Research Article **Open Access**

Synthesis and Electrochemistry of Dimetallocene-Containing Titanocenyl (IV) Complexes

E. Erasmus*

Department of Chemistry, University of the Free State, Bloemfontein, 9300, Republic of South Africa

Abstract

A series of dimetallocenyl dicyclopentadienyl titanium (IV) complexes of the from $[(C_5H_5)_2Ti^{IV}((C_5H_4)M^{II}(C_5H_5))_2]$ with M=Fe, Ru and Os were synthesized by treatment of dicyclopentadienyltitanium (IV) dichloride (titanocene dichloride) with the corresponding metallocenyllithium. The metallocenyllithium was obtained by treatment of the corresponding metallocene (ferrocene (Fc), ruthenocene (Rc) and osmocene (Oc)) with either t-buthyllithium or n-buthyllithium. The electrochemistry of the dimetallocenyl dicyclopentadienyl titanium (IV) complexes was studied by cyclic voltammetry, linear sweep voltammetry and Oster Young square wave voltammetry. The titanocenyl group showed quasi-reversible to irreversible electrochemistry with the peak anodic potential (Epc vs FcH/FcH+) of the titanocenyl group dependent on the atomic electronegativity of the metallocenyl ligand (Fe (χF_e=1.64), Ru (χR_u=1.42), Os ($\chi o_e Os$=1.52)). The metallocenyl groups (Fc, Rc and Oc) showed quasi-reversibility and the quasi-formal reduction potential, E01, was also dependent on atomic electronegativity of the metal of the metallocenyl ligand.

Synopsis and pictogram for Table of contents
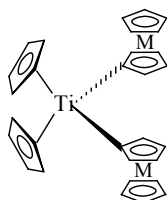
M = Fe, Ru and Os.

Synopsis

A series of dimetallocenyl dicyclopentadienyl titanium(IV) complexes of the type $[(C_5H_5)_2Ti^{IV}((C_5H_4)M^{II}(C_5H_5))_2]$ where M=Fe, Ru and Os were synthesized and characterized by spectroscopic and electrochemical methods. The electrochemical studies showed that the titanium centre has a quasi-reversible to irreversible Ti4+/Ti3+ couple, while the metallocenyl groups (Fc, Rc and Oc) showed quasi-reversible Mc/Mc+ couples.

Keywords: Ferrocene; Ruthenocene; Osmocene; Titanocene; Cyclic voltammetry

Introduction

Titanocene dichloride and its derivatives are well investigated in the fields for catalyzed polymerization [1-2] and anti-cancer treatments [3-6]. It also promotes several general organic reactions [4-14].

The cyclopentadienyl rings on the titanocene dichloride can be modified in a virtually unlimited number of ways in order to influence the physical properties of the titanium by a static intramolecular coordination of the side chain [5-8]. For instance a terminal neutral amino group at the end of an aliphatic side chain connected to the cyclopentadienyl ring can result in water-soluble species [6]. Introduction of an electron donating groups onto the cyclopentadienyl ring causes a decrease in antineoplastic activity [7], while a polar, electron-withdrawing group have shown to be a more effective antineoplastic agent [8].

Dicyclopentadienyl titanium dihalides are also ideal starting materials for ligand exchange and redox reactions. The halide is a useful site for molecular modification, because the chloride ligands on the central metal atom of the titanocene dichloride can be exchanged for any other halide or pseudohalide ligand. One equivalent of

$AlMe_3$, reacts with titanocene dichloride to yield the mono-methyl titanium(IV) complex,[11] whereas two equivalents of $AlMe_3$ yields Tebbe's reagent [9], which is a useful alternative to the classical Wittig reagents for the conversion of an ester to a vinyl ether. The replacement of both of the chlorides with a methyl group can be achieved by means of reaction with methyl magnesium chloride or methyl lithium, [9] to yield dimethyl titanocene which is a very useful precursor to a large variety of different titanium(IV) complexes [10,11]. When both the chlorides are replaced with perfluorooctanesulfonate, a water- and air-stable titanocene bis(perfluoroalkanesulfonate) is formed [12,13]. Replacement of both the chlorides with redox active specie such as

---

ferrocene is achieved by the standard method of preparation which involves the reaction between a titanocene dihalide and the lithiated ferrocene to yield dicyclopentadienyldiferrocenyltitanium [14], it has also been reported that $HgFc_2$ can be used as a ferrocenyl transfer agent [15].

Coordination compounds containing redox active ligand directly attached to the transition metal are useful to study the intramolecular interaction and communication by means of electrochemistry [16-20]

In this paper the synthetic route of the dimetallocenyl derivative of dicyclopentadienyl titanium (IV) by means of the treatment of titanocene dichloride with the appropriate lithiated metallocene (Fc, Rc and Oc) are described. With the great interest in multi-metal complexes, the electrochemical behaviour of these compounds is important. Thus with this paper we also report the results of an electrochemical study of the series of dimetallocenyl dicyclopentadienyltitanium (IV) complexes showing how the ionic radii of metal within the metallocene influences the electronic communication.

Experimental/ Material and methods

General procedures

Solid and liquid reagents (Sigma-Aldrich) were used without purification. Solvents were distilled prior to use and water was double distilled.

^{1}H NMR measurements at 289 K were recorded on a Bruker Avance DPX 300 NMR spectrometer. The chemical shifts were reported relative to $SiMe_4$ at 0.00 ppm. The chemical analyses were performed at the University of the Free State on a Leco Truspec Micro.

Synthesis

Synthesis of Bis(η⁵-cyclopentadienyl)diferrocenyl titanium(IV), 1: Under Schlenk conditions, ferrocene (2.2 g, 12 mmol) was dissolved in dry degassed THF (10 cm³). t-Butyllithium (2.5 M, 4 cm³, 10 mmol) was added slowly, while the solution was kept cool in an ice-bath and stirred for a further 30 min at 0°C. The solution was allowed to warm to room temperature. Titanocene dichloride (1.6 g, 6 mmol) was added and the mixture was stirred for 1 h at room temperature. The precipitate was filtered off and washed with warm hexane. The residue was extracted with toluene and the solvent was removed under vacuum at 50°C to yield 90 mg (13%) of 1 as the clean product. The product is air-sensitive and was stored under argon. ^{1}H NMR (300 MHz, CDCl₃) δ (TMS, ppm): 4.01 (s; 10H; 2xC₅H₅); 4.19 (s; 4H; 2x0.5xC₅H₄); 4.36 (s; 4H; 2x0.5xC₅H₄); 6.48 (s; 10H; 2xC₅H₅). Elemental analysis calculated C 77.9%, H 6.1% and found C 77.6% and H 6.3%.

Synthesis of Bis(η⁵-cyclopentadienyl)diruthenocenyl titanium(IV), 2:

Under Schlenk conditions, ruthenocene (1 g, 4.32 mmol) was dissolved in dry degassed THF (10 cm³). t-Butyllithium (2.5 M, 1.4 cm³, 3.6 mmol) was added slowly, while the stirring solution was kept cool in an ice-bath at 0°C. After stirring for 4 h at room temperature, titanocene dichloride (448 mg, 1.8 mmol) was added and the mixture was stirred for 1 h. The precipitate was filtered off and washed with warm hexane. The residue was extracted with toluene and the solvent was removed under vacuum at 50°C to yield 200 mg (17%) of 2 as the clean product. The product is air-sensitive and was stored under argon. ^{1}H NMR (300MHz, CDCl₃) δ (TMS, ppm): 4.49 (s; 4H; 2x0.5xC₅H₄); 4.52 (s; 10H; 2xC₅H₅); 4.69 (s; 4H; 2x0.5xC₅H₄); 6.32 (s; 10H; 2xC₅H₅).

Elemental analysis calculated C 67.0%, 5.3H % and found C 66.6% and H 5.7%.

Synthesis of Bis(η⁵-cyclopentadienyl)diosmocenyl titanium(IV), 3

Under Schlenk conditions, osmocene (500 g, 1.56 mmol) was dissolved in dry degassed THF (10 cm³). n-Butyllithium (2.5 M, 0.6 cm³, 1.6 mmol) was added slowly, while the stirring solution was kept cool at -78°C. After addition the mixture was allowed to heat to room temperature while stirring for 16 h. Titanocene dichloride (448 mg, 1.8 mmol) was added and the mixture was stirred for 5 h. The precipitate was filtered off and washed with warm hexane. The residue was extracted with toluene and the solvent was removed under vacuum at 50°C to yield the crude product. After recrystallization from CH_2Cl_2 and hexane and sublimation of unreacted osmocene from the crude mixture, 40 mg (3.1%) of 3 as was obtained the clean product. The product is air-sensitive and was stored under argon. ^{1}H NMR (300MHz, CDCl₃) δ (TMS, ppm): 4.71 (s; 10H; 2xC₅H₅); 4.84 (s; 4H; 2x0.5xC₅H₄); 5.05 (s; 4H; 2x0.5xC₅H₄); 6.36 (s; 10H; 2xC₅H₅). Elemental analysis calculated C 57.5%, H 4.5% and found C 57.1% and H 4.7%.

Electrochemisrty

Measurements on ca. 2.0 mmol dm⁻³ solutions of the complexes in dry air-free dichloromethane containing 0.10 mmol dm⁻³ tetrabutylammonium tetrakis(pentafluorophenyl)borate, $[N(^nBu_4)]$ $[B(C_6F_5)_4]$, as supporting electrolyte were conducted under a blanket of purified argon at 25°C utilizing a BAS 100 B/W electrochemical workstation interfaced with a personal computer. A three electrode cell, which utilized a Pt auxiliary electrode, a glassy carbon working electrode and an in-house constructed Ag/AgCl reference electrode [17] were employed. Temperature was kept constant within 0.5°C. Experimentally potentials were referenced against a Ag/AgCl reference electrode, but results are presented referenced against ferrocene (FcH/FcH⁺) as an internal standard as suggested by IUPAC [18]. To achieve this, each experiment was performed first in the absence of ferrocene and then repeated in the presence of <1 mmol dm⁻³ ferrocene. Data were then manipulated on a spreadsheet to set the formal reduction potentials of FcH/FcH⁺ couple at 0 V. Under our conditions data of FcH/FcH⁺ drifted in a series of experiments so each CV or LSV was corrected individually. The FcH/FcH⁺ couple has an

E°'=421 mV vs. Ag/AgCl

with a

ΔE=77 mV and i_{pc}/i_{pa}=0.99

Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within 5 mV.

Results and Discussion

Synthesis

A series of titanium coordination compounds of the form $[(C_5H_5)_2Ti^{IV}((C_5H_4)M^{II}(C_5H_5))_2]$ where M=Fe (1), Ru (2) and Os (3) were synthesized according to Scheme 1. The standard method of preparation involves the treatment of the corresponding metallocenyllithium (FcLi, RcLi or OcLi) with titanocene(IV) dichloride in THF. The lithiation reactions of the ferrocene and ruthenocene were achieved by the strong base t-butyllithium at 0°C for 30 min and 4 h respectively. The t-butyllithium deprotonates and lithiates one of the cyclopentadienyl ring, which is stabilized by delocalized electrons. n-Butyllithium was not used for ferrocene and ruthenocene since it gives rise to dilithiated

species [19]. Mono-lithiation is possible with *n*-butyllithium when diethyl ether is used as the solvent, but low yields are obtained. However, lithiation of osmocene needs special treatment and even then did not give good results. *n*-Butyllithium was used rather than *t*-butyllithium and the reaction time was lengthened to overnight at ambient temperature. During the addition of *n*-butyllithium, however, the temperature was kept at -78°C to suppress unwanted side reactions.

The metallocenylation of titanocene dichloride was obtained by stirring of the corresponding metallocenyllithium (FcLi, RcLi or OcLi) with titanocene (IV) dichloride in THF for an hour. Again the osmocene reaction needed a longer reaction time of 5 h. After washing and extraction, 1 and 2 were clean enough for further study but, 3 again needed special treatment. Even after re-crystallization diosmocenyltitanocenyl still showed traces of unreacted osmocene. Unreacted osmocene was removed by sublimation at 98°C and reduced pressure over a period of 2 h. The poor yields of dicyclopentadienyldimetallocenyl titanium(IV) complexes 1-3 (<20%) could possible be attributed to incomplete lithiation to for the metallocenyllithium.

The ^{1}H NMR spectra of 1-3 in $CDCl_3$ are simple and easily interpreted. All five ring protons of both the cyclopentadienyl rings connected to the titanium are equivalent on the NMR timescale and give rise to a singlet at ca 6.3-6.6 ppm. Each of these cyclopentadienyl rings consists of 6 π electrons in a continuous, cyclic π-electron system, and thus follows the Hückel rule (4n+2) for aromaticity. The ^{1}H NMR signal is, however, outside the conventional position of aromatic protons (7-8 ppm). The position of the ^{1}H NMR signal of the cyclopentadienyl rings connected to the titanium, is influenced by the atomic electronegativity of the metal of the ligand metallocene (Fe (χ_{Fe}=1.64), Os (χ_{Os}=1.52) and Ru (χ_{Ru}=1.42)), see Figure 1. As the atomic electronegativity of the metal in the metallocene ligand increases the position of the ^{1}H NMR signal for the cyclopentadienyl ring protons connected to the titanium move downfield, due to a deshielding effect.

The ^{1}H NMR signals of the protons of the cyclopentadienyl rings of the metallocene ligands appear upfield at ca. 4.0-5.1 ppm from the signal for the protons from the cyclopentadienyl rings connected to the titanium. The ^{1}H NMR signals of the ferrocene, and osmocene ligands correspond to normal pattern for mono-substituted metallocenes, namely two triplets each integrating for two protons (assigned to the substituted ring) and one singlet upfield from the triplet signals integrating for five protons (assigned to the unsubstituted ring). The ruthenocene displayed an abnormal mono-substituted metallocene pattern, where one of the triplet signals has shifted upfield from the singlet.

Electrochemistry

The electrochemical behaviour of 1-3 were studied by cyclic voltammetry in CH_2Cl_2/0.1 mol dm^{-3} [NBu$_4$][B(C_6F_5)$_4$][20]. Figure 2 shows the comparative cyclic voltammograms at a scan rate of 200 mV s^{-1} referenced *vs* FcH/FcH$^+$ as an internal standard of [(C_5H_5)$_2$Ti^{IV}((C_5H_4)M^{II}(C_5H_5))$_2$]. Electrochemical data are summarised in Table 1.
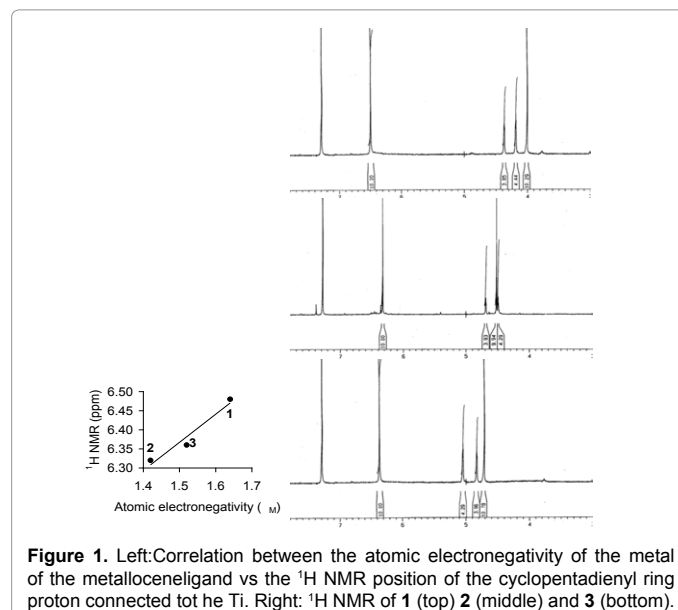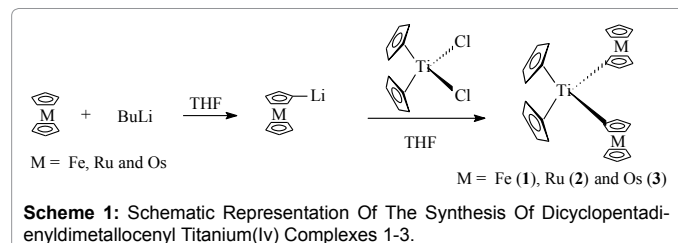
The compounds exhibited quasi-reversible to irreversible electrochemistry for the Ti^{4+}/Ti^{3+} couples and quasi-reversible electrochemistry for the metallocene ligands' Fc/Fc$^+$, Oc/Oc$^+$ and Rc/Rc$^+$ couples. The potential of the oxidation and reduction waves are dependant on the atomic electronegativity of the metal in the metallocene ligand.

The CV of 1 (Figure 2) is simple and easy to interpret. The peak

Compound	1	2	2^a	3
χ_M	1.64	1.42	1.42	1.52
E_{pc1} / mV	-1241	-1599	-1615	-1395
ΔE_{p1} / mV	92			130
E^{01}_1 / mV	-1195			-1330
i_{pa1} μA	1.4	-^{b}	3.1	1.8
i_{pa}/i_{pc}	0.5			0.5
E_{pa2} / mV	-	-1523	-1454	-
i_{pa2} μA	-	5.8	5.7	-
E_{pa3} / mV	-	-87	-	-
i_{pa3} μA	-	0.9	-	-
E_{pa4} / mV	-83	311	376	409
ΔE_{p4} / mV	79	-	79	81
E^{01}_4 / mV	-123	-	337	369
i_{pa4} μA	4.6	1.4	2.4	0.5
i_{pc}/i_{pa}	1.0	-	1.0	0.8
E_{pa5} / mV	28^c	858	649	470^c
ΔE_{p5} / mV	-	104	117	-
E^{01}_5 / mV	-	533	591	-
i_{pa5} μA	-	4.6	7.9	-
i_{pc}/i_{pa}	-	0.3	0.3	-

a) Data obtained from an experiment conducted at -35°C.

b) Peaks overlap to the extent that they could not be separated. Hence no peak currents are provided for this peak.

c) Estimate, real value could not be determined due to overlapping of peaks.

Table 1. Cyclic voltammetry data obtained from voltammograms (*vs* FcH/FcH$^+$) of [(C_5H_5)$_2$Ti{(C_5H_4)M(C_5H_5)}$_2$] with M = Fe (**1**), Ru (**2**) and Os (**3**), measured CH_2Cl_2/0.1 mol dm^{-3} [NBu$_4$][B(C_6F_5)$_4$] at a glassy carbon working electrode at 25°C and a scan rate of 100 mV s^{-1}. The concentration of the metallocene dichloride complexes was 2.0 mmol dm^{-3}. Atomic electronegativity of the metals, χ_M, is also shown.

Scheme 1: Schematic Representation Of The Synthesis Of Dicyclopentadienyldimetallocenyl Titanium(Iv) Complexes 1-3.

Figure 1. Left:Correlation between the atomic electronegativity of the metal of the metalloceneligand vs the ^{1}H NMR position of the cyclopentadienyl ring proton connected tot he Ti. Right: ^{1}H NMR of **1** (top) **2** (middle) and **3** (bottom).
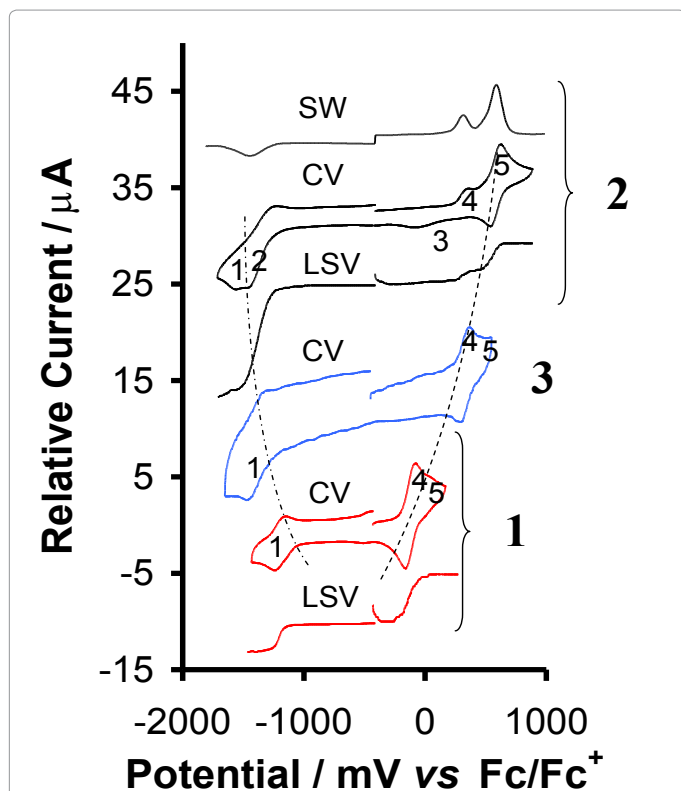
Figure 2: Cyclic voltammograms of a 2.0 mM solution of $[(C_5H_5)_2Ti\{(C_5H_4)M(C_5H_5)\}_2]$ with M=Fe^{II} (**1**), Ru^{II} (**2**) and Os^{II} (**3**) measured in CH_2Cl_2/0.1 mol dm^{-3} [NBu$_4$][B(C$_6$F$_5$)$_4$] at a glassy carbon working electrode at 25ºC and a scan rate of 200 mV s^{-1}. The square wave of **2** and the linear sweep voltammogram of **1** and **2** are also shown.
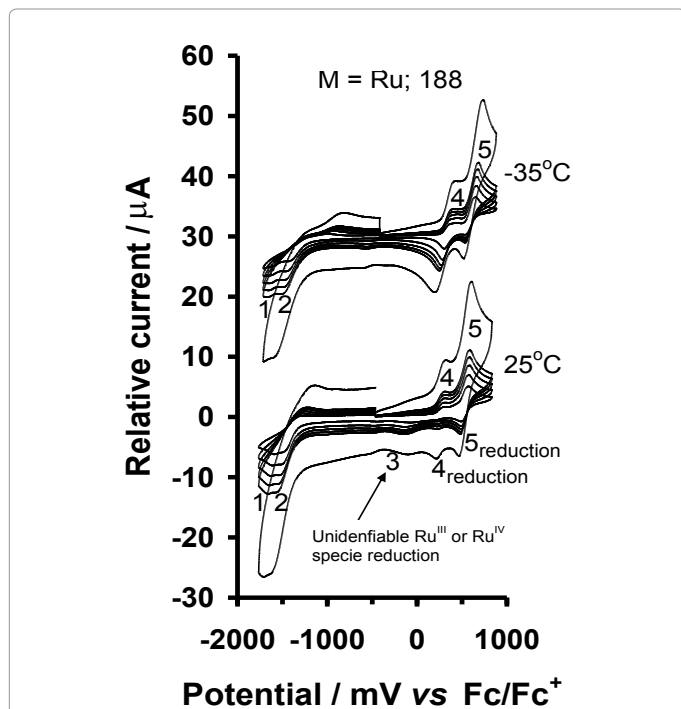

Figure 3. The cyclic voltammograms of $[(C_5H_5)_2Ti\{(C_5H_4)Ru(C_5H_5)\}_2]$ at 25ºC (Bottom) and at -35ºC (Top) at a scan rate of 100, 200, 300, 400, 500 and 2000 mV s^{-1}.

labelled 1 is associated with the Ti^{4+}/Ti^{3+} couple. This reduction wave is electrochemically quasi-reversible with

$\Delta E=92$ mV

and chemically irreversible with

$i_{pa}/i_{pc}=0.5$

The almost overlapping peaks labelled 4, 5 are assigned to the two ferrocenyl fragments that are chemically and electrochemically reversible at slow scan rates of 50-200 mV s^{-1} with

$\Delta E=72-79$ mV

and

$i_{pa}/i_{pc} \approx 1$

However, at higher scan rates the oxidation wave becomes electrochemically quasi-reversible with $\Delta E=85-102$ mV but stays chemically reversible with

$i_{pa}/i_{pc} \approx 1$

Peak 5 is observed as a small shoulder of peak 4. The existence of the two peaks 4 and 5 is explained by the two ferrocenyl moieties, which are not oxidised at exactly the same potential. From the LSV of 1 (Figure 1), it can be seen that the i_p of ferrocenyl oxidation is twice that of Ti^{4+} reduction. This proves that the two ferrocenyl moieties transfer twice as much electrons as the titanium centre, and it is consistent with Ti^{4+} being reduced to Ti^{3+} in a one-electron process similar to titanocenyl β-diketonato complexes [21], since it is know that the ferrocenyl moiety is involved in a well-defined one electron transfer process [22,23].

The CV of 3 (Figure 1) is similar to that observed for 1. Peak 1 belongs to the Ti^{4+}/Ti^{3+} couple which was found to be electrochemically quasi-reversible at slow scan rates up to 100 mV s^{-1} with

$\Delta E=130$ mV

and chemically irreversible due to

$i_{pa}/i_{pc} \approx 0.5$

However, at higher scan rates the reduction wave becomes electrochemical and chemically irreversible with $\Delta E>150$ mV. Overlapping peaks 4, 5 are assigned to the reversible oxidation of the two osmocenyl moieties. The two osmocenyl moieties are for all practical purposes oxidised at the same potential. This oxidation wave was found to be electrochemically reversible with

$\Delta E=79-89$ mV

at all scan rates (50-500 mV s^{-1}) with

$i_{pa}/i_{pc} \approx 1$

The CV of 2 (Figure 1) was much more complex than that of 1 and 3. The reduction wave associated with the Ti^{4+}/Ti^{3+} couple shows two peaks labelled 1 and 2. Both these reduction wave 1 and 2 are chemically and electrochemically irreversible with E$_{pc}$=-1599 and -1523 mV respectively.

Peaks 3-5 are assigned to the ruthenocenyl groups. Peaks 4 and 5 are well resolved without shoulders, unlike what was found with 1 and 3. A possible explanation why the ruthenocenyl moieties are oxidised at different potentials is that the distance between the two cyclopentadienyl rings are larger for ruthenocene than for the other

two metallocenes. The distance between the parallel cyclopentadienyl planes are 3.68 Å for ruthenocene, 3.32 Å for ferrocene and 3.64 Å for osmocene [24]. Thus free rotation for the ruthenocene moieties around the bond connecting them to the titanium(IV) metal centre may be more impaired than for the other two metallocenes. It may even be possible to lock the two ruthenocenyl ligands in different positions making their electronic surroundings different.

The more detailed CV traces of the ruthenocene-derivative (2) at 25°C (Figure 3 bottom) shows 5 reduction waves, three of which are associated with the ruthenocenyl group (peaks 3-5) and the other two reduction waves for Ti (peaks 1 and 2).

The electrochemically generated Ru^{III} specie should in analogy with free ruthenocene [25], be very unstable and short lived. The Ru^{III} specie will undergo conversions in an attempt to regain an 18-electron configuration similar to what was found for free ruthenocene [26], this phenomena has been found with other ruthenocene-containing compounds as well [27-32]. These conversions may include reaction with any nucleophile in solution, dimerization with another Ru^{III} specie to form a Ru^{III}-Ru^{III} compound [33,34], or any other rearrangements to eventually form unidentifiable Ru^{III}- or Ru^{IV}-species. Some of these newly formed Ru^{III}- or Ru^{IV}- species are probably reduced at peak 3.

The intensity of the reduction half wave of peak 4 becomes more and more prominent as scan rate increases. Concomitantly with this, the reduction wave 3 decreases in current intensity as wave 4 reduction intensity increases with increased scan rate. This result is consistent with any of the 18-electron converted species mentioned earlier taking place predominantly with the mixed valent ruthenocene species, *but at a slow rate*. Peak 3 is associated with the reduction of the unidentifiable Ru^{III}- or Ru^{IV}-species. Hence, at fast scan rates, Rc$^+$ reduction occurs faster than any of the conversions to the unidentifiable Ru^{III}- or Ru^{IV}-species as indicated by large i_{4red} currents. However, at slow scan rates, before potentials are reached during the reduction cycle, the Rc$^+$ species are converted to the unidentifiable Ru^{III}- or Ru^{IV}-species. This then accounts for the relatively more intense reduction half wave of peak 3 that is observed at slow scan rates. The two peaks labelled 1 and 2 in the CV of 2 (Figure 2 and 3) are also mutually consistent with two unequal Ti centres which would arise if the ruthenocenyl groups cannot rotate freely about the bond binding them to the titanium centre. The lack of free rotation argument is further supported when the temperature study for 2 is considered. At -35°C, the Ti reduction wave does not have a clearly resolved second peak. The Ti reduction wave is, however, much broadened. This poorer resolution is expected due to slower electron transfer rates at lower temperatures. However, peaks 4 and 5 at -35°C becomes much more ideal, which would be consistent with two preferred rotational conformations for the ruthenocenyl groups being frozen on the CV time scale.

The CV of the ruthenocenyl complex at -35°C showed that both oxidation waves 4 and 5 have pronounced reduction peaks, with $\Delta E \approx 150$ mV. This makes both peaks 4 and 5 quasi-reversible. Interesting to note is that at -35°C, both ruthenocene peaks 4 and 5 have $i_{pc}/i_{pa} \approx 0.9$, implying almost all Ru^{III} formed during oxidation are reduced back to Ru^{II}. Therefore no unidentifiable Ru^{III}- or Ru^{IV}-species could have formed. Peak 3 was also not observed at low temperatures. Thus for 2 at low temperatures, the conversion to the unidentifiable Ru^{III}- or Ru^{IV}-species is severely impaired. The LSV of 2 and 3 showed unexpected large current flows for the Ti^{4+}/Ti^{3+} couple. This is rationalised in terms of 2 and 3 becoming deposited on the electrode surface during Ti^{4+} reduction. The shape of peak 1 for 3 and peak 1 and 2 for 2 is also consistent with electrode deposition of the analyte. It is not expected

that the large currents associated with the LSV of peaks 1 and 2 of 2 is indicative of Ti^{2+} which is normally only formed at ca. -2500 mV *vs* FcH/FcH$^+$ [28].

The E_{pc} of the Ti^{4+}/Ti^{3+} couples are dependent on the atomic electronegativity of the metal in the metallocene ligand (Fe (χ_{Fe}=1.64), Os (χ_{Os}=1.52) and Ru (χ_{Ru}=1.42)). As the metal in the metallocene ligands' atomic electronegativity increases, the substituent metallocene withdraws more electron density from the titanium centre, making the titanium centre easier to reduce. This can be seen in E_{pc} of the Ti^{4+}/Ti^{3+} couple which became more positive, 3<2<1.

The E^{01} of metal in the metallocene ligand is also dependent on the atomic electronegativity the metal in metallocene ligand. Surprisingly, opposite of what is expected as the atomic electronegativity increases the E^{01} for the Fc/Fc$^+$, Oc/Oc$^+$ and Rc/Rc$^+$ couples of the metallocene ligands decreases. However, when comparing the oxidation potential of ferrocenyl-containing β-diketones [29] with the same ruthenocenyl-containing β-diketones, [23] the Fc/Fc$^+$ couple appears at lower potential than the Rc/Rc$^+$ couple. This shows that physical properties other than electronegativity are responsible for the potential at which a metal in a metallocene is oxidized.

Conclusion

This study has shown that dimetallocenyl dicyclopentadienyl titanium(IV) complexes could be synthesized by the treatment of the appropriate lithiated metallocene (FcLi, RcLi or OcLi) with titanocene(IV) dichloride.

There exists a linear correlation between the ^{1}H NMR position of the cyclopentadienyl rings' protons and the atomic electronegativity of the metal in the metallocene ligand.

All compounds revealed chemically and electrochemically irreversible reduction wave for the Ti^{4+}/Ti^{3+} couple in the voltage range -1599 mV<E_{pc}<-1241 mV depending on the metallocene ligand. While metallocenyl ligands' metal centres (M=Fe, Ru and Os) revealed a quasi reversible oxidation wave. The potential of the oxidation waves of the metallocenes' metal centres were also found to be dependent on the atomic electronegativity of the metal (Fe (χ_{Fe}=1.64), Ru (χ_{Ru}=1.42) and Os (χ_{Os}=1.52)).

References

1. Ghosh S, Hagihara H (2009) Polystyrene with half-titanocene/MAO catalysts: Influence of 2,6-diisopropylphenol. App Cat A Gen 360: 126-129.

2. Mohring PC, Coville NJ (1994) Homogeneous group 4 metallocene ziegler-natta catalysts: The influence of cyclopentadienyl-ring substituents. J Organomet Chem 479: 1-29.

3. Chen P, Wu QS, Ding YP, Chu M, Huang ZM, et al. (2010) A controlled release system of titanocene dichloride by electrospun fiber and its antitumor activity in vitro. See comment in PubMed Commons below Eur J Pharm Biopharm 76: 413-420.

4. Vassylyev O, Panarello A, Khinast JG (2005) Enantioselective hydrogenations with chiral titanocenes. See comment in PubMed Commons below Molecules 10: 587-619.

5. Jutzi P, Redeker T (1997) Efficient recycling of a versatile titanocene precatalyst - significance of side-chain functionalization. Organomet 16: 1343-1344.

6. Bradley S, McGowan PC, Oughton KA, Thornton-Pett M, Walsh ME (1999) Facile synthesis of amino-functionalised ferrocenes and vanadocenes. J Chem Soc Chem Commun 77.

7. Köpf-Maier P, Wagner W, Köpf H (1988) In vitro cell growth inhibition by metallocene dichlorides. Struct Bonding 70: 103-185.

8. Boyles JR, Bair MC, Campling BG, Jain N (2001) Enhanced anti-cancer activities of some derivatives of titanocene dichloride. See comment in PubMed Commons below J Inorg Biochem 84: 159-162.

9. Tebbe FN, Parshall GW, Reddy GS (1978) Olefin homologation with titanium methylene compounds. J Am Chem Soc 100: 3611-3613.

10. Vailaya A, Wang T, Chen Y, Huffman M (2001) Quantitative analysis of dimethyl titanocene by iodometric titration, gas chromatography and NMR. See comment in PubMed Commons below J Pharm Biomed Anal 25: 577-588.

11. Wailes PC, Weigold H, Bell AP (1997) Sulphur dioxide insertion reactions with dicyclopentandienyltitanium and -zirconium alkyl and aryl compounds. J Organomet Chem 33: 181-188.

12. Long NJ (1998) Metallocenes: An introduction to sandwich complexes, Blackwell Science, London.

13. Wilkinson G (1982) Editor, Comprehensive Organometallic Chemistry, vol. III, Pergamon Press, Oxford.

14. Qiu RH, Zhang GP, Xu XH, Zou KB, Shao LL, et al. (2009) Metallocene bis(perfluoroalkanesulfonate)s as air-stable cationic Lewis acids. J Organomet Chem 694: 1524-1528.

15. Qiu RH, Xu XH, Li YH, Zhang GP, Shao LL, et al. (2009) Synthesis and structure of air-stable Lewis acidic binuclear complex of zirconocene pentafluorophenylsulfonate and its catalytic application in the allylation of carbonyl compounds with tetraallyltin. Chem Comm 13: 1679-1681.

16. Razuvaev GA, Domrachev GA, Sharutin VV, Suvorova ON (1977) J Organomet Chem 14: 313.

17. Togni A, Hayashi T (1995) Ferrocenes Homogeneous Catalysis Organic Synthesis Materials Science, VCH, Weinheim.

18. Conradie J, Cameron TS, Aquino MAS, Lamprecht GJ, Swarts JC (2005) Synthetic, electrochemical and structural aspects of a series of ferrocene-containing dicarbonyl β-diketonato rhodium(I) complexes. Inorg Chim Acta 358: 2530-2542.

19. von Eschwege KG, Swarts JC (2010) Chemical and electrochemical oxidation and reduction of dithizone. Polyhedron 29: 1727-1733.

20. Gritzner G, Kuta J (1984) Recommendations on reporting electrode potentials in nonaqueous solvents. Pure Appl Chem 56: 461-466.

21. Rausch MD, Fischer EO, Gurbert H (1960) The Aromatic Reactivity of Ferrocene, Ruthenocene and Osmocene1,2. J Am Chem Soc 82: 76-82.

22. Gericke HJ, Barnard NI, Erasmus E, Swarts JC, Cook MJ, et al. (2010) Solvent and electrolyte effects in enhancing the identification of intramolecular electronic communication in a multi redox-active diruthenium tetraferrocenoate complex, a triple-sandwiched dicadmium phthalocyanine and a ruthenocene-containing β-diketone. Inorg Chim Acta 363: 2222.

23. Erasmus E, Conradie J, MullerA, Swarts JC (2007) Synthesis, crystal structure and electrochemistry of tetrahedral mono-β-diketonato titanocenyl complexes. Inorg Chim Acta 360: 2277-2283.

24. Muller TJ, Conradie J, Erasmus E (2012) A spectroscopic, electrochemical and DFT study of para-substituted ferrocene-containing chalcone derivatives: Structure of FcCOCHCH(p-tBuC6H4). Polyhedron 33: 257-266.

25. Erasmus E (2001) Ferrocene- and ruthenocene-containing chalcones: A spectroscopic and electrochemical study. Inorg Chim Acta 378: 95-101.

26. Ambrose ZS, M.Sc. Study, unpublished results.

27. Fay RC, Lowry RN (1967) Stereochemistry and lability of dihalobis(.beta.-diketonato)titanium(V) complexes. I. Acetylacetonates. Inorg Chem 6: 1512-1519.

28. Swarts JC, Nafady A, Roudebush JH, Trupia S, Geiger WE (2009) One-electron oxidation of ruthenocene: reactions of the ruthenocenium ion in gentle electrolyte media. See comment in PubMed Commons below Inorg Chem 48: 2156-2165.

29. Erasmus E, Swarts JC (2013) Intramolecular communication and electrochemical observation of the 17-electron ruthenocenium cation in fluorinated ruthenocene-containing β-diketones; polymorphism of $C_{10}H_{21}$ and $C_{10}F_{21}$ derivatives. New J Chem 37: 2862-2873.

30. Weast RC (1970) Editor, Handbook of Chemistry and Physics, 51st Edition, The Chemical Rubber Co., Cleveland D111.

31. du Plessis WC, Erasmus JJC, Lamprecht GJ, Conradie J, Cameron TS, et al. (1999) Cyclic voltammetry of ferrocene-containing β-diketones as a tool to obtain group electronegativities. The structure of 3-ferrocenoyl-1,1,1-trifluoro-2-hydroxyprop-2-ene. Can J Chem 77: 378-386.