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Evidence of intramolecular electron transfer between two metallic atoms in a bimetallic complex by electrochemical methods†

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The electrochemical properties of the monomeric complex [(η^5-C_5H_5)(μ-η^5:η^1-$C_5H_4(CH_2)_2P(C_6H_5)_2TiCl_2$] **1** and the heterobimetallic complex [(η^5-C_5H_5)(μ-η^5:η^1-$C_5H_4(CH_2)_2P(C_6H_5)_2TiCl_2$][$RuCl_2(C_6H_4(CH_3)(C_3H_7))$] **2** have been studied by cyclic voltammetry, controlled potential electrolysis and rotating disk electrode voltammetry. An unexpected electron transfer between the two heterobimetallic atoms has been observed. This transfer takes place *via* an intramolecular interaction, hence *via* a chloride bridge. Electrochemical simulation has been carried out to verify experimental results and to obtain the kinetic constant of the proposed square scheme.

Introduction

Organometallic chemistry abounds with examples of dinuclear compounds in which the two metallic centers are held together by a variety of bridging ligands. Such compounds provide good models for the study of cooperative effects between adjacent metal atoms in catalysis. The recent surge of interest in the chemistry of early-late heterobimetallic compounds is motivated by the aptitude of the compound to confine two metallic fragments within a chloride bridge, thus yielding complexes with new properties which are interesting to explore. The catalytic behaviour[1] of the titanium–ruthenium heterobimetallic complexes have shown surprising differences according to the ligands used. Since such transformations proceed mostly through electron transfer on the metal, it is of primary importance to gain insight into the nature of the species formed by the stepwise electron addition or abstraction. Electrochemical methods can therefore be of great help in the understanding of such mechanisms.

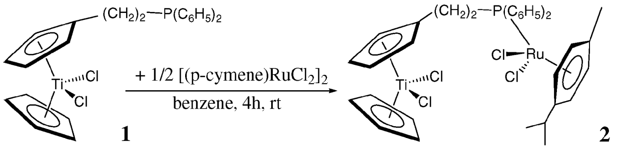
Pioneering work in the field may be found in the reduction of $[Cr(CN)_6{}^{3-}]$[2] and in the electrochemical study of organometallic complexes.[3–12] The electrochemical properties of mononuclear titanium[13–16] or ruthenium[17–18] complexes have been widely investigated but, in contrast with the abundant work in this area and to our best knowledge, only a few electron-transfer studies[19–22] have been published on bimetallic complexes. A chloride bridge between two metallic atoms has already been observed,[21–24] but it is the first electrochemical study which gives evidence of an electron transfer *via* this bridge.

In this article, we report an electrochemical study of a monometallic compound [(η^5-C_5H_5)(μ-η^5:η^1-$C_5H_4(CH_2)_2P(C_6H_5)_2TiCl_2$] **1** and the corresponding heterobimetallic complex [(η^5-C_5H_5)(μ-η^5:η^1-$C_5H_4(CH_2)_2P(C_6H_5)_2TiCl_2$][$RuCl_2(C_6H_4(CH_3)(C_3H_7))$] **2**, giving evidence of the chloride bridge between the two metallic centers and providing elements to better understand the catalytic results already obtained.[1] The electrochemical mechanism of this bimetallic complex will be extensively described. The kinetics of its electrochemical reactions are also investigated.

Experimental

Synthesis and catalysis behaviour of the complex 2

The heterobimetallic compound **2** was prepared according to an earlier published procedure[25] by reaction between titanocene monophosphine with the ruthenium dimer, as described as below.



A preliminary assessment of the catalytic performance of the bimetallic complex **2** in ring closing metathesis (RCM) has already been carried out.[1] First attempts in neutral catalysis were conducted in CH_2Cl_2 under neon light with a solution of *N*,*N*-diallyltosylamide and a catalytic amount of bimetallic complexes. These latter, unlike the monometallic complex [$RuCl_2P(C_6H_{11})_3(C_6H_4(CH_3)(C_3H_7))$], showed almost no catalytic activity. A second set of experiments, which met with more success, required changing the neutral complex **2** into cationic Ti–Ru-allenylidene precatalyst. In this case, a cationic site generated on ruthenium by a chloride ion extraction is needed. Cationic complexes thus obtained have as a result a vacant site in which alkyne can be coordinated to initiate the RCM reaction. Such complexes can be generated *in situ* or not by successive addition of silver triflate and propargylic alcohol. It is worth noting that the rate of formation of the cumulene species is very different according to the bimetallic complex. The reactivity of **2** is very mixed: the reaction occurred but required a long time and was not quantitative. Thus, the ease of access to the allenylidene complex and therefore to an effective precatalyst was thoroughly studied. At this point,

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† Electronic supplementary information (ESI) available: Electronic supplementary information available: ESR spectra of **1′** and **3′**. See http://dx.doi.org/10.1039/b507665j

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electrochemistry seems to be the methodology of choice to study the subtle reactivity of **2** and more generally to obtain insight into the influence of the titanocene fragment on its metal neighbour.

Electrochemistry

All manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free argon gas and using dry solvents. The main supporting electrolyte used was the tetrabutylammonium hexafluorophosphate (NBu_4PF_6), obtained by adding 100 mL of tetrabutylammonium hydroxide and 15 mL of hexafluorophosphate acid to 1 L of water. The white solid obtained was filtered, recrystallized three times in ethanol and dried at 80 °C for at least 2 days before use. A second electrolyte used was sodium tetraphenylborate ($NaBPh_4$) purchased from Avocado. Theses electrolytes were degassed under vacuum before use and then solubilized at a concentration of 0.2 mol L^{-1}. Tetrahydrofuran (THF) was distilled under argon over sodium and benzophenone. Throughout our work, a three-compartment cell was used with a platinum wire as a counter electrode. The reference electrode was a saturated calomel electrode (SCE) separated from the solution by a sintered glass disk. For all voltammetric measurements carried out with a Taccussel UAP4 unit cell, the working electrode was a vitreous carbon electrode ($\varnothing$ = 3 mm). The controlled potential electrolyses were performed with an Amel 721 electronic integrator in a cell with three compartments separated by fritted glass of medium porosity. A carbon gauze was used as the cathode, a platinum plate as the anode and a saturated calomel electrode as the reference electrode.

All the electrochemical results will be presented *versus* the saturated calomel electrode (SCE) and the complex concentration was generally close to 2×10^{-3} mol L^{-1}.

Simulation

Digital simulations were obtained with the program Digisim (Bianalytical Systems). The potential step size was 5 mV. The uncompensated resistance, here $R_u = 800\ \Omega$, was determined with a PAR 373A potentiostat using the same experimental conditions as for the CV measurements. The double layer capacitance value was estimated as $C_{dl}/A = 1.71\ \mu F\ cm^{-2}$ using a blank solution prior to voltammetric measurements. The experimental curves were corrected for residual current, also determined using voltammetric measurements of blank solutions.

Other measurements

ESR spectra were obtained using a Bruker ESP 300 spectrometer and at 295 K, in the electrochemical study conditions (THF and electrolyte salt 0.2 mol L^{-1}).

Results and discussion

The electrochemical characteristics of the complexes were studied in THF, 0.2 mol L^{-1} of NBu_4PF_6 solution by cyclic voltammetry (CV) and rotating disk electrode voltammetry (RDE). The monomeric species used in the bimetallic synthesis, such as Cp_2TiCl_2 or $[RuCl_2(C_6H_4(CH_3)(C_3H_7))]_2$, have already been extensively investigated.[13,14,18]

Electrochemical studies

The monometallic complex 1. The monometallic complex **1** studied by CV revealed one reduction peak A at −0.70 V and one oxidation peak B′ at −0.15 V (Fig. 1a). This electrochemical system was characteristic of a square scheme[13,14] (Scheme 1), since the same voltammogram is obtained with the second potential cycle, as described previously.[16] This type of mechanism was first introduced by Jacq[26] and developed afterwards.[27–33] By RDE voltammetry, a second reduction wave was assigned to Ti^{III} reduction at −2.13 V (Fig. 1b). When the electrolysis was performed at −1.20 V on the A reduction plateau (Fig. 1c) with one electron consumption ($n = 0.88e^-$), the Ti^{III} oxidation wave B′ was obtained (see reaction (1)) and an ESR signal characteristic of the Ti^{III}–P complex[10] **1′** was detected in the resulting solution (see Fig. 1S in ESI†). It consists of an intense doublet due to the interaction of the unpaired electron with one ^{31}P nucleus (nuclear spin $I = 1/2$). Each of the doublet lines is symmetrically flanked by an hyperfine sextet resulting from the ^{47}Ti nucleus ($I = 5/2$, natural abundance 7.4%) and a hyperfine octet caused by the ^{49}Ti nucleus ($I = 7/2$, natural abundance 5.4%). However, the intense "^{31}P doublet" prevents the observation of the inner lines of the $^{47,49}Ti$ hyperfine pattern. The ESR parameters were found equal to: $g = 1.9896$, $a_P = 19.8$ G, $a_{Ti} = 9.3$ G.

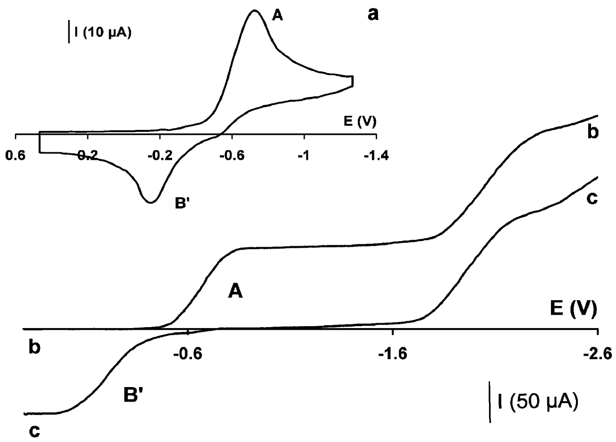
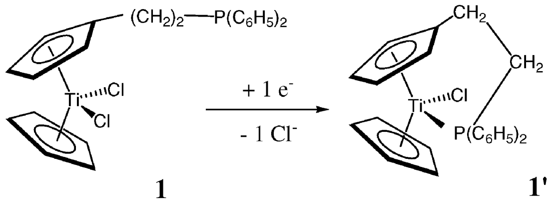
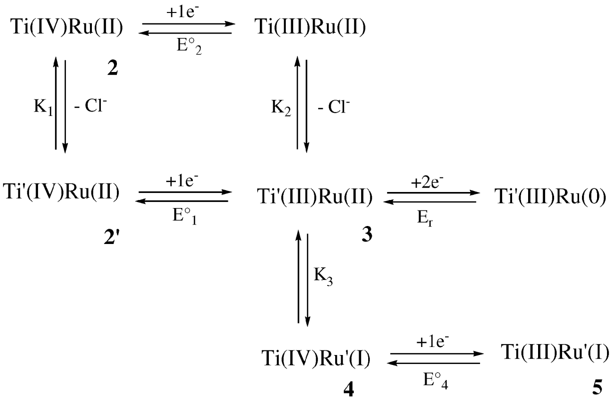


Fig. 1 Voltammograms of complex **1** on carbon electrode in THF containing 0.2 mol L^{-1} NBu_4PF_6 by CV (a, scan rate: 100 mV s^{-1}) or by RDE voltammetry (b–c, scan rate: 20 mV s^{-1}); (a, b) initial; (c) after electrolysis at −1.20 V ($n = 0.88e^-$).



(1)



Scheme 1 Mechanism scheme of the bimetallic complex **2**. This complex is symbolized by its oxidation degree, for example the initial product as Ti(IV)Ru(II).

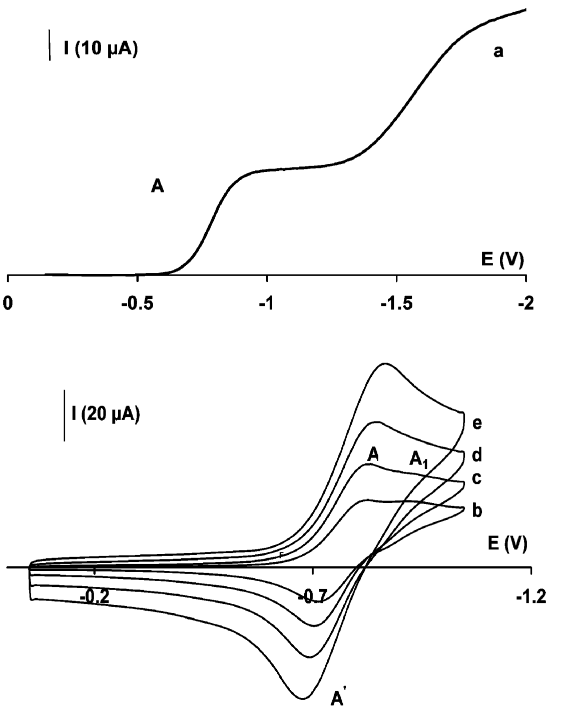


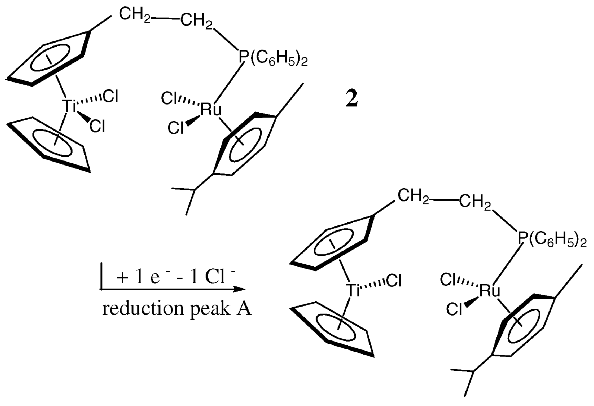
Fig. 2 Voltammograms of complex **2** on carbon electrode in THF containing 0.2 mol L^{-1} NBu_4PF_6 by RDE voltammetry (a, scan rate: 20 mV s^{-1}) or by CV (b–e) at scan rates: (b): 20 mV s^{-1}; (c): 50 mV s^{-1}; (d) 100 mV s^{-1} and (e): 200 mV s^{-1}.

Otherwise, by adding a half equivalent of the $[RuCl_2(C_6H_4(CH_3)(C_3H_7))]_2$ dimer on the Ti^{III} generated complex, no changes were observed in this oxidation wave B′.

This means that there were no spontaneous interactions between Ti^{III} and Ru^{II} which is due to the fact that the phosphorus atom coordinated then protected the Ti^{III} from the Ru^{II} interaction.

The bimetallic complex 2. The bimetallic complex **2**, studied by RDE voltammetry, exhibited two reduction waves at −0.79 V and −1.57 V (Fig. 2a): the first one was due to a Ti^{IV} reduction. The second wave observed is attributed to the Ru^{II} reduction. Its height is nearly twice that of the first one, hence it might be explained by the reduction[6,7] of Ru^{II} to Ru^{0}.

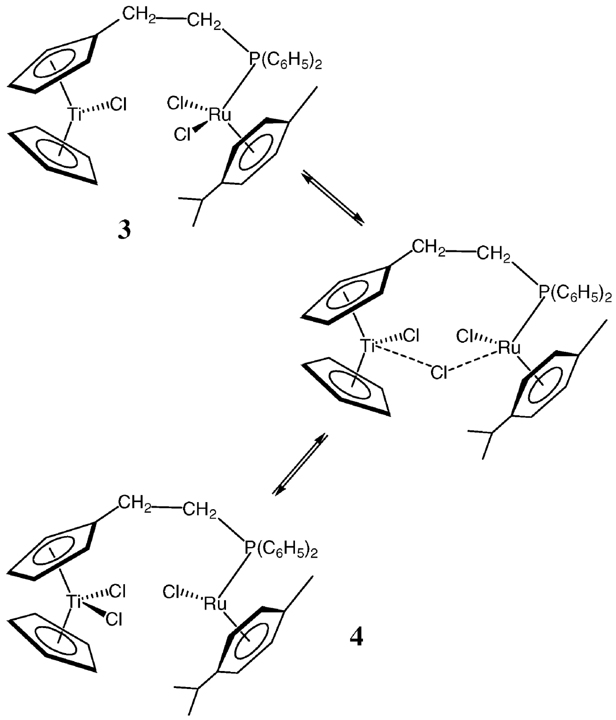
Using CV (Fig. 2b–2e), a pseudo-reversible system Ti^{IV}/Ti^{III} A/A′ was observed at −0.76 V, following a classical electrochemical square scheme.[3,13,14] The initial complex **2**, symbolized as Ti(IV)Ru(II), is reduced according to the A/A′ square scheme to the complex Ti′(III)Ru(II), formulated as **3**, where the chemical reaction corresponds to the elimination of a chloride atom (see reaction (2)).



(2)

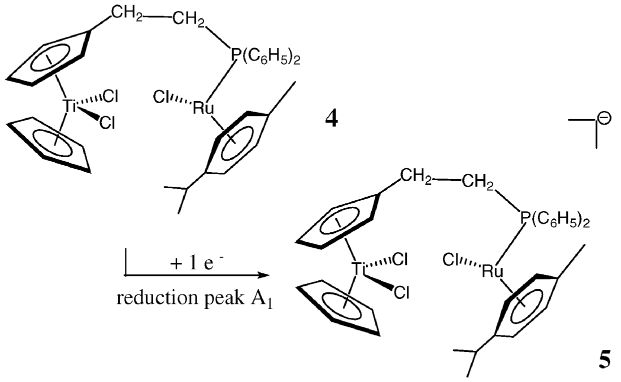
For low scan rate (20 mV s^{-1}, Fig. 2b), a new reduction peak A_1 appears at −0.91 V. Its intensity increases as the scan rate is reduced and may be attributed to the reduction of transient Ti^{IV} species. Simultaneously, by RDE, the second reduction wave Ru^{II}/Ru^{0} decreases as the first one increases. The ratio i_d/i_d without electronic transfer of the wave A decreases and tends toward 1 when the rotation scan is increased (1.21 for 20.94 rad s^{-1} and 1.08 for 209.43 rad s^{-1}). When the experiments were carried out at low temperature, this A_1 peak was missing. Moreover, this peak A_1 was obtained whatever the complex concentration (with a concentration range investigated from 7.5×10^{-4} to 4×10^{-3} mol L^{-1}), which tends to prove the existence of intramolecular interactions.

The existence of a second reduction peak (A_1), situated in the potential area of Ti^{IV} complex reduction revealed by CV and the diffusion current variation with the rotation rate could be explained by an electronic transfer between the two metallic atoms to regenerate a Ti^{IV} complex. This electronic transfer is intramolecular and the only way for it to take place is *via* a chloride bridge. Moreover, previous studies have already pointed out a chloride bridge between two heterobimetallic atoms. Numerous examples are available: a choice with few of them concerning titanium or ruthenium are cited as references.[20–24] In the complex **3**, the chloride atom is then transferred from Ru to Ti; Ti′(III)Ru(II) thus becomes Ti(IV) Ru′(I) (see reaction (3)). This is in accordance with the fact that the second reduction wave decreases as A_1 increases, since in these conditions, this process corresponds to a Ru(I)/Ru(0) reduction.



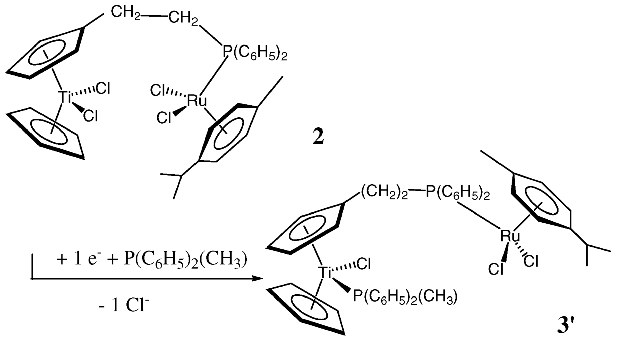
(3)

This new Ti^{IV} complex is then reduced at −0.91 V (A_1 peak, see reaction (4)). When the scan rate is increased, this interaction does not have enough time to take place, hence the A/A′ system only is observable. At low temperature, the peak A_1 is once again not apparent since at this temperature, the chemical reactions are slowed and so the chloride atom transfer can no longer occur.



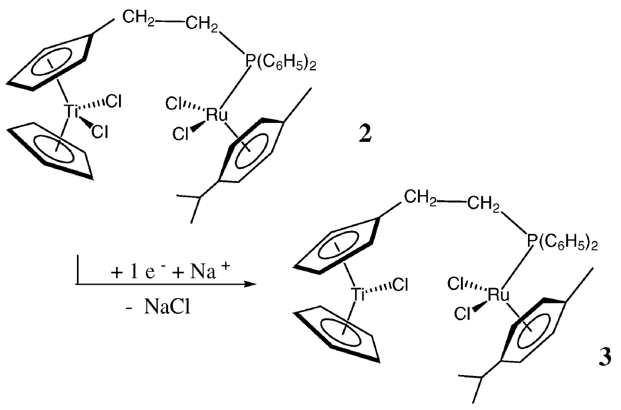
(4)

When the experiments were carried out with three equivalents of $P(C_6H_5)_2(CH_3)$, the peak A_1 disappeared. In these conditions and after an electrolysis at −0.95 V, an oxidation wave was obtained at −0.27 V. The ESR spectrum (see Fig. 2S in ESI†) showed as for the monometallic complex (see above) that the Ti signal was split into a doublet (a_p = 20 G) owing to the interaction of the unpaired electron[10] of Ti^{III} species with ^{31}P (g = 1.9885, a_{Ti} = 10 G) and the formation of the complex **3′** (see reaction (5)). These results prove that when the phosphorus atom was coordinated to the Ti atom, no interaction between the Ti and the Ru atoms was able to take place. The complex is then stopped in the Ti′(III)Ru(II) stage, as complex **3′** and may be oxidized to Ti′(IV)Ru(II).



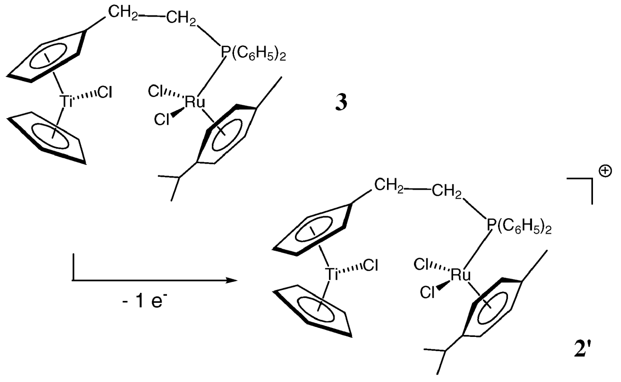
(5)

When the complex **2** was studied in the presence of $NaBPh_4$, the A, A_1 and B peaks were obtained as before. However, the first system becomes totally irreversible for scan rates varying from 20 to 200 mV s^{-1} (reaction (2′)). At 500 mV s^{-1}, a peak with low intensity appears at −0.34 V.



(2′)

In this medium, $NaBPh_4$ trapped the chloride anion released from reaction (2) to yield to a NaCl precipitate; this reaction then becomes irreversible and consequently, **3** can be oxidized at –0.34 V to form the cationic species **2′** (reaction (6)).



(6)

Scheme 1 summarizes all the results obtained for the reactivity study of the complex **2**.

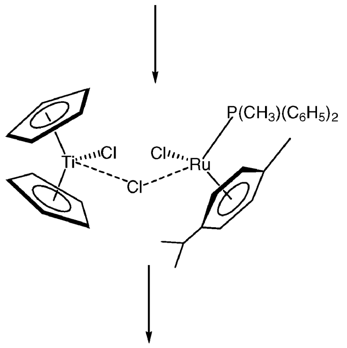
Could the electronic transfer observed in a bimetallic complex be obtained with only the corresponding monometallic complexes?

The interest of the bimetallic complex, compared to the corresponding separated monometallic complexes was verified. Cp_2TiCl_2 was reduced electrochemically with consumption of one electron at −1.2 V and the corresponding $Cp_2Ti^{III}Cl$ was obtained, which presents its oxidation wave at −0.71 V.

One equivalent of $Ru^{II}Cl_2$(*p*-cymene)($PPh_2(CH_3)$) was introduced to this solution. After ten minutes, the Ti^{III} oxidation wave was nearly unchanged. Twenty-five minutes were needed to begin to observe a decrease in this wave. Simultaneously, the corresponding reduction wave of Cp_2TiCl_2 increases only weakly (10% max. according to the wave height).

These results indicated that an electronic transfer between the two monometallic complexes Ti^{III} and Ru^{II} may be observed after a relatively long time. This electronic transfer may only be explained by the formation of an intermediate (intermolecular inner-sphere electronic transfer), since, as the difference of potential between the Ti^{III} oxidation potential and the Ru^{II} reduction potential is equal to 0.65 V (potentials, respectively, equal to −0.71 V and −1.36 V), an outer-sphere electronic transfer could be eliminated.

$$Cp_2TiCl \quad + \quad Ru^{II}Cl_2(\text{p-cymène})(P(C_6H_5)_2(CH_3))$$



$$Cp_2TiCl_2 \quad + \quad \text{"}Ru^{I}Cl_2(\text{p-cymène})((P(C_6H_5)_2(CH_3))\text{"}$$

In conclusion, we have showed that an electronic transfer between two metallic atoms in the case of heterobimetallic derivatives was observed at the cyclic voltammetry time scale, but was not observed with the two separated monometallic complexes at the same time scale. This last electronic transfer was all the same observed but with a much longer time scale and a weaker yield.

Electrochemical simulation

Since the complex **2** presented an unexpected reactivity with an electron transfer occurring *via* a chloride bridge between two

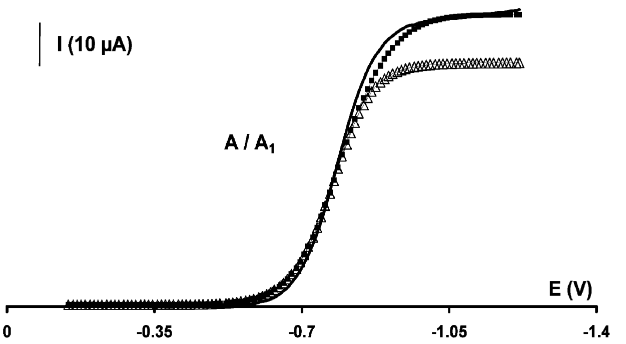


Fig. 3 RDE voltammograms of complex **3** on carbon electrode in THF containing 0.2 mol L^{-1} NBu$_4$PF$_6$: experimental curves (—); simulated curves (■ ■ ■); simulated curves without electronic transfer (△△△) at a scan rate of 20 mV s^{-1} and a rotation rate of 104.72 rad s^{-1}.

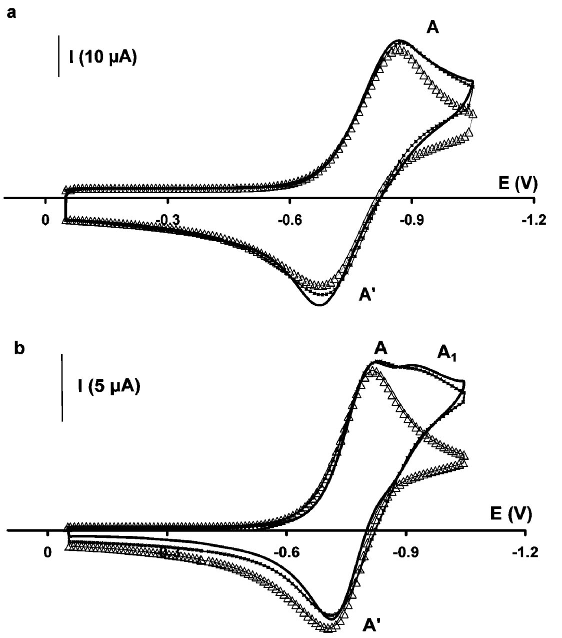


Fig. 4 Cyclic voltammograms of complex **3** on carbon electrode in THF containing 0.2 mol L^{-1} NBu$_4$PF$_6$: experimental curves (—); simulated curves (■ ■ ■); simulated curves without electronic transfer (△△△) at scan rates: (a: 200 mV s^{-1}; b: 20 mV s^{-1}).

metallic atoms, we tried to verify all the experimental results obtained for it by using the Digisim simulation software and to complete them by determining all the thermodynamic and kinetic parameters defined in Scheme 1.

To first determine the square scheme parameters,[34,35] the results obtained with the complex **2** in the presence of NaBPh$_4$ were analyzed. In this case, the precipitation of NaCl occurs during the Ti(IV)Ru(II) reduction, the initial complex is reduced and for a relatively fast scan rate, the reoxidation pathway of Ti′(III)Ru(II) to Ti′(IV)Ru(II) was observed at −0.34 V (reaction (6)). No chloride atom being available, the reverse reduction peak Ti′(IV)Ru(II)/Ti′(III)Ru(II) should have been obtained at the second scan. Unlikely, this reduction peak was not obtained but $E°_1$, the corresponding standard potential, may also be approximated as equal to $E_{(6)}$ − (0.06/2), hence (−0.34, −0.03) or (−0.37) V, if the ohmic drop is neglected.

Otherwise, the potential of the peaks A/A′ is also function of $E°_2$ (the Ti(IV)Ru(II)/Ti(III)Ru(II) standard potential) and K_2. K_2 is defined an equilibrium constant and is then equal to k_{f2}/k_{b2} = [Ti′(III)Ru(II)] × [Cl$^-$]/[Ti(III)Ru(II)]. Theses two values have been evaluated by numeric simulation at different scan rates by RDE voltammetry and CV: $E_2° = -0.80$ V; $K_2 = 6 \times 10^{-3}$ mol L^{-1}. The K_1 constant (equal to k_{f1}/k_{b1} = [Ti′(IV)Ru(II)] × [Cl$^-$]/[Ti(IV)Ru(II)]) is deducted from the relation[34] $K_2/K_1 = \exp[F/RT(E_1° - E_2°)]$. We also verified that the rate constant of the charge transfer k_{hi}, equal to 0.025 cm s^{-1}, and the charge transfer coefficient α_i, equal to 0.5, previously determined[35] for the di(propylthiotetramethylcyclopentadienyl) titanium dichloride (Cp′$_2$TiCl$_2$) under the same experimental conditions, were suitable for the simulation. Better results were obtained for k_{hi} equal to 0.01 cm s^{-1} by RDE fitting.

On the contrary, the chemical reaction constants are rather far from the already mentioned case[35]: $k_{f1} = 10^{-4}$ s^{-1} hence $k_{b1} = 1.78 \times 10^5$ mol^{-1} L s^{-1} (instead of $k_{b1} = 10^{11}$ mol^{-1} L s^{-1}); $k_{f2} = 10^7$ s^{-1} (instead of $k_{f2} = 10^3$ s^{-1}), since the square scheme is pseudo-reversible and no second oxidation peak was observed in this explored scan rate field. The results therefore imply that the reduction and the oxidation are taking place by the same pathway: Ti(IV)Ru(II) to Ti(III)Ru(II) to Ti′(III)Ru(II) (see reaction (2)).

The electron transfer from the titanium to the ruthenium is expressed by the A wave increase in RDE voltammetry (Fig. 3) and the A$_1$ peak appearance in CV (Fig. 4). The corresponding constants K_3 and k_{f3}, as the K_4 and k_{f4} constants, linked to the formed Ti(IV)Ru′(I) reduction are evaluated by numeric simulation (Figs. 3 and 4). K_3 and k_{f3} influenced the A$_1$ peak and slightly modified the A′ peak height, K_4 and k_{f4} applying the essential part in this height. Lastly, the normal potential of the global system: Ti′(III)Ru(II)/Ti′(III)Ru(0), E_r = 1.57 V was calculated, assuming that this reaction is a bielectronic system including two successive monoelectronic steps, which is only an hypothesis (a disproportionation reaction could also be considered).

All the electrochemical and chemical constants of Scheme 1 were then determined, as described in Table 1.

It is interesting to note that the initial square scheme behaves like a simple Electrochemical–Chemical scheme and that the rate of the electron transfer between the titanium to the ruthenium is not so fast.

Conclusion

The unexpected electrochemical activity of the complex **2** was well-studied by cyclic voltammetry, controlled potential electrolysis and RDE. In fact, an intramolecular electron transfer between the two metallic atoms *via* a chloride atom transfer

Table 1 Electrochemical and chemical constants for the complex **2** in Scheme 1[a]

$E_i°$/V	k_{hi}/cm s^{-1}	α_i	K_i	k_f/s^{-1}
$E_1° = -0.38$	$k_{h1} = 0.01$	$\alpha_1 = 0.5$	$K_1 = 5.6 \times 10^{-10}$ mol L^{-1}	$k_{f1} = 10^{-4}$
$E_2° = -0.80$	$k_{h2} = 0.01$	$\alpha_2 = 0.5$	$K_2 = 6 \times 10^{-3}$ mol L^{-1}	$k_{f2} = 10^{+7}$
			$K_3 = 10^{-2}$	$k_{f3} = 10$
$E_4° = -0.76$	$k_{h4} = 0.01$	$\alpha_4 = 0.5$	$K_4 > 10^2$	$k_{f4} = 10^{-1}$
$E_r = -1.57$				

[a] k_{hi} = heterogeneous charge transfer rate constant; α_i = charge transfer coefficient; K_i = equilibrium constant, respectively equal to: $K_1 = k_{f1}/k_{b1}$ = [Ti′(IV)Ru(II)] × [Cl$^-$]/[Ti(IV)Ru(II)]; $K_2 = k_{f2}/k_{b2}$ = [Ti′(III)Ru(II)] × [Cl$^-$]/[Ti(III)Ru(II)]; $K_3 = k_{f3}/k_{b3}$ = [Ti(IV)Ru′(I)]/[Ti′(III)Ru(II)]; k_{bi} and k_{fi} = chemical reaction constants.

was revealed for this complex. The experimental results were verified by simulation and all the chemical and electrochemical constants were defined.

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