ_{\max} [nm] (ϵ [$M^{-1} \text{ cm}^{-1}$])	Reference
$(C_5Me_5)_2(CO)Ti(TCNE)$ (1)	CH_2Cl_2	227 (10 180), 263 (13 710), 439 (3560), 559 (3700)	This work
TCNE	CH_3CN	219 (4540), 248sh (11 800), 255 (15 880), 261 (16 750), 270 (15 000)	[16]
$TCNE^{\bullet-}$	CH_3CN	215 (18 600), 225 (15 900), 428 (8425)	[16]
$TCNE^{2-}$	CH_3CN	230 (21 545)	[16]
$(C_5Me_5)_2BrV(TCNE)$	DCE ^a	394, 505sh, 597	[15]
$(C_5Me_5)(CO)_2Mn(TCNE)$	DCE ^a	396, 742	[10a]
$(C_6Me_6)(CO)_2Cr(TCNE)$	DCE ^a	488, 654	[10a]
$(C_5Me_5)_2(CO)Ti(TCNQ)$ (2)	CH_2Cl_2	271 (7870), 410 (3270), 678sh, 750 (3430), 840 (3790)	This work
TCNQ	CH_3CN	395 (63 600)	[17b]
$TCNQ^{\bullet-}$	CH_3CN	420 (24 300), 761sh, 842 (43 300)	[17a]
$TCNQ^{2-}$	CH_3CN	210 (32 500), 240 (16 250), 330 (33 750)	[17c]

^a DCE = 1,2-dichloroethane.

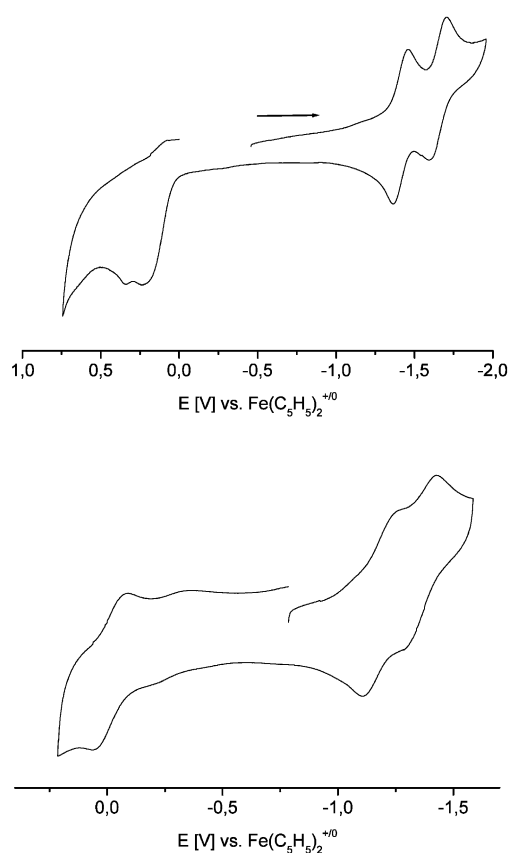


Fig. 3. Cyclic voltammograms of **1** (top) and **2** (bottom) in $CH_2Cl_2/0.1$ M Bu_4NPF_6 at 100 mV s^{-1} scan rate.

tion constant K_c (Table 3). First and second reduction are much less separated for the complexes, suggesting different sites of reduction according to Scheme 1.

$$RT \cdot \ln K_c = nF \cdot \Delta E,$$

$$K_c = 10^{\Delta E/0.059 \text{ V}} \quad (T = 298 \text{ K}). \quad (4)$$

Oxidation occurs irreversibly for **1** but reversibly for **2** at rather low potentials, confirming the susceptibility of these compounds to oxidation e.g. by air.

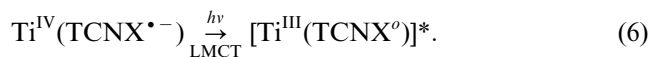
2.5. UV-vis spectroelectrochemistry

Stepwise spectroelectrochemical reduction of **1** or **2** (Fig. 4, Table 4) using an optically transparent thin-layer electrolytic (OTTLE) cell [18] showed the disappearance of the intraligand transitions attributed to $TCNX^{\bullet-}$ after the first electron addition. This observation suggests a ligand-centered reduction to yield a $Ti^{III}(TCNX^{2-})$ species. The broad bands attributed to LMCT transitions (Eq. (5)) remaining disappear after the second reduction step, producing a dianion with completely reduced metal and TCNX ligand and thus no charge transfer transitions in the visible region.



These results are compatible with the oxidation state assignments given in Scheme 1.

The reversible oxidation of **2** shows partially but not completely diminished intraligand bands of $TCNX^{\bullet-}$, suggesting a $Ti^{IV}(TCNQ^{\bullet-})$ instead of a $Ti^{III}(TCNQ^o)$ situation. Accordingly, the new features at 567 and 649 nm are assigned to LMCT transitions (Eq. (6)).



2.6. IR spectroelectrochemistry

Using the OTTLE cell it was possible to monitor the behavior of $\nu(CN)$ and $\nu(CO)$ bands on reduction and oxidation. Fig. 5 shows the results for the stepwise reduction of **1**, Table 5 summarizes the results. Due to solubility problems the TCNQ complex **2** had to be studied in THF solution where the second reduction was found to be closer to the first one.

As a general result of added negative charge, the reduction steps are accompanied by low-energy shifts of $\nu(CN)$ and $\nu(CO)$ (Fig. 5). For **1**⁻ the number of

Table 3
Electrochemical data ^a of ligands and complexes

Compound	Solvent ^b	E_{ox}	E_{red1}	E_{red2}	K_c ^d	Reference
(C ₅ Me ₅) ₂ (CO)Ti(TCNE) (1)	CH ₂ Cl ₂	0.23 ^c	−1.41	−1.64	10 ^{3.9}	This work
TCNE	CH ₃ CN	n.o.	−0.28	−1.45	10 ^{19.8}	[1]
(C ₅ Me ₅) ₂ BrV(TCNE)	DCE	0.10 ^c	−0.93	irr		[15]
(C ₅ Me ₅) ₂ (CO) ₂ Mn(TCNE)	CH ₃ CN	0.47 ^c	−0.63	irr		[10a] ^e
(C ₆ Me ₆)(CO) ₂ Cr(TCNE)	CH ₃ CN	0.35 ^c	−0.94	irr	-	[10a] ^e
(C ₅ Me ₅) ₂ (CO)Ti(TCNQ) (2)	CH ₂ Cl ₂	−0.01	−1.20	−1.37	10 ²⁹	This work
TCNQ	CH ₃ CN	n.o.	−0.25	−0.97	10 ^{12.2}	[1]
(C ₅ Me ₅) ₂ (CO) ₂ Ti	CH ₂ Cl ₂	0.01 ^c	n.o.			This work

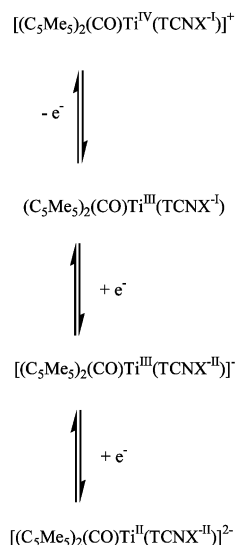
^a Potentials in V versus (C₅H₅)₂Fe ⁺¹⁰ from cyclic voltammetry at 100 mV s^{−1}.

^b 0.1 M Bu₄NPF₆ solutions.

^c Peak potential for irreversible oxidation.

^d Comproportionation constant for monoanion from Eq. (4).

^e Potentials converted from SCE reference, 0.49 V difference.



Scheme 1.

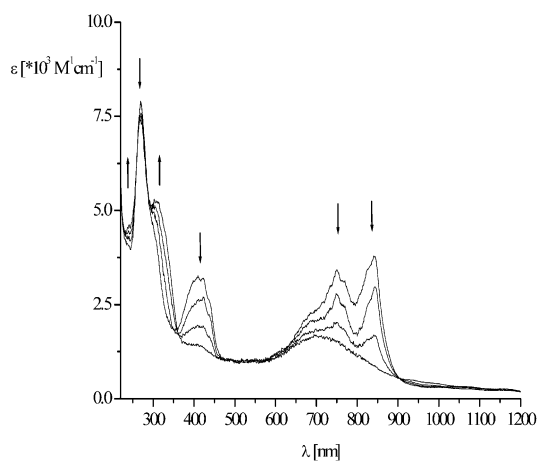


Fig. 4. Changes in the UV-vis/NIR absorption spectrum of **2** on reduction to the monoanion from spectroelectrochemistry in CH₂Cl₂/0.1 M Bu₄NPF₆.

Table 4

Absorption data from UV-vis/NIR spectroelectrochemistry in CH₂Cl₂/0.1 M Bu₄NPF₆

Compound	λ_{max} [nm] (ϵ [M ^{−1} cm ^{−1}])	Assignment
(C ₅ Me ₅) ₂ (CO)Ti ^{III} (TCNE ^{−1}) (1)	559 (3700)	MLCT
	439 (3560)	IL
	263 (13 710)	(TCNQ ^{•−})
	227 (10 180)	IL
[(C ₅ Me ₅) ₂ (CO)Ti ^{III} (TCNE ^{−II})] [−] (1 [−])	682 (899)	LMCT
	260 (10 690)	IL
	230 (11 800)	IL
	233 (14 590)	IL
[(C ₅ Me ₅) ₂ (CO)Ti ^{II} (TCNE ^{−II})] ^{2−} (1 ^{2−})	840 (3790)	IL
	750 (3430)	(TCNQ ^{•−})
	678sh	IL
	439 (3560)	MLCT
[(C ₅ Me ₅) ₂ (CO)Ti ^{III} (TCNQ ^{−1}) (2)	410 (3270)	IL
	271 (7870)	IL
	694 (1700)	LMCT
	303 (5300)	IL
[(C ₅ Me ₅) ₂ (CO)Ti ^{III} (TCNQ ^{−II})] [−] (2 [−])	268 (7500)	IL
	974 (363)	LMCT
	405 (1054)	IL
	324 (6440)	IL
(C ₅ Me ₅) ₂ (CO)Ti ^{II} (TCNQ ^{−II})] ^{2−} (2 ^{2−})	268 (5870)	IL

observable bands from nitrile stretching vibrations increases; for a nitrile-N coordinated TCNX^{n−} ligand the expected number of $\nu(CN)$ bands is four, however, these are not always all observed due to overlap or weak intensity. Unfortunately, there is overlap of several bands around 2100 cm^{−1} in 1^{2−} which prevents us from making more definite assignments in that case, including the localization of $\nu(CO)$.

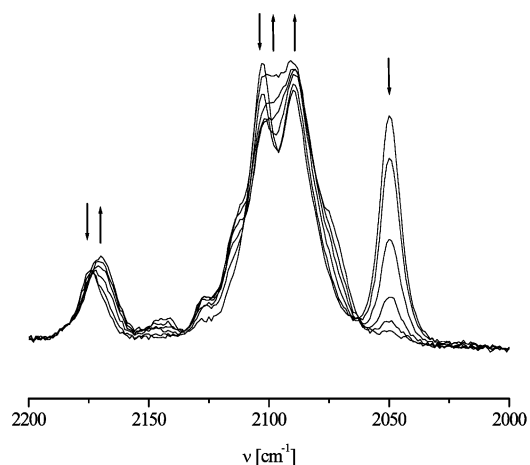
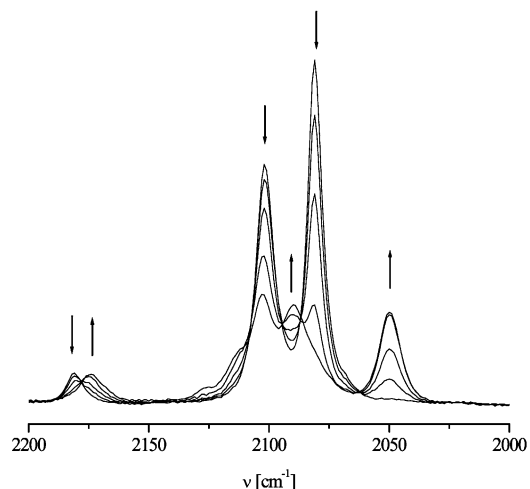


Fig. 5. Changes in the IR spectrum of **1** on stepwise reduction to the monoanion (top) and from the monoanion to the dianion (bottom) from spectroelectrochemistry in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$.

Table 5
Stretching frequencies from IR spectroelectrochemistry in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$

Compound	$\nu \text{ (cm}^{-1}\text{)}$	
	ν_{CN}	ν_{CO}
$(\text{C}_5\text{Me}_5)_2(\text{CO})\text{Ti}^{\text{III}}(\text{TCNE}^{-1})$ (1)	2180w, 2097s	2077s
$[(\text{C}_5\text{Me}_5)_2(\text{CO})\text{Ti}^{\text{III}}(\text{TCNE}^{-\text{II}})]^{-}$ (1 ⁻)	2174w, 2113sh, 2103m, 2090m	2050m
$[(\text{C}_5\text{Me}_5)_2(\text{CO})\text{Ti}^{\text{II}}(\text{TCNE}^{-\text{II}})]^{2-}$ (1 ²⁻)	2169w, 2101m, 2091m	n.o.
$(\text{C}_5\text{Me}_5)_2(\text{CO})\text{Ti}^{\text{III}}(\text{TCNQ}^{-1})$ (2)	2182w, 2102s	2050s
$[(\text{C}_5\text{Me}_5)_2(\text{CO})\text{Ti}^{\text{III}}(\text{TCNQ}^{-\text{II}})]^{-}$ (2 ²⁻)	2167m, 2157m, 2122s, 2109s	n.o.
$[(\text{C}_5\text{Me}_5)_2(\text{CO})\text{Ti}^{\text{IV}}(\text{TCNQ}^{-1})]^{+}$ (2 ⁺)	2221vw, 2180vw, 2103w	2061w

The first and second reduction processes appear rather close for **2** in THF, Fig. 6 shows the combined spectroelectrochemical response which shows only par-

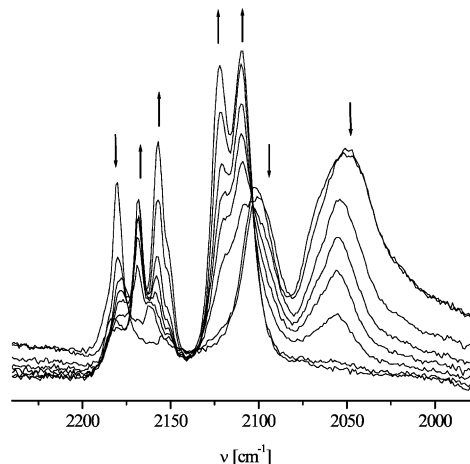


Fig. 6. Changes in the IR spectrum of **2** on stepwise reduction to the monoanion and dianion from spectroelectrochemistry in THF/0.1 M Bu_4NPF_6 .

tially parallels to that of **1**: The high-energy $\nu(\text{CN})$ band is similarly shifted stepwise to lower wavenumbers and $\nu(\text{CO})$ could not be located (Table 5). It should be remembered that the stepwise reduction involves different sites, first the ligand and then the metal. The latter process may involve significant charge transfer to the carbonyl ligand which then does no longer exhibit an easily detectable IR band. Conversely, the TCNX^{2-} ligand would give back some charge so as not to experience any strong low-energy shift of $\nu(\text{CN})$.

On oxidation of the complex **2** the $\nu(\text{CN})$ and $\nu(\text{CO})$ bands are all diminished in intensity, only $\nu(\text{CO})$ experiences a high-energy shift in agreement with a metal-centered oxidation to a rare carbonyltitanium(IV) species (Scheme 1). Appearance of the 2221 cm^{-1} band of free TCNQ indicates slow decomposition, the TCNE analogue **1** could not be studied at all due to irreversible oxidation.

2.7. NMR and EPR spectroscopy

The complexes **1** and **2** exhibit broadened $^1\text{H-NMR}$ signals due to the presence of small amounts of dissociated $\text{TCNX}^{\bullet-}$. Accordingly, these species could be detected in low concentration by EPR spectroscopy, higher concentrations of $\text{TCNQ}^{\bullet-}$ were observed after oxidation of **2** in agreement with the labilization mentioned above. Only the high-field shifted methyl proton signals were observed in the $^1\text{H-NMR}$ spectra of **1** and **2** (see Section 4), the TCNQ ring protons in **2** could not be located.

In agreement with Scheme 1, the one-electron reduction of **1** and **2** gave EPR signals (Fig. 7) compatible with the presence of organometallic titanium(III) species [19] ($3d^1$ configuration) with g tensor components lower than the free electron value of 2.0023 (Table 6). In

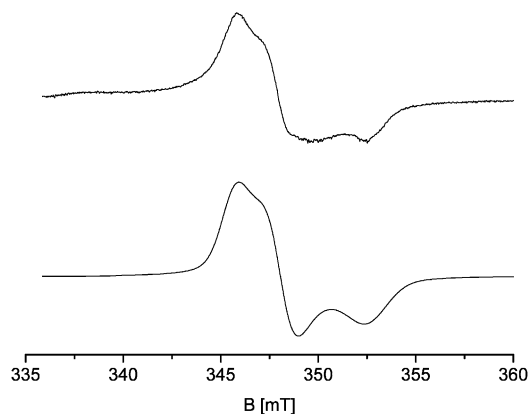


Fig. 7. EPR spectrum of electrogenerated 1^- in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$ at 4 K (top) with simulation (bottom).

contrast, the oxidized 2^+ showed an unresolved signal at 2.0030, compatible with a complex of $\text{TCNQ}^{\bullet-}$ [20].

3. Conclusion

The complexes $(\text{C}_5\text{R}_5)_2(\text{CO})\text{Ti}^{2+q}(\text{TCNX}^{-q})$ are formed in an electron transfer-assisted and probably -catalyzed substitution reaction. In comparison to previously studied related organometallic complexes $(\text{C}_5\text{H}_5)_2\text{BrV}(\text{TCNE})$, $(\text{C}_6\text{R}_6)(\text{CO})_2\text{Cr}(\text{TCNE})$ or $(\text{C}_5\text{R}_5)(\text{CO})_2\text{Mn}(\text{TCNE})$ the TCNE complex **1** exhibits a distinctly higher degree of charge transfer q between the low-valent metal and the acceptor ligand. Evidence for this comes from $\nu(\text{CN})$ and $\nu(\text{CO})$ band shifts in the infrared spectra, from charge transfer band energies and especially from the redox potentials. No stable species of higher nuclearity could be isolated. While oxidation at rather low potentials yields labile carbonyltitanium(IV) species of the $\text{TCNX}^{\bullet-}$ ligands, the reduction occurs stepwise, first on the ligand (to yield $\text{TCNX}^{2-}/\text{Ti}^{\text{III}}$) and then on the metal (to form Ti^{II}).

Table 6
EPR data of reduced and oxidized complexes^a

Compound	g_1	g_2	g_3	g_{av}	g_{iso}	T (K)
1^-	2.00	1.99	1.96	1.983	n.d.	4
2^-	2.001	1.988	1.964	1.984	1.98 ^b	110
2^+	^c	^c	^c	^c	2.0030	110

^a From in situ electrolysis in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$, low-temperature measurements in glassy frozen solutions.

^b At 300 K.

^c No g anisotropy observed at X band frequency.

4. Experimental

4.1. Instrumentation

EPR spectra were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. $^1\text{H-NMR}$ spectra were taken on a Bruker AC 250 spectrometer, infrared spectra were obtained using a Perkin–Elmer 1760X FTIR instrument. UV–vis/NIR absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out at 100 mV s^{-1} scan rate in dichloromethane/ $0.1 \text{ M Bu}_4\text{NPF}_6$ using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell [18] for UV–vis spectra and a two-electrode capillary for EPR studies [21].

4.2. Syntheses

All manipulations had to be carried out in rigorously dried solvents under an argon atmosphere.

4.2.1. $(\text{C}_5\text{H}_5)_2(\text{CO})\text{Ti}(\text{TCNE})$

A solution of 58 mg (0.453 mmol) TCNE in 10 ml THF was treated with a solution of 102 mg (0.436 mmol) $(\text{C}_5\text{H}_5)_2(\text{CO})_2\text{Ti}$ (Strem) in 20 ml THF. An instantaneous color change from red to bluish green was observed. After stirring for one hour the dark green insoluble precipitate was collected and dried under vacuum. Yield: 110 mg (73%). Anal. Calc. for $\text{C}_{17}\text{H}_{10}\text{N}_4\text{OTi}$ (334.03): C, 61.07; H, 3.94; N, 16.77. Found: C, 61.11; H, 3.89; N, 16.52%.

4.2.2. $(\text{C}_5\text{H}_5)_2(\text{CO})\text{Ti}(\text{TCNQ})$

A solution of 91 mg (0.446 mmol) TCNQ in 10 ml THF was treated with a solution of 101 mg (0.432 mmol) $(\text{C}_5\text{H}_5)_2(\text{CO})_2\text{Ti}$ in 20 ml THF. An instantaneous color change from red to blue-green was observed. After stirring for 1 h the forest-green insoluble precipitate was collected and dried under vacuum. Yield: 137 mg (75%). Anal. Calc. for $\text{C}_{23}\text{H}_{14}\text{N}_4\text{OTi}$ (410.07): C, 67.31; H, 3.44; N, 13.66. Found: C, 66.74; H, 3.89; N, 12.74%.

4.2.3. $(\text{C}_5\text{Me}_5)_2(\text{CO})\text{Ti}(\text{TCNE})$ (**1**)

A solution of 37 mg (0.289 mmol) TCNE in 10 ml THF was treated with a solution of 107 mg (0.287 mmol) $(\text{C}_5\text{Me}_5)_2(\text{CO})_2\text{Ti}$ [22] in 20 ml THF. An instantaneous color change from bright red to blood-red was observed. After stirring for one hour and removal of the solvent the blood-red solid was collected

and dried under vacuum. Yield: 89 mg (65%). Anal. Calc. for $C_{27}H_{30}N_4OTi$ (474.19): C, 68.33; H, 6.38; N, 11.81. Found: C, 67.38; H, 6.18; N, 11.62%. 1H -NMR (CD_2Cl_2): $\delta = 1.55$ (s).

4.2.4. $(C_5Me_5)_2(CO)Ti(TCNQ)$ (2)

A solution of 56 mg (0.274 mmol) TCNQ in 10 ml THF was treated with a solution of 96 mg (0.256 mmol) $(C_5Me_5)_2(CO)_2Ti$ [22] in 20 ml THF. An instantaneous color change from bright red to dark blue was observed. After stirring for one hour and removal of the solvent the dark blue solid was collected and dried under vacuum. Yield: 123 mg (82%). Anal. Calc. for $C_{33}H_{34}N_4OTi$ (550.22): C, 71.97; H, 6.23; N, 10.18. Found: C, 70.26; H, 6.70; N, 10.02%. 1H -NMR (CD_2Cl_2): $\delta = 1.57$ (br, s).

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