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

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Abstract

A series of dimetallocenyl dicyclopentadienyl titanium(IV) complexes of the from \([\text{C}_5\text{H}_5\text{Ti}^4\text{C}_5\text{H}_4\text{M}^2\text{C}_5\text{H}_5]\) 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 (χ_Fe=1.64), Ru (χ_Ru=1.42), Os (χ_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.

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M = Fe, Ru and Os.

Synopsis

A series of dimetallocenyl dicyclopentadienyl titanium(IV) complexes of the type \([\text{C}_5\text{H}_5\text{Ti}^4\text{C}_5\text{H}_4\text{M}^2\text{C}_5\text{H}_5]\) 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 Mo/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 AlMe3, reacts with titanocene dichloride to yield the mono-methyl titanium(IV) complex, whereas two equivalents of AlMe3 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, 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 noted that HgFc₂ 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.

1H NMR measurements at 289 K were recorded on a Bruker Avance DPX 300 NMR spectrometer. The chemical shifts were reported relative to SiMe₄ 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(q⁻-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. 1H NMR (300MHz, CDCl₃) δ (TMS, ppm): 4.01 (s; 10H; 2xC₅H₅); 4.19 (s; 4H; 2x0.5xC₅H₄); 4.36 (s; 1H; 2xC₅H₄); 6.48 (s; 10H; 2xC₅H₅). Elemental analysis calculated C 57.5%, H 4.5% and found C 57.1% and H 4.7%.

Synthesis of Bis(q⁻-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. 1H NMR (300MHz, CDCl₃) δ (TMS, ppm): 4.01 (s; 10H; 2xC₅H₅); 4.19 (s; 4H; 2x0.5xC₅H₄); 4.36 (s; 1H; 2xC₅H₄); 6.48 (s; 10H; 2xC₅H₅). Elemental analysis calculated C 67.0%, 5.3H % and found C 66.6% and H 5.7%.

Synthesis of Bis(q⁻-cyclopentadienyl)dirhodiumocenyl 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 CHCl₃ 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. 1H NMR (300MHz, CDCl₃) δ (TMS, ppm): 4.71 (s; 3H; 2xC₅H₄); 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%.

Electrochemistry

Measurements on ca. 2.0 mmol dm⁻³ solutions of the complexes in dry air-free dichloromethane containing 0.10 mmol dm⁻³ tetrabutylammonium tetrafluoroborate, [N( nBu4)] [B(C₆F₅)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 iᵢ/iᵢ⁺=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 [(C₅H₄)₄H⁺Ti⁺[((C₅H₄)₄M(C₅H₅)]₄] 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 metallocenylolithium (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

ΔE=77 mV and iᵢ/iᵢ⁺=0.99

Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within 5 mV.
Rc/Rc+ couples. The potential of the oxidation and reduction waves electrochemistry for the metallocene ligands’ Fc/Fc+, Oc/Oc+ and voltammetry in CH₂Cl₂/0.1 mol dm⁻³ [NBu₄][B(C₆F₅)₄] [20]. Figure 2

Electrochemistry metallocenyllithium. dicyclopentadienyldimetallocenyl titanium(IV) complexes 1-3 98°C and reduced pressure over a period of 2 h. The poor yields of osmocene. Unreacted osmocene was removed by sublimation at crystallization diosmocenyltitanocenyl still showed traces of unreacted 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 metalloccenylthium.

The ¹H NMR spectra of 1-3 in CDCl₃ 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 ¹H NMR signal is, however, outside the conventional position of aromatic protons (7-8 ppm). The position of the ¹H NMR signal of the cyclopentadienyl rings connected to the titanium, is influenced by the atomic electronegativity of the metal of the ligand metallocene (Fe (χFe=1.64), Os (χ Os=1.52)) connected to the titanium, is influenced by the atomic electronegativity of the metal of the ligand metallocene (Fe (χFe=1.64), Os (χ Os=1.52), Ru (χ Ru=1.42)), see Figure 1. As the atomic electronegativity of the metal in the metallocene ligand increases the position of the ¹H NMR signal for the cyclopentadienyl ring protons connected to the titanium move downfield, due to a deshielding effect.

The ¹H 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 ¹H NMR signals of the ferrocene, and osmocene ligands protons connected to the titanium are equivalent on the NMR timescale and give rise to a singlet. 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 other 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 CH₂Cl₂/0.1 mol dm⁻³ [NBu₄][B(C₆F₅)₄] [20]. Figure 2 shows the comparative cyclic voltammograms at a scan rate of 200 mV s⁻¹ referenced vs Fc/Fc⁺ as an internal standard of [(C₅H₅)₂Ti[(C₅H₅)₂]] with M = Fe (1), Ru (2) and Os (3), measured CH₂Cl₂/0.1 mol dm⁻³ [NBu₄][B(C₆F₅)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.

| Compound | 1 | 2 | 2⁺ | 3 |
|----------|---|---|----|---|
| X₀⁺ | 1.64 | 1.42 | 1.42 | 1.52 |
| Epcᵢ / mV | -1241 | -1599 | -1615 | -1395 |
| ΔEpaᵢ / mV | 92 | 130 | - | - |
| ΔEpcᵢ / mV | -1195 | -1330 | - | - |
| iₛₑᵧμA | 1.4 | 3.1 | 1.8 | 0.5 |
| nₛₑᵧμA | 0.5 | 0.5 | 0.5 | 0.5 |
| ΔEpa₁ / mV | 79 | 81 | - | - |
| ΔEpc₁ / mV | -83 | 409 | - | - |
| iₛₑᵧμA | 4.6 | 2.4 | 2.4 | 0.5 |
| nₛₑᵧμA | 1.0 | 1.0 | 0.8 | 0.8 |
| Epc₂ / mV | 104 | 117 | - | - |
| ΔEpa₂ / mV | -123 | 369 | - | - |
| ΔEpc₂ / mV | -337 | -337 | - | - |
| iₛₑᵧμA | 4.6 | 7.9 | - | - |
| nₛₑᵧμA | 0.3 | 0.3 | 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 Fc/Fc⁺) of [(C₅H₅)₂Ti[[C₅H₅]₂M(C₅H₅)₂]] with M = Fe (1), Ru (2) and Os (3), measured CH₂Cl₂/0.1 mol dm⁻³ [NBu₄][B(C₆F₅)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.

Figure 1. Left: Correlation between the atomic electronegativity of the metal of the metallocene ligand and the ¹H NMR position of the cyclopentadienyl ring proton connected to the Ti. Right: ¹H NMR of (top) 1 (middle) and 3 (bottom).
labelled 1 is associated with the Ti$$^4+$$/Ti$$^3+$$ couple. This reduction wave is electrochemically quasi-reversible with
\[ \Delta E = 92 \text{ mV} \]
and chemically irreversible with
\[ \frac{i_p}{i_c} = 0.5 \]

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
\[ \Delta E = 72-79 \text{ mV} \]
and
\[ \frac{i_p}{i_c} \approx 1 \]

However, at higher scan rates the oxidation wave becomes electrochemically quasi-reversible with \( \Delta E = 85-102 \text{ mV} \) but stays chemically reversible with
\[ \frac{i_p}{i_c} = 1 \]

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 known 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
\[ \Delta E = 130 \text{ mV} \]
and chemically irreversible due to
\[ \frac{i_p}{i_c} = 0.5 \]

However, at higher scan rates the reduction wave becomes electrochemical and chemically irreversible with \( \Delta E = 150 \text{ mV} \). 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
\[ \Delta E = 79-89 \text{ mV} \]
at all scan rates (50-500 mV s$$^{-1}$$) with
\[ \frac{i_p}{i_c} = 1 \]

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 \( E_p = -1599 \) 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 cyclodenediaryl 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 RuIII specie should in analogy with free ruthenocene [25], be very unstable and short lived. The RuII 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 RuIII specie to form a RuII-RuII compound [33,34], or any other rearrangements to eventually form unidentified RuII- or RuIV-species. Some of these newly formed RuIII- or RuIV- 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 increases with increased scan rate. This result is 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 TiIV which is normally only formed at ca. -2500 mV vs FcH/FcH+ [28].

The Epc of the TiIV/TiIII couples are dependent on the atomic electronegativity of the metal in the metallocene ligand (Fe (χFe=1.64), Os (χOs=1.52) and Ru (χRu=1.42)). As the metal in the metallocene ligands’ atomic electronegativity increases, the substituted metallocene withdraws more electron density from the titanium centre, making the titanium centre easier to reduce. This can be seen in Epc of the TiIV/TiII couple which became more positive, 3<2<1.

The Epc 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 Epc for the Fc/Fc+, Os/OcO- and Re/ReO- 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, [30] the Fc/Fc+ couple appears at lower potential than the Re/ReO- 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 dimetalocenyl 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 ‘H NMR position of the cyclodenediaryl rings’ protons and the atomic electronegativity of the metal in the metallocene ligand.

All compounds revealed chemically and electrochemically irreversible reduction wave for the TiIV/TiIII couple in the voltage range -1599 mV< Epc < -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 (χFe=1.64), Ru (χRu=1.42) and Os (χOs=1.52)).

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