ISSN 1023-1935, Russian Journal of Electrochemistry, 2021, Vol. 57, No. 1, pp. 85–91. © Pleiades Publishing, Ltd., 2021.

An Electrochemical Study of Bis(cyclopentadienyl)titanium(IV) Dichloride in the Presence of Magnesium Ions, Amides or Alkynes

Abdou K. D. Dimé[a], *, **Yvan Six**[b], **and Olivier Buriez**[c]

[a] *Equipe Matériaux, Electrochimie et Photochimie Analytiques (EMEPA) de l'Université Alioune Diop de Bambey, B.P. 30 Bambey, Sénégal*

[b] *Laboratoire de Synthèse Organique (LSO), UMR 7652 CNRS / ENSTA / École Polytechnique, Institut Polytechnique de Paris, Palaiseau Cedex, 91128 France*

[c] *PASTEUR, Département de Chimie, Ecole Normale Supérieure, PSL University, Sorbonne Université, CNRS, Paris, 75005 France*

**e-mail: abdou.dime@uadb.edu.sn*

Received January 30, 2020; revised May 1, 2020; accepted June 11, 2020

Abstract—In tetrahydrofuran, the electrochemical reduction of $Cp_2Ti^{IV}Cl_2$ (2 mM) generated three titanium(III) complexes which were in equilibrium: $[Cp_2TiCl_2]^{\bullet-}$, $[Cp_2TiCl]^{\bullet}$ and $(Cp_2TiCl)_2$. Although the anion radical $[Cp_2TiCl_2]^{\bullet-}$ was the main species produced under these conditions, cyclic voltammetry investigations clearly showed that the proportion of the three electrogenerated Ti^{III} complexes can be modified as a function of the amounts of chloride ion present in the solution. Accordingly, the presence of Mg^{2+} ions, which led to the consumption of chloride ions through the formation of $MgCl_2$, favoured the formation of $[Cp_2TiCl]^{\bullet}$ and, consequently, of the corresponding dimer $(Cp_2TiCl)_2$. The electrochemical behaviours of $Cp_2Ti^{IV}Cl_2$ and of the electrogenerated low-valent Ti complexes were also investigated in the presence of amide and alkyne derivatives. Under these conditions, titanium complexes could not only interact with the amide carbonyl group, but also with the alkyne triple bond, provided the latter was not sterically hindered. Interestingly, the carbonyl group and the triple bond had antagonist effects on redox properties of titanium(III) complexes.

Keywords: titanium, titanocene, cyclic voltammetry, amide, alkyne

DOI: 10.1134/S1023193521010031

INTRODUCTION

In recent years, there has been a revival in the chemistry of bis(cyclopentadienyl)titanium chloride ($Cp_2Ti^{III}Cl$), especially in the field of radical organic synthesis [1–4]. Indeed, the use of this organometallic complex, obtained by the monoelectronic reduction of $Cp_2Ti^{IV}Cl_2$ and which possesses an unpaired electron on its metal center, has become a powerful tool not only in reactions involving electron transfer processes such as epoxide openings [5, 6], but also in pinacol coupling reactions [7, 8], in Reformatsky-type reactions [9], and in other transformations involving polarity reversal [10–14]. Furthermore, the development of catalytic protocols allowing the regeneration of the $Cp_2Ti^{IV}Cl_2$ starting complex after single electron transfer has significantly contributed to increasing the popularity of $Cp_2Ti^{III}Cl$ [15–18]. The preparation of this complex can be easily achieved by the reduction of $Cp_2Ti^{IV}Cl_2$ in the presence of suitable metals (e.g. zinc [19], aluminium [20] or manganese [21]), although this procedure also generates metal cations in solution. To overcome this drawback, the electrochemical reduction of $Cp_2Ti^{IV}Cl_2$ appeared as an efficient alternative strategy. In both cases, the work reported by Daasbjerg et al. has highlighted the mechanistic aspects of the chemical or electrochemical reduction of $Cp_2Ti^{IV}Cl_2$ [23–25]. Based on cyclic voltammetry investigations, it was clearly demonstrated that the electrochemical reduction of the Ti^{IV} complex mainly leads to the formation of the anion radical $[Cp_2TiCl_2]^{\bullet-}$, whereas its chemical reduction by metals (Zn, Al, Mn) leads to an equilibrium mixture of the radical $[Cp_2TiCl]^{\bullet}$ and the corresponding dimer $[Cp_2TiCl]_2$. In the latter case, and independently of the nature of the reducing metal, the dimerization equilibrium constant was found equal to 3×10^3 M^{-1} [25].

It was also found that the reactivity of Ti^{III} complexes, which is strongly dependent on both the nature of the substrate and the experimental conditions, is difficult to predict. For instance, the dimer $[Cp_2TiCl]_2$

has been judged as poorly reactive towards ketones or aliphatic aldehydes [26]. Nevertheless, Cuerva and Oltra showed that acetophenone may undergo a pinacol coupling reaction in the presence of $[Cp_2TiCl]_2$, provided that the metals used for the reduction (Mn or Zn) are employed in excess amounts [27]. Surprisingly, it was also shown that $[Cp_2TiCl]_2$ was the most reactive species towards benzaldehyde, compared to $[Cp_2TiCl_2]^{\bullet -}$ or $[Cp_2TiCl]^{\bullet}$.

Taking into account the current resurgence in the use of Ti^{III} species, we decided to explore their behaviours under experimental conditions that are typically applied in radical organic synthesis. Within this context, it was notably important to investigate how metal cations may impact the equilibrium between the Ti^{III} complexes generated by monoelectronic reduction of $Cp_2Ti^{IV}Cl_2$. Moreover, it was relevant to study the behaviours of the Ti^{III} complexes in the presence of important classes of organic compounds such as amide and alkyne derivatives, because the presence of a carbonyl group or of a triple bond may lead to specific interaction/complexation with the titanium metal center. This work was performed by cyclic voltammetry, a powerful analytical technique that is particularly suitable for this kind of exploration [28].

EXPERIMENTAL

Reagents

Tetrahydrofuran (THF, Carlo-Erba RPE quality), was distilled, under argon, over sodium and benzophenone. Tetrabutylammonium tetrafluoroborate ($TBABF_4$) was used as the supporting electrolyte for the electrochemical investigations; it was prepared from $NaBF_4$ (Acros) and $n Bu_4NHSO_4$ (Acros), then recrystallised from EtOAc/hexane (both Acros) and dried at 60°C. Diphenylacetylene (Acros, purity 99%), phenylacetylene (Acros, purity 98%) and magnesium perchlorate (Acros) were used as received. *N*-but-3-enyl-*N*-(4-methoxyphenyl)acetamide (BMA) was synthesized as described elsewhere [29].

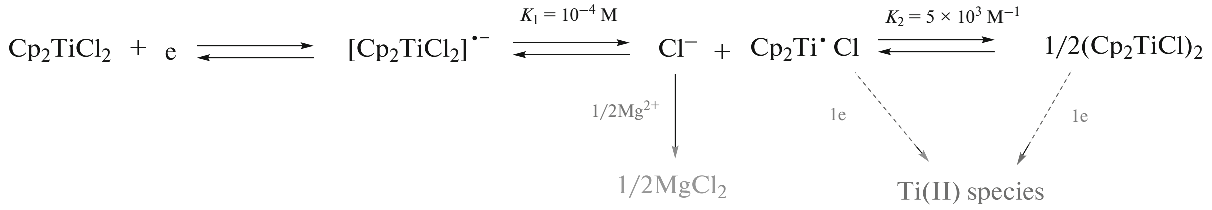
Instrumentation

All electrochemical manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free argon, at room temperature. The supporting electrolyte was degassed under vacuum before use and then dissolved to a concentration of 0.3 mol/L. Voltammetric analyses were carried out in a standard three-electrode cell, with an Autolab PGSTAT 302N potentiostat, connected to an interfaced computer installed with the Electrochemistry Nova software. The reference electrode was a saturated calomel electrode (SCE) separated from the analysed solution by a sintered glass disk filled with the background solution. The auxiliary electrode was a platinum wire separated from the analysed solution by a sintered glass disk filled with the background solution. For all voltammetric measurements, the working electrode was a glassy carbon electrode (∅ = 1 mm, Goodfellow).

RESULTS AND DISCUSSION

Electrochemical Behaviour of $Cp_2Ti^{IV}Cl_2$ in the Absence and in the Presence of Magnesium Salts

The first part of the work was aimed at evidencing a possible impact of metal cations on the equilibrium involving Ti^{III} complexes obtained after the monoelectronic reduction of $Cp_2Ti^{IV}Cl_2$. Typically, since titanium complexes are sometimes associated with Grignard reagents [30–32], it was relevant to investigate whether the presence of magnesium ions is prone to affect the Ti^{III} complexes repartition displayed in Scheme 1.



Scheme 1. Main Ti^{III} complexes involved after the electrochemical reduction of Cp_2TiCl_2 in THF (transformations put under scrutiny in this work are displayed in blue) [24].

In this work, both the reduction of $Cp_2Ti^{IV}Cl_2$ and the analysis of the corresponding generated Ti^{III} complexes were performed by cyclic voltammetry. As shown in Fig. 1, the cyclic voltammogram (CV) of $Cp_2Ti^{IV}Cl_2$, obtained in THF with 0.3 M $TBABF_4$ as supporting electrolyte, exhibited a first fully reversible reduction process (noted as O_1/R_1; $E^{\circ} = (E_{pa} + E_{pc})/2 = -0.74$ V) followed by a pseudo-reversible system ($E_{R2} = -2.08$ V). The reversibility of R_2 was more or less clearly visible, depending on how well the electrode surface had been polished.

As described by K. Daasbjerg et al. [24], the first process R_1/O_1 involves a relatively complex mecha-

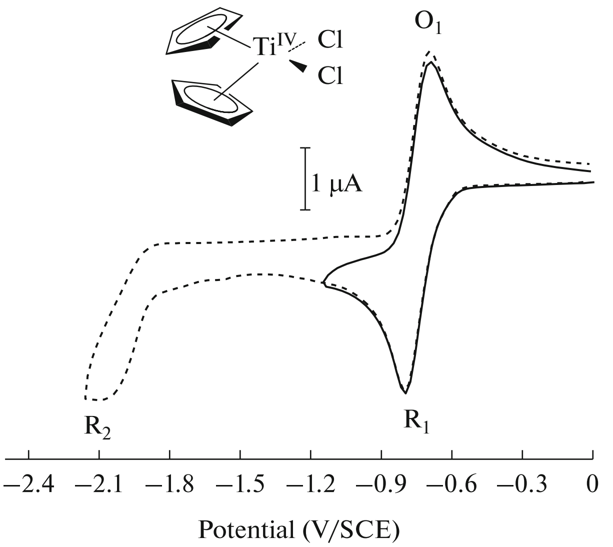


Fig. 1. Cyclic voltammogram of Cp_2TiCl_2 (2×10^{-3} M) in THF/$n$$Bu_4NBF_4$ (0.3 M) at a glassy carbon working electrode (∅ = 1 mm) and at $v = 100$ mV/s.

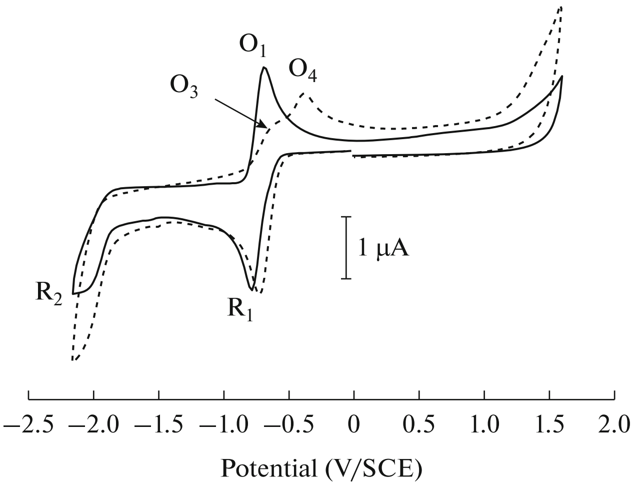


Fig. 2. Cyclic voltammograms of Cp_2TiCl_2 (2×10^{-3} M) in THF/$n$$Bu_4NBF_4$ (0.3 M) in the absence (solid line) and in the presence (dashed line) of $Mg(ClO_4)_2$ (2×10^{-3} M). CVs obtained at a glassy carbon working electrode (∅ = 1 mm) and at $v = 100$ mV/s.

nism despite its apparent neat reversibility. Actually, and as illustrated in Scheme 1, the mono-electronic reduction of Cp_2TiCl_2 initially produces the corresponding radical anion species. At low scan rates ($v <$ 0.5 V/s), the latter has enough time to dissociate and generate the radical $[Cp_2TiCl]^{\bullet}$ while releasing a chloride anion. Under these conditions, the radical species $[Cp_2TiCl]^{\bullet}$ was shown to be in equilibrium with the corresponding dimer $(Cp_2TiCl)_2$. Based on simulated voltammograms, K. Daasbjerg et al. could even determine the equilibrium constants involved between these three complexes (Scheme 1) [24]. From these constants, it was notably established that the electrochemical reduction of a 2 mM Cp_2TiCl_2 solution (conditions used in this work) generated the anion radical $[Cp_2TiCl_2]^{\bullet-}$ as the major species (1.35 mM), whereas both the radical $[Cp_2TiCl]^{\bullet}$ and the dimer $(Cp_2TiCl)_2$ species were present at lower concentrations (0.21 and 0.22 mM, respectively).

Although the electrochemical reduction of Cp_2TiCl_2 generates three different complexes, the CV in Fig. 1 revealed only one oxidation wave when the potential sweep was inverted after R_1. This is due to the fact that cyclic voltammetry is a dynamic technique, with the three complexes resulting from the reduction of Cp_2TiCl_2 being in equilibrium. In other words, the second-order back association reaction between $[Cp_2TiCl]^{\bullet}$ and Cl^- is fast enough to leave $[Cp_2TiCl_2]^{\bullet-}$ as the only species detectable on the reverse sweep (Scheme 1). This process, that is all the more efficient that the scan rate is low (i.e., that the timescale becomes longer) therefore generates only one wave (O_1) corresponding to the oxidation of the anion radical.

Accordingly, the reduction wave R_2 observed in Fig. 1 ($E_{R2} = -2.08$ V) can be assigned to the reduction of either the radical $[Cp_2TiCl]^{\bullet}$ or the dimer $(Cp_2TiCl)_2$. In both cases, the reduction process would produce the corresponding anion $[Cp_2TiCl]^-$ which would decompose into titanocene and chloride anion as the final stable species.

Under otherwise identical conditions, how is the CV of Cp_2TiCl_2 modified in the presence of magnesium ions? In Fig. 2 is shown a typical CV of the titanium(IV) complex recorded in the presence of one molar equivalent of Mg^{2+} added in solution in the form of $Mg(ClO_4)_2$.

Clearly, several changes can be observed compared to the CV obtained in the absence of magnesium salts. First, the reduction wave R_1 was slightly shifted towards a less negative potential value ($E_{R'1} = -0.73$ V vs. $E_{R1} = -0.79$ V), indicating the presence of a new chemical reaction following the electron transfer, that would facilitate the electrogenerated anion radical dissociation. Within the same long time-scale ($v = 0.1$ V/s), the oxidation wave O_1 corresponding to the oxidation of the anion radical $[Cp_2TiCl_2]^{\bullet-}$ is split into two new oxidation waves, noted as O_3 and O_4 and located at $E_{O3} = -0.56$ V and $E_{O4} = -0.41$ V, respectively. Indeed, under these conditions, the anion radical does not exist anymore in the diffusion layer. By analogy with the work reported by K. Daasbjerg and coworkers, O_3 and O_4 can be assigned to the oxidation of the dimer $(Cp_2TiCl)_2$ and of the radical $[Cp_2TiCl]^{\bullet}$ species, respectively.

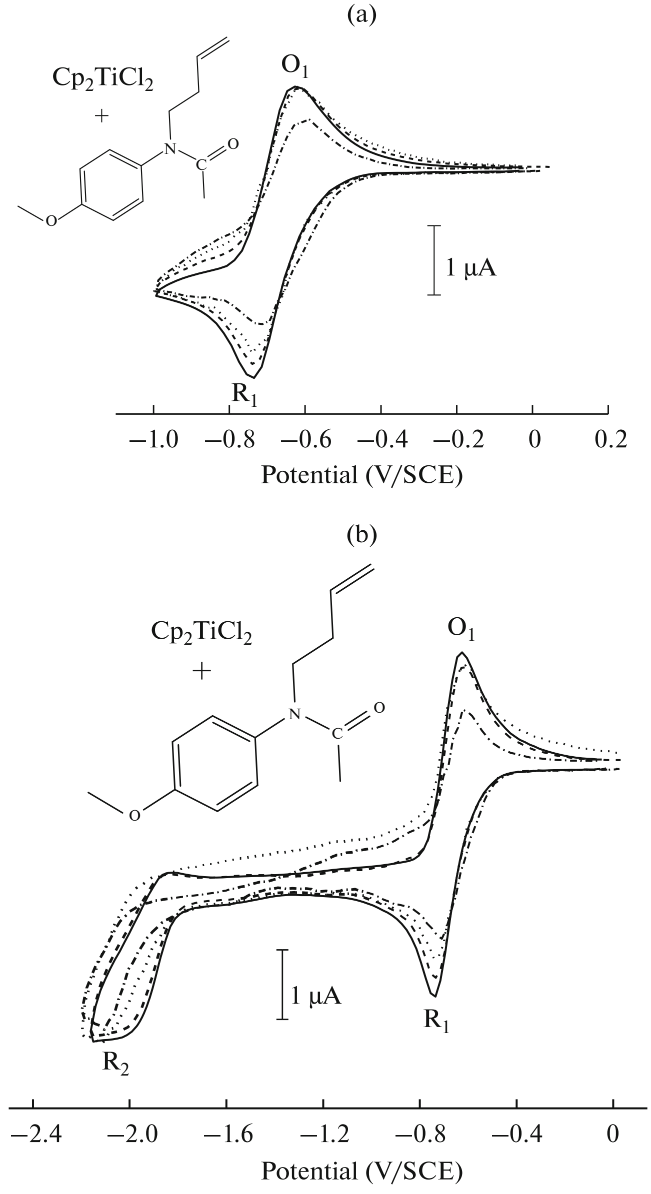


Fig. 3. Cyclic voltammograms of Cp_2TiCl_2 (2×10^{-3} M) recorded in THF/nBu_4NBF_4 (0.3 M), at a glassy carbon electrode (1 mm in diameter), in the absence (solid lines) and in the presence of BMA: 2×10^{-3} M (dashed lines); 20×10^{-3} M (dotted lines); 40×10^{-3} M (dash dotted lines). The potential sweep was inverted at −1 V (a) or −2.2 V (b). Scan rate: 50 mV/s.

In summary, this behaviour clearly indicates that the complexation between Mg^{2+} and Cl^- displaces the equilibrium shown in Scheme 1 towards the production of $[Cp_2TiCl]^{\bullet}$. Moreover, these findings can be compared to those obtained when Cp_2TiCl_2 is chemically reduced by a metal such as zinc [19, 27]. In other words, the Mg^{2+} ions added under electrochemical conditions play a similar role to the Zn^{2+} ions generated during the chemical reduction of Cp_2TiCl_2 by Zn.

It is also worthy of note that the addition of magnesium salts in the Cp_2TiCl_2 solution leads to a peak current increase of R_2 (Fig. 2). This reveals that the concentration of the species reduced at this potential value (i.e., $[Cp_2TiCl]^{\bullet}$ or $(Cp_2TiCl)_2$) increase in the diffusion layer. This is consistent with the interpretation described above; however, it is difficult at this stage to draw unambiguous conclusions about the exact nature of the Ti^{III} species that is reduced at the level of R_2.

Electrochemical Behaviour of $Cp_2Ti^{IV}Cl_2$ in the Absence and in the Presence of Amide or Alkyne Derivatives

In the previous part, we demonstrated that equilibria involving titanium(III) complexes can be displaced by reducing the concentration of free chloride ions in solution. Another objective of this work was also to obtain qualitative information on possible complexation of electrogenerated low-valent titanium complexes with important organic substrates such as *N*-but-3-enylamides and alkyne derivatives. Indeed, these compounds can be chemically transformed into high added value compounds such as aminocyclopropanes and *Z*-alkenes, respectively. However, these processes involve the presence of titanium(II) complexes, generated under drastically different conditions i.e., typically from $Ti(OiPr)_4$ associated with a polar organometallic compound such as a Grignard reagent [32–36] or, more rarely, an organolithium compound [37, 38].

In the Presence of N-but-3-enyl-N-(4-methoxyphenyl)acetamide (BMA)

The electrochemical behaviour of Cp_2TiCl_2 was first investigated in the presence of BMA, a substrate that proved to be useful for the preparation of endoperoxides having antimalarial activity [29]. As shown in Fig. 3a, the peak current intensities of both R_1 and O_1 concomitantly decreased as the BMA concentration increased. Under the same conditions, the wave R_2 shifted towards more negative potential values (Fig. 3b).

These behaviours are very likely related to a complexation occurring between the Ti metal center and the carbonyl group of BMA, in agreement with the Lewis acidity and oxophilic properties of titanium. Such a complexation between the starting complex and BMA would therefore lead to “Cp_2TiCl_2-amide” complex having a lower diffusion coefficient than Cp_2TiCl_2 in agreement with a decrease of both $I(R_1)$ and $I(O_1)$.

Moreover, a complexation would also occur between BMA and electrogenerated Ti^{III} complexes (in R_1) before reduction of the latter (in R_2), in agree-

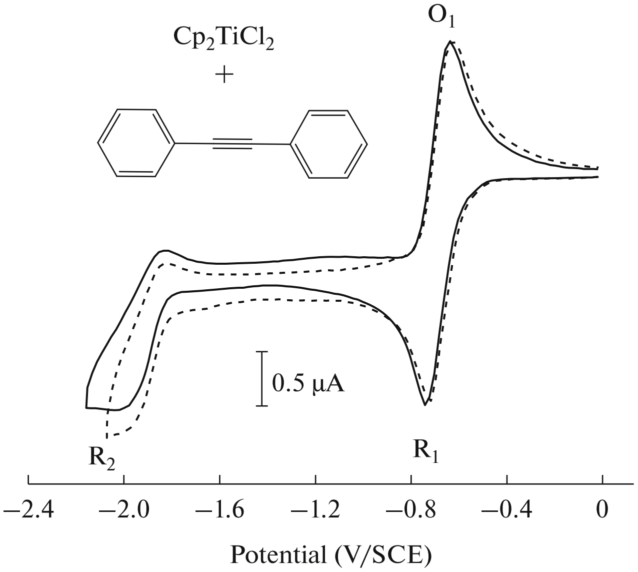


Fig. 4. Cyclic voltammograms of Cp_2TiCl_2 (2×10^{-3} M) in THF/$n$$Bu_4NBF_4$ (0.3 M), at a glassy carbon electrode (1 mm in diameter), in the absence (solid line) and in the presence (dashed line) of diphenylacetylene (2×10^{-3} M). Scan rate: 50 mV/s.

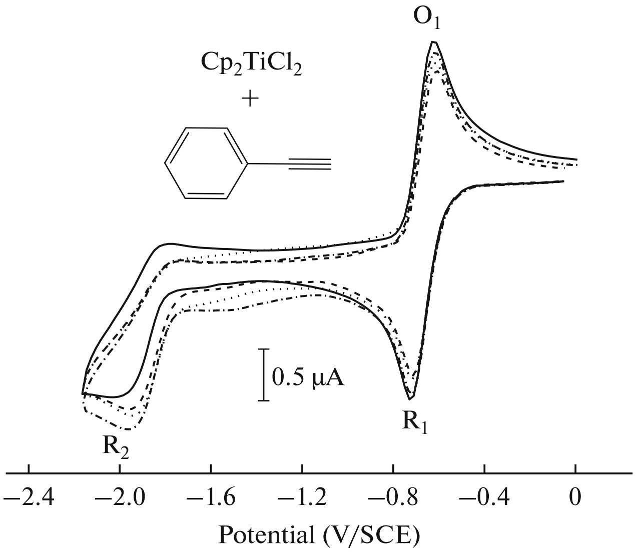


Fig. 5. Cyclic voltammograms of Cp_2TiCl_2 (2×10^{-3} M) in THF/$n$$Bu_4NBF_4$ (0.3 M), at a glassy carbon electrode (1 mm in diameter), in the absence (solid line) and the presence of phenylacetylene: 2×10^{-3} M (dashed line); 4×10^{-3} M (dotted line); 6×10^{-3} M (dash dotted line). Scan rate: 50 mV/s.

ment with the potential shift of R_2 towards more negative potential values (Fig. 3b). In other words, the complexation between the BMA carbonyl electron-donating group and the Ti^{III} metal center made the complex reduction more difficult.

In the Presence of Alkyne Derivatives

Even more than *N*-but-3-enyl amide compounds, alkyne derivatives are substrates of high importance in organic synthesis because their reduction gives access to alkene products. The electrochemical behaviour of Cp_2TiCl_2 was comparable in the absence and in the presence of one molar equivalent of diphenylacetylene (Fig. 4). The same voltammograms were also obtained when diphenylacetylene was used in excess (not shown). These results clearly demonstrate the absence of complexation between diphenylacetylene and titanium complexes (Ti^{IV} and Ti^{III}). This also confirms the important role of the carbonyl group in the complexation reaction occurring between the titanium metal center and the amide derivative BMA (previous paragraph).

It was hypothesised that the absence of changes in the CVs shown in Fig. 4 could be due to the steric hindrance of the triple bond (presence of one aromatic ring at each side of the triple bond) which would prevent an easy access to the titanium complex. Phenylacetylene was therefore investigated instead of diphenylacetylene. Contrary to what had been observed previously with BMA, no changes were observed on the R_1/O_1 system even in the presence of phenylacetylene used in excess (20 molar equivalents, not shown). However, in the presence of increasing amounts of phenylacetylene, the wave R_2 shifted towards less negative potential values, while the process remained reversible (Fig. 5). Contrarily to the situation observed with BMA, the reduction process occurring in R_2 became therefore easier (negative *vs.* positive shift of the potential wave R_2). This experimental observation is consistent with a complexation between the electrogenerated Ti^{II} complex and the triple bond, which thus facilitates the reduction of Ti^{III} (EC-type mechanism).

CONCLUSIONS

This work was aimed at using cyclic voltammetry to explore the behaviour of the reduced titanium species under the experimental conditions that are typically applied when Cp_2TiCl_2 is used in radical organic synthesis. Interestingly, it was clearly shown that the presence of metal salts that are able to subtract chloride ions freely diffusing in solution impacts the ratio of the Ti^{III} complexes generated by monoelectronic reduction of $Cp_2Ti^{IV}Cl_2$. Typically, a decrease of the Cl^- concentration (via the addition of Mg^{2+} to produce $MgCl_2$) favoured the formation of $[Cp_2TiCl]^•$ and, consequently, of the corresponding dimer $[Cp_2TiCl]_2$. Importantly, this behaviour mimics the situation observed under classic conditions involving reducing metals (Zn, Mn and Al), where metal chloride salts are produced. Furthermore, it was shown that organic compounds bearing either a carbonyl group or a nonsterically hindered triple bond may have antagonist effects on redox properties of titanium(III) complexes. Accordingly, the complexation between the BMA carbonyl electron-donating group and the Ti^{III} metal center made the complex reduction more difficult. Conversely, the reduction of the Ti^{III} species was facilitated in the presence of phenylacetylene because of complexation between the Ti^{II} thus produced and the alkyne triple bond.

FUNDING

This work was supported by the Agence Nationale de la Recherche (grant number: ANR-12-BS07-0013 "ACTIMAC"), the Centre National de la Recherche Scientifique (CNRS), the École Normale Supérieure, École Polytechnique and Sorbonne University.

CONFLICT OF INTERESTS

The authors state that they have no conflict of interests.

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