pearance of the $Si(CH_3)_3$ resonance of **3** required 13–14 h.

Rate of Reactions of $(CO)_5MnCH_3$ (2a) with 3 and $(C_6H_5)_3P$. A 5-mm NMR tube was charged with **2a** (0.040 g, 0.19 mmol), **3** (0.054 g, 0.21 mmol), and CH_2Cl_2 (0.35 mL). The tube (0.54 M in **2a**; 0.60 M in **3**) was capped with a septum, shaken, and left at 21 °C. The reaction was periodically monitored by ^1H NMR. The half-life of **2a** was ca. 2.2 h, as assayed by the disappearance of the $MnCH_3$ resonance.

A 5-mm NMR tube was charged with **2a** (0.039 g, 0.19 mmol), $(C_6H_5)_3P$ (0.054 g, 0.21 mmol), standard $(C_6H_5)_3SiCH_3$ (0.053 g, 0.19 mmol), and CH_2Cl_2 (0.35 mL). The tube (0.54 M in **2a**; 0.60 M in $(C_6H_5)_3P$) was capped with a septum and monitored as above. The half-life of **2a** was ca. 2.5 h.

A 5-mm NMR tube was charged with **2a** (0.022 g, 0.10 mmol) and 0.36 mL of a CH_2Cl_2 solution which was 0.96 M in $(C_6H_5)_3P$ (0.35 mmol), 0.96 M in **3** (0.35 mmol), and 0.046 M in $Cr(acac)_3$ (0.017 mmol). The reaction was monitored by ^{31}P NMR at ambient probe temperature by using a pulse delay of 20 s. Integration of the resonances due to $(C_6H_5)_3P$ and **3** in the starting solution (without **2a**) and after 20-, 40-, and 60-min reaction times indicated that **3** was consumed ca. 1.1 times faster than $(C_6H_5)_3P$.

Acknowledgment. We are grateful to the Department of Energy and the National Science Foundation for support of this research. FT NMR spectrometers utilized were provided by NSF departmental instrumentation grants, and K.A.K. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a Summer Research Fellowship.

Registry No. **2a**, 13601-24-6; **2b**, 29992-26-5; **2c**, 13985-77-8; **2d**, 88916-68-1; **3**, 17154-34-6; **4a**, 88932-93-8; **4b**, 88916-69-2; **4c**, 88916-70-5; **4d**, 88916-71-6; **6b**, 88916-72-7; **8**, 88916-73-8; **9**, 100790-19-0; C_6H_5COCl, 98-88-4; $K^+(CO)_5Mn^-$, 15693-51-3; $(C_6H_5)_2PCl$, 1079-66-9; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_3SiCH_2Li$, 1822-00-0; $(CH_3)_3SiCH_2Cl$, 2344-80-1; $(CO)_5MnBr$, 14516-54-2; $(CO)_5MnCOC_6H_5$, 15612-92-7; $(CO)_5MnH$, 16972-33-1; $(C_6H_5)_2PH$, 829-85-6; $(C_6H_5)_3P$, 603-35-0; 2-naphthoyl chloride, 2243-83-6.

Electrochemical Synthesis and Properties of $(\eta^5\text{-}C_5H_4R)_2TiSe_5$ (R = H, Me, *i*-Pr)

G. Tainturier, B. Gautheron, and C. Degrand*

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (U.A. 33), Faculté des Sciences, 6 bd Gabriel, 21100 Dijon, France

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Ultrasound-induced electrochemical reduction of gray Se powder in DMF or THF, followed by addition of $(\eta^5\text{-}C_5H_4R)_2TiCl_2$ (**1**, R = H, *i*-Pr), led to $(\eta^5\text{-}C_5H_4R)_2TiSe_5$ (**2**, R = H, *i*-Pr) in high current efficiencies in THF and low to moderate yields in DMF. Compounds **2** could be also prepared in moderate yields when **1** was reduced at a Pt cathode in THF, in the presence of an excess of Se (at least 5 equiv). Finally, **2** was obtained in low yields when **1** was chemically reduced to the dimeric form $(\eta^5\text{-}C_5H_4R)_2TiCl$ (**3**), gray Se powder being added after reduction. From the electrochemical results, it is suggested that a key step of the overall process leading to **2** is a one-electron reduction of complex **1**, followed by formation of complex **3**. In the first electrochemical method, an homogeneous electron transfer would occur between an electrochemically generated Se anionic species and complex **1**. The lower yields of **2** in DMF than in THF are in agreement with the better binding properties of DMF, compared to THF, as far as complex **3** is concerned. Complexes **2** were irreversibly reduced and worked as a soluble Se reservoir. The electrochemical synthesis of **2** (R = Me) was thus achieved in 70% yield.

Introduction

The pentaselenide complexes **2** (R = H, CH_3) are suitable substrates for Se atom transfer.[1-4] They are readily available materials from chemically prepared alkali polyselenides and the titanocene dichlorides **1** (R = H, CH_3) according to the overall reaction (1).[4-7]

$$\underset{\mathbf{1}}{(\eta^5\text{-}C_5H_4R)_2TiCl_2} + (M_2^{2+}, Se_5^{2-}) \rightarrow \underset{\mathbf{2}}{(\eta^5\text{-}C_5H_4R)_2TiSe_5} + 2MCl \quad (1)$$

Very recently,[8] we have observed that the ultrasound-induced electrochemical reduction of Se powder proceeds very easily in solvents such as *N,N*-dimethylformamide (DMF), CH_3CN, and tetrahydrofuran (THF) in which gray selenium is insoluble. Addition of an alkyl halide, RX, to the electrogenerated anions Se_2^{2-} and Se^{2-} leads to the corresponding dialkyl diselenide RSeSeR and dialkyl selenide RSeR in a double nucleophilic substitution reaction. However, in certain cases, the indirect reduction of RX by Se_2^{2-} or Se^{2-} occurs simultaneously.[9]

In the present report, we describe the electrochemical synthesis in DMF and THF of the pentaselenide complexes **2a,b** from electrochemically generated polyselenide anions and titanocene dichlorides **1a,b**. A second electrochemical method and its chemical equivalent are successfully proposed to perform the syntheses of complexes **2a,b**. The influence of the solvent on their yields is discussed. The electrochemical behavior of complexes **2a,b** is examined, and it is shown that these pentaselenide derivatives can serve as a soluble Se reservoir.

$(\eta^5\text{-}C_5H_4R)_2TiCl_2$	$(\eta^5\text{-}C_5H_4R)_2TiSe_5$
1a, R = H	**2a**, R = H
1b,R = *i*-Pr	**2b**, R = *i*-Pr
1c, R = *t*-Bu	**2c**, R = *t*-Bu
1d, R = CH_3	**2d**, R = CH_3

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Table I. Large-Scale Ultrasound-Induced Electrochemical Reduction of Se Followed by Addition of Titanocene Dichloride (1)[a]

entry	solv	Se/ mmol	charge consumed/C (mmol of electrons)	1 added (mmol)	2 isolated (mmol)	curr efficiency/%
1	THF	2.5	96.5 (1)	**1a** (0.5)	**2a** (0.32)	64
2	DMF	5	193 (2)	**1a** (1)	**2a** (0.16)	16
3	THF	5	193 (2)	**1b** (1)	**2b** (0.82)	82
4	DMF	5	193 (2)	**1b** (1)	**2b** (0.75)	75
5	THF	5	193 (2)	**1c** (1)		

[a] The cathode is a graphite cloth.

Table II. Half-Wave Potential, $E_{1/2}$, of the First Reduction Wave of the Complexes 1a–c (1 mM)

1	electrode[a]	solv	$-E_{1/2}$/V
1a	C	THF	0.68
	Pt	THF	0.80[b]
	C	DMF	0.63
	Pt	DMF	0.63[b]
1b	C	THF	0.79
1c	C	THF	0.72

[a] RDE. [b] From ref 11.

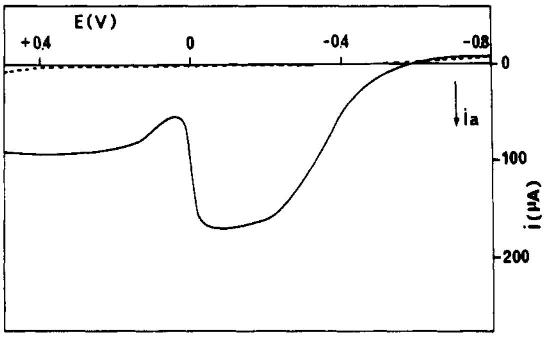

Figure 1. Voltammogram at a glassy carbon RDE obtained in situ after the large-scale electrochemical reduction of Se powder (2.5 mmol) in DMF, on a graphite cloth. Sonication was maintained during electrolysis, and 0.5 mmol of electrons was consumed.

Results

1. Ultrasound-Induced Electrochemical Reduction of Se Powder. The ultrasonic electrochemical reduction of Se powder was performed in a H-type cell whose compartments were carefully protected against air by an inert atmosphere of argon. The cathode was either a graphite tissue of cylindric shape or a Pt grid cylinder. The electrochemical reduction of Se powder was slightly easier on a graphite cloth where it occurred below −0.65 ± 0.05 V than on a Pt grid where it started at −0.9 V. To maintain a reasonable faradic current, the working potential had to be progressively shifted to more negative values. As the electrolysis proceeded, the cathodic as well as the central compartment of the cell turned brown, indicating a slow migration of the electrogenerated anionic Se species toward the anodic compartment of the cell. Voltammograms obtained in situ in DMF at a rotating carbon disk electrode (RDE) show that the electrochemically generated selenide anions present an anionic wave which is distorted by a maximum (Figure 1).

2. Electrochemical Synthesis of the Pentaselenide Complexes 2a,b. The electrochemical synthesis of the complexes **2a,b** was achieved by two methods. In the first, the purple complexes **2a** and **2b** were prepared by electrochemical reduction of Se as described above, followed by addition of the corresponding titanocene dichloride **1a** and **1b**. The electrolyses performed according to this procedure correspond to the overall process (2).

$$Se_5^{2-} + \underset{\textbf{1a,b}}{(\eta^5\text{-}C_5H_4R)_2TiCl_2} \rightarrow \underset{\textbf{2a,b}}{(\eta^5\text{-}C_5H_4R)_2TiSe_5} + 2Cl^- \qquad (2)$$

In a typical experiment, gray selenium powder (5 mmol) was reduced with sonication on a graphite cloth. The potential was shifted from −0.55 to −0.80 V. After consumption of 193 C (2 mmol of electrons), 1 mmol of titanocene dichloride (**1a**) was added and sonication was maintained five more minutes. The catholyte was then diluted with water, and the electrolysis products were extracted with diethyl ether. A series of electrolyses is summarized in Table I (entries 1–4) which shows, on the one hand, that **2b** is isolated in higher yields than **2a** and, on the other, that better yields of **2** were obtained in THF than in DMF. This influence of the solvent is particularly noticeable in the case of **2a**. Attempts to electrochemically synthesize the pentaselenide complex **2c** failed (Table I, entry 5). When the substituted complex **1c** was added, it was completely consumed but no pentaselenide complex was isolated.

Another set of electrolyses has allowed the synthesis of **2a,b** according to a different method. In this series, the complexes **1a** and **1b** were reduced at a Pt electrode in the presence of Se powder, *at potentials not too negative to avoid the direct reduction of Se* which occurs, as already mentioned, below −0.9 V on Pt. The reduction potentials of **1a,b** are slightly less negative and are given in Table II. Moderate yields of **2a** and **2b** were thus obtained in THF and low yields of **2a** in DMF (Table III). Sonication of the cell did improve these results (compare entries 2 and 3 and entries 4 and 5 in Table III). The equivalent chemical method was tested, and it led to **2a** and **2b** in low yields. In this method, the dimeric forms **4a,b** of the Ti(III) complexes **3a,b** were prepared by chemical reduction of **1a,b** and then allowed to react in THF with Se powder in excess. In the case of **4a**, ^1H NMR analysis of the resulting mixture clearly indicated the formation of

Table III. Large-Scale Electrochemical Reduction of 1 on a Pt Grid in the Presence of Se in Excess

entry	solv	1 (mmol)	stirring	$-E$/V	charge consumed/C (mmol of electrons)	Se/ mmol	2 (mmol)	curr efficiency[a]/%
1	THF	**1a** (1)	sonic.	0.48–0.62	96.5 (1.00)	5	**2a** (0.125)	25
2	DMF	**1a** (2)	sonic.	0.52–0.70	320 (3.32)	10	**2a** (0.10)	6
3	DMF	**1a** (2)	mech	0.52–0.70	276 (2.86)	10	**2a** (0.04)	3
4	THF	**1b** (1)	sonic.	0.54–0.70	216 (2.24)	10	**2b** (0.455)	41
5	THF	**1b** (1)	mech[b]	0.61–0.80	168 (1.74)	6	**2b** (0.215)	25

[a] On the basis of 2e consumed. [b] 15 min of sonication after electrolysis.

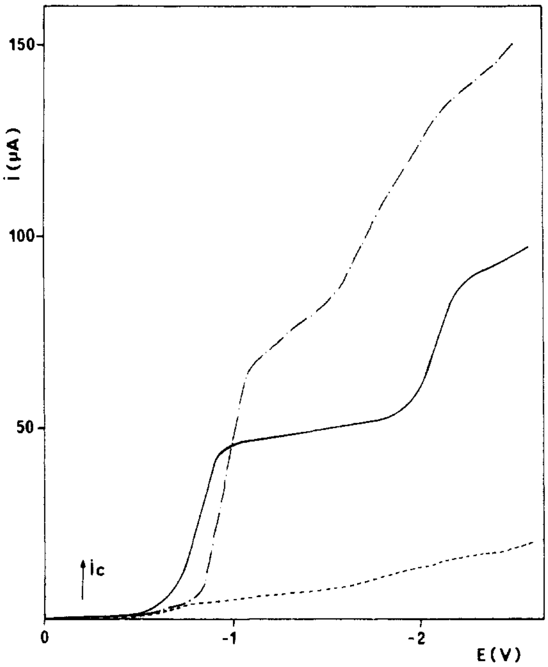

Figure 2. Voltammograms in THF at a glassy carbon RDE of **1b** (—) and **2b** (-·). The concentration of **1b** and **2b** was 10^{-3} M. The dotted line corresponds to the background cathodic current.

Table IV. Peak Potential, E_p, of the First Reduction Peak of the Complexes 2a,b[a]

		$-E_p$/V		
2	solv	C	Pt	Hg
2a	DMF	0.88	0.92	0.94
2b	THF	1.10	0.99	0.98
	DMF	0.97	0.98	1.00

[a] The scan rate is 200 mV s^{-1}.

2a and **1a**. The former complex was isolated in low yield (6% after purification by column chromatography). In the case of **4b**, the purple complex **2a** was isolated in 18% yield together with a large amount of **1b**.

$$2(\eta^5\text{-}C_5H_4R)_2\dot{T}iCl \rightleftharpoons [(\eta^5\text{-}C_5H_4R)_2TiCl]_2 \quad (3)$$
$$\mathbf{3a},\ R = H \qquad \mathbf{4a},\ R = H$$
$$\mathbf{3b},\ R = i\text{-}Pr \qquad \mathbf{4b},\ R = i\text{-}Pr$$

3. Electrochemical Reduction of Complexes 2a,b. The electrochemical reduction of **2a,b** was observed to occur in two stages (Figure 2 and Table IV). A comparison of the first wave of **2a,b** with the first wave of the corresponding complexes **1a,b** (Figure 2) shows, on the one hand, that the reduction of **2a,b** takes place at potentials slightly more negative than in the case of **1a,c** (compare also the results contained in Tables II and IV) and, on the other hand, that the limiting current of **2a,b** is about twice higher than for **1a,b**. The first stage is therefore a two-electron process. In cyclic voltammetry, an anodic peak B is associated to the first reduction peak A (Figure 3). On successive scannings, a cathodic peak B′ appears which precedes A.

The large scale electrochemical reduction of **2b** at a potential corresponding to its first reduction wave confirms that two electrons are involved in the electrochemical process. Addition of **1d** after electrolysis provided **2d** in good yields, up to 70% current efficiency (Table V). The current efficiency was slightly increased by sonication of the cell after addition of **1d**. Similarly, the electrochemical reduction of **2b** (0.2 mmol) in the presence of a large excess of benzyl chloride, which is more difficultly reduced, consumed 1.46 mmol of electrons and led to a mixture of dibenzyl diselenide (0.325 mmol) and dibenzyl selenide (0.13 mmol) in 65% and 13% yields, respectively. Dibenzyl selenide could arise from a further electrochemical reduction of dibenzyl diselenide, as previously observed.[9]

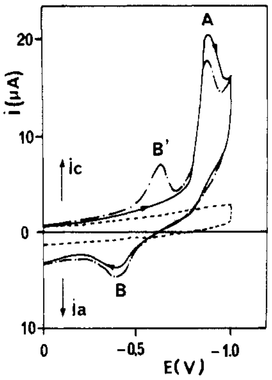

Figure 3. Cyclic voltammogram of **2a** (10^{-3} M) at a stationary glassy carbon electrode in DMF: first scan (—) and second scan (-·). The scan rate is 71 mV s^{-1}. The dotted line corresponds to the background cathodic current.

Discussion

In DMF, it has been shown that polyselenide anions Se_x^{2-} are obtained when a sacrificial Se electrode is cathodically polarized.[10] However, only dialkyl or diaryl diselenides are isolated if an alkyl or aryl halide is present.[10] Similarly, we have observed that a dialkyl diselenide is isolated in almost quantitative current efficiency when Se (5 mmol) is partially reduced (2 mmol of electrons consumed) and then allowed to react with an alkyl halide (2 mmol).[8] Thus, the reaction of alkylating agents with electrochemically generated Se_x^{2-} anions leads exclusively to diselenide derivatives. It is consistent with a disproportionation of Se_x^{2-} to Se_2^{2-} and (x - 2)Se.

The reaction of the titanocene dichlorides **1a** and **1b** with Se_x^{2-} leads to the complexes **2a** and **2b** which have a selected $TiSe_5$ ring size (Table I, entries 1–4). Attempts to electrochemically synthesize the pentaselenide complex **2c** fails although **1c** is completely consumed when it is added to Se_x^{2-} (Table I, entry 5). This result, together with the well-known electrochemical properties of titanocene dichloride (**1a**) which has been shown[11] to be easily reduced in three monoelectronic stages, suggests that, in the overall process (2), an homogeneous electron transfer occurs between Se_x^{2-} and complexes **1a–c**. Since the anionic Se species are easily oxidized (Figure 1) and since the first electron uptake of **1a**,[11] **1b**, and **1c**[12] starts at potentials close to −0.7 V (Table II), such a transfer can be reasonably proposed. *For the sake of simplicity, we will consider only the Se_5^{2-} species in the following discussion.* This choice is purely speculative but it is not disproved by the experimental results. We propose that the homogeneous electron exchange (eq 4) is followed by a rapid loss of Cl^-[11,13,14] (eq 5). The following equations represent assumptions, which account for the results summarized in Table I. In reaction 6, a coupling reaction between the Ti(III) complex **3** and the uncharged extremity of a Se_5^-

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Table V. Large-Scale Electrochemical Reduction[a] of 2b Followed by Addition of 1d

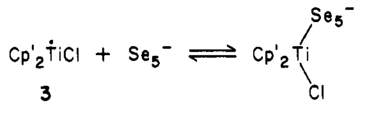
entry	2b/ mmol	$-E$/V	charge consumed/C (mmol of electrons)	n^b	1d/ mmol	2d mmol[c]	2d curr efficiency[d]/%
1	0.30	1.00–1.10	52 (0.54)	1.80	0.30	0.163	60
2	0.29	0.80–0.84	28 (0.29)	1.00	0.29[e]	0.084[f]	58
3	0.30	0.90–1.10	46.5 (0.48)	1.60	0.24[g]	0.166	70

[a] Mechanical stirring, Pt cathode, THF. [b] Number of electrons consumed by **2b** unit. [c] After purification. [d] On the basis of 2e consumed. [e] 2-min sonication. [f] Together with unreacted **2b** and **1d**. [g] 10-min sonication.

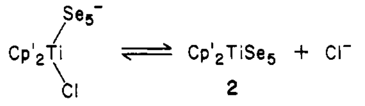
chain, is postulated. Reaction 7 summarizes a possible final step leading from **5** to the purple complex **2** which can result from an intramolecular nucleophilic substitution or electron transfer, with loss of Cl^-. In the case of **1c**, the successive electron transfer (eq 4) and loss of Cl^- (eq 5) would occur, since the initial complex is consumed. However, the substitution on the Cp rings by bulky *t*-Bu groups would prevent the formation of the selected $TiSe_5$ ring (eq 7).

$$\underset{\mathbf{1}}{Cp'_2TiCl_2} + Se_5^{2-} \rightleftharpoons (Cp'_2TiCl_2)^{-\bullet} + Se_5^- \qquad (4)$$

$$(Cp'_2TiCl_2)^{-\bullet} \rightleftharpoons \underset{\mathbf{3}}{Cp'_2\dot{T}iCl} + Cl^- \qquad (5)$$



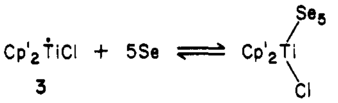
$$\underset{\mathbf{3}}{Cp'_2\dot{T}iCl} + Se_5^- \rightleftharpoons \underset{\mathbf{5}}{Cp'_2Ti(Se_5^-)(Cl)} \qquad (6)$$



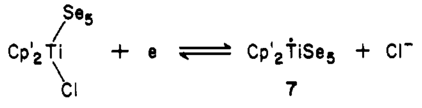
$$\underset{\mathbf{5}}{Cp'_2Ti(Se_5^-)(Cl)} \rightleftharpoons \underset{\mathbf{2}}{Cp'_2TiSe_5} + Cl^- \qquad (7)$$

$Cp' = \eta^5\text{-}C_5H_4R$

The results of Table III, which summarize the electroreduction of **1a,b** in the presence of Se, are also in agreement with the initial formation of an unstable radical anion which might further evolve according to reactions 5 and 8–10 which again postulate the intermediate formation of a Ti(III) complex, **3**. The complex **2a** was observed to be moderately stable in DMF with sonication. It decomposed slowly, giving gray Se powder. This relative instability might decrease slightly the current efficiency of **2a** in entry 2 of Table III.



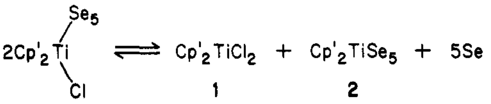
$$\underset{\mathbf{3}}{Cp'_2\dot{T}iCl} + 5Se \rightleftharpoons \underset{\mathbf{6}}{Cp'_2Ti(Se_5)(Cl)} \qquad (8)$$



$$\underset{\mathbf{6}}{Cp'_2Ti(Se_5)(Cl)} + e \rightleftharpoons \underset{\mathbf{7}}{Cp'_2\dot{T}iSe_5} + Cl^- \qquad (9)$$

$$\underset{\mathbf{7}}{Cp'_2\dot{T}iSe_5} \rightleftharpoons \underset{\mathbf{2}}{Cp'_2TiSe_5} \qquad (10)$$

The developed chemical method looks rather uninviting since low yields of **2a,b** were obtained. These yields will be optimized in a further study. However, the interest of this method is to point out that a key step of the overall process would be the intermediate formation of complex **3** which is in equilibrium with its dimeric form (eq 3). To account for the presence of **1a,b** in the reaction mixture, it is suggested that **3** further reacts with elementary Se (eq 8) and that the formation of **6** would be followed by a disproportionation reaction (eq 11) which would regenerate **1** together with **2**.



$$2\underset{\mathbf{6}}{Cp'_2Ti(Se_5)(Cl)} \rightleftharpoons \underset{\mathbf{1}}{Cp'_2TiCl_2} + \underset{\mathbf{2}}{Cp'_2TiSe_5} + 5Se \qquad (11)$$

If we bring together eq 3, 8, and 11, the formation of **2** would result from the overall process (12).

$$\underset{\mathbf{4}}{(Cp'_2TiCl)_2} + 5Se \rightleftharpoons \underset{\mathbf{2}}{Cp'_2TiSe_5} + \underset{\mathbf{1}}{Cp'_2TiCl_2} \qquad (12)$$

Our results present some analogy with the results obtained when dialkyltitanocene compounds Cp_2TiR_2 are photolyzed in benzene in the presence of elemental sulfur.[15] The dark red complex Cp_2TiS_5[5,6,16] was isolated in 70% yield. Under such conditions, a photolytic cleavage of the Ti–R bond has been shown to occur[17] so that the Ti(III) complex $Cp_2\dot{T}iCH_3$ was initially generated, which probably reacted with sulfur. Furthermore, we have observed[18] that addition of sulfur to the dimeric form **4a** of the complex **3a** leads to Cp_2TiS_5.[5,6,16] As a whole, those results suggest that many chemical or electrochemical processes leading to the pentachalcogenide derivatives Cp'_2TiE_5 (E = S, Se), involve the intermediate formation of a Ti(III) complex which further reacts with neutral chalcogen units.

In the two electrochemical methods described above to prepare **2a,b**, the use of DMF as solvent decreases the yields of the complexes (Tables I and III). For reasons unknown to date, this solvent effect is particularly noticeable in the case of **2a** (compare entries 1 and 2 in Table I). This is in agreement with the fact that DMF has been shown[11,14] to bind more strongly to the Ti(III) complex **3** than does THF (eq 13).

$$\underset{\mathbf{3}}{Cp'_2\dot{T}iCl} + L \rightleftharpoons Cp'_2TiClL \qquad (13)$$

L = DMF or THF

We suggest that as soon as **3** is released in reaction 5, the Se units compete with molecules of solvents to bind **3**. If we consider reactions 6 and 8, they are therefore prevented more in DMF than in THF. Furthermore, if we consider the first electrochemical method (Table I) and the corresponding steps 4–6, they take place most probably in a solvent cage. The close proximity of **3** and Se_5^- (eq 6) facilitates the formation of **5**. Higher yields of complexes **2a,b** can thus be expected in Table I than in Table III where **1** is reduced at the cathode. In this case, **3** is released into the bulk of the catholyte where the coupling

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reaction (8) with Se powder occurs. Sonication does facilitate this heterogeneous reaction (compare, for instance, entries 4 and 5 of Table III).

Compounds **2a,b** are electrochemically active, their first reduction stage corresponding to a two-electron process. Cleavage of the Se chain occurs since the anionic Se chain thus generated can be utilized to prepare the new pentaselenide complexes **2** and dialkyl diselenides. In Figure 3, the anodic peak B would correspond to the oxidation of the anionic Se chain to elementary Se. The Se units thus generated would accumulate on the electrode surface before being reduced at potentials of peak B′, during the second cathodic scan.

Experimental Section

Gray selenium powder and benzyl chloride were purchased from Fluka, and titanocene dichloride (**1a**) was purchased from Strem Chemicals. The synthesis of the 1,1′-disubstituted titanocene dichlorides **1b–d** has been reported.[19–21] Dimeric dicyclopentadienyltitanium chloride (**4a**) was prepared according to the known procedure.[22] The same procedure was applied to prepare **4b**. Analytical grade DMF was carefully dried on neutral alumina; THF was distilled from sodium benzophenone ketyl before use. Tetrabutylammonium hexafluorophosphate (Fluka) was recrystallized from ethanol. All manipulations were performed under an argon atmosphere.

Elemental analyses were performed by Service Central d'Analyses, C.N.R.S., Lyon. Spectra were recorded by means of the following instruments: infrared, Perkin-Elmer 580B; ^{1}H NMR, JEOL FX 100; mass spectra, Finnigan 3002; *m/e* values given correspond to most abundant isotope.

Cyclic voltammograms at a stationary or rotating disk electrode and at a hanging mercury drop electrode[23] were obtained with a Tacussel UAP 4 unit and a GSTP function generator and were recorded on an Ifelec 2025 C X-Y recorder. An Amel 552 potentiostat and a Tacussel IG 5-N integrator were used in coulometry and preparative electrolysis. All the potentials referred to the aqueous saturated calomel electrode (SCE).

Electrochemical Reduction of Se Powder. The ultrasound-induced electrochemical reduction of Se powder is performed in a H-type cell, the three compartments of which are separated by a fritted glass and filled with DMF or THF containing 0.1 M Bu_4NBF_4 or Bu_4NPF_6 (0.2 M in the case of THF). The cathode is a graphite cloth of cylindric shape or a Pt grid and the anode a Pt grid. The catholyte was deaerated with argon prior to the introduction of Se; its volume was 60 mL. An inert atmosphere of argon is then carefully maintained. Ultrasonication (vat Bransonic B32) and cooling by an ice bath of the cell are maintained during the electrolysis.

Electrochemical Synthesis of 2a,b,d. A few typical electrolyses are described below.

Electrochemical Synthesis of 2a (Entry 1 of Table I). Se (197.5 mg, 2.5 mmol) was reduced with ultrasound at a graphite cloth, the potentials being shifted from −0.55 to −0.80 V. The electrolysis was stopped after consumption of 96.5 C (10^{-3} mol of electrons). Complex **1a** (123.5 mg, 0.5 mmol) was then added and sonication maintained 5 more minutes. The catholyte was diluted with water (600 mL), and the electrolysis products were extracted with diethyl ether (3 × 200 mL). After the purple solution was dried with $MgSO_4$, the organic solvents were removed. The crude product (193 mg) was washed with a mixture of acetone/hexane (1/9) in which **2a** is almost insoluble whereas all the side products are not. The dark purple solid residue was dried, weighed (183 mg, 0.32 mmol), then recrystallized from CH_2Cl_2/hexane; decomp pt 210–212 °C. Its ^{1}H NMR in $CDCl_3$ and IR were identical with those given for **2a** in ref 5 and 6, respectively. Mass spectrum: *m/e* 578 (M^+), 480 (Se_6^+), 418 $(M - 2Se)^+$, 400 (Se_5^+), 353 $(M - 2Se - Cp)^+$, 338 $(M - 3Se)^+$, 258 $(M - 4Se)^+$, 193 $(M - 4Se - Cp)^+$, 178 $(M - 5Se)^+$.

Electrochemical Synthesis of 2b (Entry 4 of Table II). Compound **1b** (335 mg, 1 mmol) was reduced in THF with ultrasound in the presence of Se in excess (790 mg, 10 mmol). The potential was shifted from −0.54 to −0.70 V, and the electrolysis was stopped after consumption of 216 C (2.24 mmol of electrons). The catholyte was treated as above. The dark purple residue **2b** (299 mg, 0.46 mmol) was recrystallized from diethyl ether/hexane: mp 145 °C; proton NMR (C_6D_6) δ 5.84 (t, 2 H), 5.59 (s, 4 H), 5.45 (t, 2 H), 2.97 (hp, 1 H), 2.58 (hp, 1 H), 1.02 (d, 6 H, ^3J = 6.8 Hz), 0.83 (d, 6 H, ^3J = 6.8 Hz); mass spectrum, *m/e* 662 (M^+), 555 $(M - Cp')^+$, 502 $(M - 2Se)^+$, 480 (Se_6^+), 422 $(M - 3Se)^+$, 400 (Se_5^+), 395 $(M - 2Se - Cp')^+$, 342 $(M - 4Se)^+$, 315 $(M - 3Se - Cp')^+$, 262 $(M - 5Se)^+$. Anal. Calcd for $C_{16}H_{22}Se_5Ti$: C, 29.25; H, 3.37; Se, 60.09; Ti, 7.21. Found: C, 29.38; H, 3.40; Se, 60.07; Ti, 7.40.

Electrochemical Synthesis of 2d (Entry 1 of Table V). Compound **2b** (197 mg, 0.3 mmol) was reduced in THF on Pt with mechanical stirring at −1.1 V. After depletion of the faradic current and consumption of 52 C (0.54 mmol of electrons), compound **1d** (83 mg, 0.3 mmol) was added. After being left standing for 20 min, the catholyte was treated as above. The dark purple residue (0.163 mmol) was identical with an authentic sample of **2d**;[4] mass spectrum, *m/e* 606 (M^+), 480 (Se_6^+), 446 $(M - Se)^+$, 400 (Se_5^+), 367 $(M - 2Se - Cp)^+$, 366 $(M - 3Se)^+$, 287 $(M - 3Se - Cp)^+$, 286 $(M - 4Se)^+$, 206 $(M - 5Se)^+$.

Chemical Synthesis of 2a. In a representative procedure, 395 mg (5.00 mmol) of Se powder was added to a stirred solution of $(Cp_2TiCl)_2$[22] (215 mg, 0.5 mmol) in 20 mL of THF. The mixture became red-brown after a few minutes. The stirring was maintained for four more hours, and the solution obtained after filtration of the selenium in excess was concentrated and chromatographed (flash chromatography, silica gel Merck 60, toluene). Two zones were eluted: a violet zone which contained the literature compound **2a**[5,6] (18 mg, 6.2% yield) and a red zone leading to Cp_2TiCl_2 (**1a**).

Chemical Synthesis of 2b. In order to prepare **4b**, compound **1b** (0.41 g, 1.22 mmol) was reduced in THF by a 10-fold excess of amalgamated aluminum foil according to the procedure described in ref 22. Without further purification, the very air-sensitive green-brown crude product was allowed to react with gray Se powder (0.57 g, 7.2 mmol) in THF at room temperature for 4 days. After removal of the solvent, chromatography of the residue using the same technique as for **2a** afforded **2b** (0.07 g, 0.11 mmol) and **1b** (0.12 g, 0.36 mmol). On the basis of the overall reaction (12), **2b** and **1b** were obtained in 18% and 59%, yields, respectively.

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Registry No. **1a**, 1271-19-8; **1b**, 12130-65-3; **1c**, 79269-71-9; **1d**, 1282-40-2; **2a**, 12307-22-1; **2b**, 97732-75-7; **2d**, 78614-88-7; $(Cp_2TiCl)_2$, 1271-18-7.

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