

ansa-METALLOCENE DERIVATIVES

IX *. ELECTROCHEMICAL REACTIONS OF TETRAMETHYLETHYLENE-BRIDGED TITANOCENE DICHLORIDE AND DICARBONYL DERIVATIVES

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Summary

In the reduction of tetramethylethylene-bridged $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ under argon, studied by cyclic voltammetry, a first reduction to the Ti^{III} stage occurs at a potential of -0.92 V vs. SCE, close to that of $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$, and a second reduction to the Ti^{II} stage at a potential of -2.53 V, about 0.3 V more negative than in the corresponding reduction of the unbridged analogue. Decay of the tetramethylethylene-bridged Ti^{II} product is considerably faster than that of its unbridged analogue. Changes induced by the presence of an N_2 or H_2 atmosphere indicate the occurrence of secondary reactions.

In the presence of CO, reduction to $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Ti}(\text{CO})_2$ occurs at -2.0 V. This tetramethylethylene-bridged titanocene dicarbonyl complex, which is also formed by reduction of $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ with Mg metal under CO, undergoes irreversible reduction and oxidation at -2.78 and -0.08 V, respectively. When the latter process is conducted in the presence of Cl^- , the dichloride $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ is regenerated.

Introduction

Redox properties of titanocene dichloride (Cp_2TiCl_2) have been studied fairly thoroughly by cyclic voltammetry as well as by other electrochemical methods [2–17]. In order to clarify some previously observed reactivity differences between bridged and unbridged titanocene derivatives [18] we have undertaken a cyclic voltammetry study of the redox reactions of a tetramethylethylene-bridged titano-

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cene derivative, $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ ($\text{tmen}(\text{Cp})_2\text{TiCl}_2$), as well as of its conversion into and its formation from the dicarbonyl complex $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Ti}(\text{CO})_2$.

Experimental

1. *Preparation of $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{TiCl}_2$.* The procedure described in ref. 19 was modified to avoid a green discoloration which was otherwise occasionally observed: The crude product obtained after evaporation of tetrahydrofuran (THF) from the initial reaction mixture was taken up in CH_2Cl_2 , and to this solution about 1/4 to 1/3 of its volume of 6 M aqueous HCl was added. After complete conversion to the red Ti^{IV} stage, subsequent separation and drying with Na_2SO_4 , the organic layer was concentrated to a small volume, to give crystalline *ansa*-titanocene dichloride, as described in ref. 19.

2. *Preparation of $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Ti}(\text{CO})_2$.* All operations were performed with strict exclusion of air and humidity in Schlenk and vacuum line equipment. In a 500 ml flask ca. 60 ml of air-free, anhydrous THF was condensed on to 2.0 g (6.0 mmol) $\text{tmen}(\text{Cp})_2\text{TiCl}_2$, 500 mg (ca. 20 mmol) of Mg turnings and a small amount of HgCl_2 in vacuo. An atmosphere of CO was introduced and the reaction mixture allowed to warm to room temperature, at which it was stirred for one day. After removal of the solvent, ca. 60 ml pentane were introduced and the resulting red-brown slurry stirred at room temperature. After filtration and evaporation of the filtrate to about one third of its volume, crystallization was induced by cooling to -80°C . The crystalline solid was freed under Ar from the red-brown supernatant liquid by decantation, and then dried in vacuo at room temperature. In this manner, 1.2 g (3.83 mmol, ca. 65%) of $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2$ was obtained as dark brown crystals. ^1H NMR (in C_6D_6 , δ in ppm relative to δ 7.15 for $\text{C}_6\text{D}_5\text{H}$) 4.67 (t, 4 H), 5.00 (t, 4 H), 0.80 (s, 12 H). IR: $\nu(\text{CO})$ 1965, 1888 cm^{-1} (in pentane).

The dicarbonyl compounds can be sublimed in vacuo at ca. 60°C . The solid material is immediately decomposed upon contact with air, but can be stored without noticeable decomposition under N_2 or Ar. Transfer to the electrolysis cell was accomplished in a sealed ampoule, which was broken inside the cell under an atmosphere of Ar.

3. *Cyclic voltammetry.* To provide air- and water-free conditions, all measurements were performed in an electrochemical cell with an internal drying column [20] containing 10 g Al_2O_3 (Woelm basic, super I), through which the electrolyte, a ca. 0.1 M solution of tetra-*n*-butylammonium hexafluorophosphate ($\text{TBA}^+ \text{PF}_6^-$, Fluka, crystallized from ethanol) in deaerated anhydrous THF was passed repeatedly. Samples of $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ or $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2$ were then introduced into the cell and dissolved under Ar to give a concentration of 10^{-3} M. Unless otherwise noted, measurements were performed at 5°C with a combined Pt auxiliary and working electrode (1 mm diameter) [20], an Amel 553 potentiostat, and a programmable potentiostatic function generator, which will be described in detail in a forthcoming publication. Potentials were measured (without IR compensation) versus an $\text{Ag}/\text{AgNO}_3(\text{sat})/0.1$ M $\text{TBA}^+ \text{PF}_6^-/\text{THF}$ (25°C) reference electrode [20] and referred to SCE by adding 0.599 V. For comparison analogous measurements were conducted with solutions of Cp_2TiCl_2 . Measurements at -48°C were conducted, under otherwise identical conditions, with THF solutions of the more soluble tetra-*n*-butyl ammonium perchlorate ($\text{TBA}^+ \text{ClO}_4^-$, 0.1 M) as supporting electrolyte.

Results and discussion

1. *Reduction of tmen(Cp)₂TiCl₂ under Ar.* As previously observed with Cp₂TiCl₂ [8,11–16] two prominent electrochemical processes are apparent, at potentials of about -1 V and -2.5 to -3 V, in cyclic-sweep voltammogrammes of tmen(Cp)₂TiCl₂ in THF solution under argon (Fig. 1). Reduction peak *A* at $E_p(A) - 0.92$ V, which can be assigned to the first electron uptake by tmen(Cp)₂TiCl₂, shows several characteristic analogies to that of Cp₂TiCl₂, observed by Laviron and collaborators [11–13]. A peak separation of $\Delta E_p(A' - A) 0.11$ V at 50 mV/s (0.19 V at 500 mV/s), a decrease in the peak current ratio $i(A')/i(A)$ with increasing sweep rate (0.98 at 50 mV/s, 0.90 at 500 mV/s), the concomitant rise of a second oxidation peak A'_1 at $E_p(A'_1) - 0.24$ V, particularly at lower temperatures, and the complete suppression of this additional oxidation peak A'_1 in the presence of added Cl⁻ (ca. 0.02 M TBA⁺ Cl⁻), are all in accord with the notion [11–13], that the dichloro anion initially formed at *A* rapidly and reversibly dissociates to a neutral, solvated monochloride tmen(Cp)₂TiCl(THF)*. Oxidation of this species occurs either after uptake of Cl⁻ (i.e. regeneration of the dichloro anion), at peak *A'* or, as such, at peak A'_1 . The latter process would generate, instead of tmen(Cp)₂TiCl₂, the solvated cation tmen(Cp)₂TiCl(THF)⁺. A small reduction peak A_1 at $E_p(A_1) - 0.30$ V is assignable to the reduction of this cation, since this peak, 0.6 V more positive than *A*, is observed only when a fast reduction backsweep follows the oxidation process at peak A'_1 . These observations are qualitatively reproduced by a digital simulation (implicit Crank–Nicolson method [21,22]), assuming a quasi-reversible electron transfer and a kinetically controlled ligand exchange involving tmen(Cp)₂TiCl₂⁻ and tmen(Cp)₂TiCl(THF).

The reduction process at peak B **, which can be assigned to a second one-electron reduction, tmen(Cp)₂TiCl(THF) + e⁻ → tmen(Cp)₂TiCl(THF)⁻, differs from the analogous process with Cp₂TiCl₂ in some respects, the most obvious being a more negative peak potential (-2.53 V at 200 mV/s): The potential difference $\Delta E_p(A - B)$ (1.56 V at 50 mV/s, 1.65 V at 500 mV/s) for the two reduction steps of tmen(Cp)₂TiCl₂ is larger by 0.29 to 0.33 V than the corresponding potential difference for the two reduction steps of Cp₂TiCl₂, for which we have obtained values of 1.27 V and 1.32 V, at 50 and 500 mV/s, respectively. A similar, albeit much smaller increase in $\Delta E_p(A - B)$, by 0.05 V, was observed by Vlcek and collaborators [17] in their polarographic studies on the reduction of ethylene-bridged titanocene dichloride, H₄C₂(C₅H₄)₂TiCl₂, (en(Cp)₂TiCl₂) [18].

A second difference between the reduction of tmen(Cp)₂TiCl₂ and that of Cp₂TiCl₂ concerns the reoxidation of the reduced species generated at *B*. For doubly-reduced Cp₂TiCl₂, the reoxidation peak *B'* is quite pronounced. While a peak current ratio $i(B')/i(B)$ of less than unity and a peak separation $\Delta E_p(B' - B)$ of 0.23 V (200 mV/s) indicate a decay of the Cp₂Ti^{II} species formed at *B*, the species oxidized at *B'* appears to be relatively stable. In contrast, no reoxidation

* A dimer [tmen(Cp)₂TiCl]₂ may actually be present either as the predominant or as a minor Ti^{III} species in equilibrium with the solvated monochloride tmen(Cp)₂TiCl(THF). This possibility should be borne in mind throughout the subsequent discussion.

** Peak B is relatively flat, and its peak potential is shifted to more negative values at higher sweep rates.

tmen(cp)₂TiCl₂ under Ar

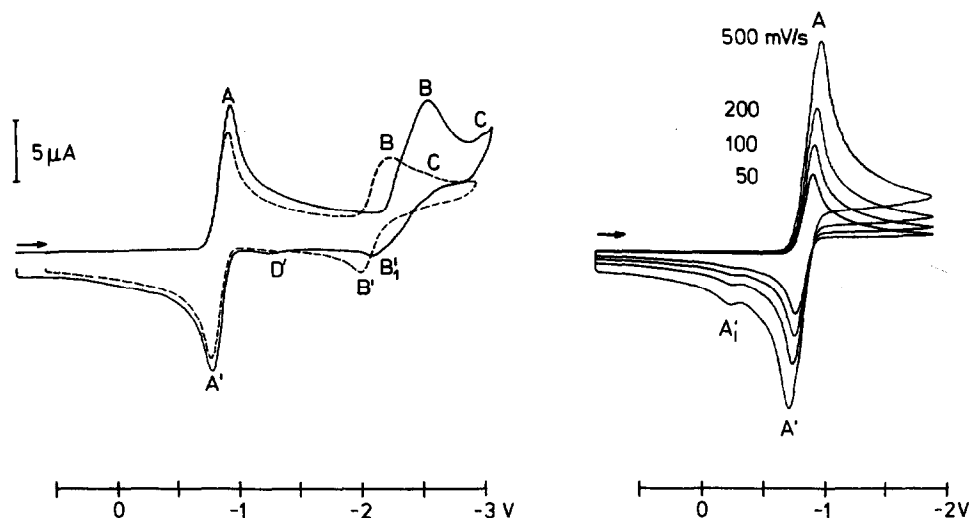


Fig. 1. Cyclic voltammograms of tmen(Cp)₂TiCl₂ in THF with 0.1 M TBA⁺ PF₆⁻ under Ar at 5°C, at a sweep rate of 500 mV/s (left, solid line; for comparison (broken line) cyclic voltammogramme of Cp₂TiCl₂, obtained, at 200 mV/s, under otherwise identical conditions) and at sweep rates of 500, 200, 100 and 50 mV/s (right). All voltammogrammes start with a reductive sweep.

peak is apparent, at 5°C, for doubly-reduced tmen(Cp)₂TiCl₂ anywhere between -2.5 and -1 V at sweep rates below 200 mV/s. At higher sweep rates, a weak indication of an oxidation peak B₁' appears at a potential of E_p(B₁') - 2.04 V. The anodic potential shift of peak B₁' relative to peak B, ΔE_p(B₁' - B) 0.48 V (200 mV/s), would be in accord with the notion that the species oxidized at B₁' is the neutral complex tmen(Cp)₂Ti(THF), arising from the chloro anion tmen(Cp)₂TiCl(THF)⁻ formed at B by rapid loss of chloride ion. In cyclic voltammogrammes at -48°C, at higher scan rates, instead of oxidation peak B₁', oxidation is observed at a more cathodic peak B' with a potential closer to that of peak B (ΔE_p(B' - B) 0.31 V).

The fact that oxidation either at peak B' or at B₁' is observable only at high sweep rates indicates that Ti^{II} species such as tmen(Cp)₂TiCl(THF)⁻ and tmen(Cp)₂Ti(THF) undergo a rather rapid decay, probably by cleavage of the coordinated THF molecule, or by comproportionation with tmen(Cp)₂Ti(IV)Cl₂*. The decreased lifetime of the ethylene-bridged Ti^{II} species can reasonably be related to the considerably more negative potential at which this ring-bridged Ti^{II} species is formed.

2. Reduction of tmen(Cp)₂TiCl₂ under N₂ or H₂. Voltammogrammes obtained under N₂ or H₂ differ from those obtained under Ar only in the region below -2.5

* A much smaller reduction peak C, observed at 5°C (but not at -48°C) in addition to peak B in the reduction of tmen(Cp)₂TiCl₂ at a potential E_p(C) -2.94 V, with a peak current ratio i(C)/i(B) increasing at low sweep rates, and an additional oxidation peak D' observed at ca. -1.2 V after generation of reduction peak B, are probably associated with some decay product(s) of a solvated tmen(Cp)₂Ti^{II} species.

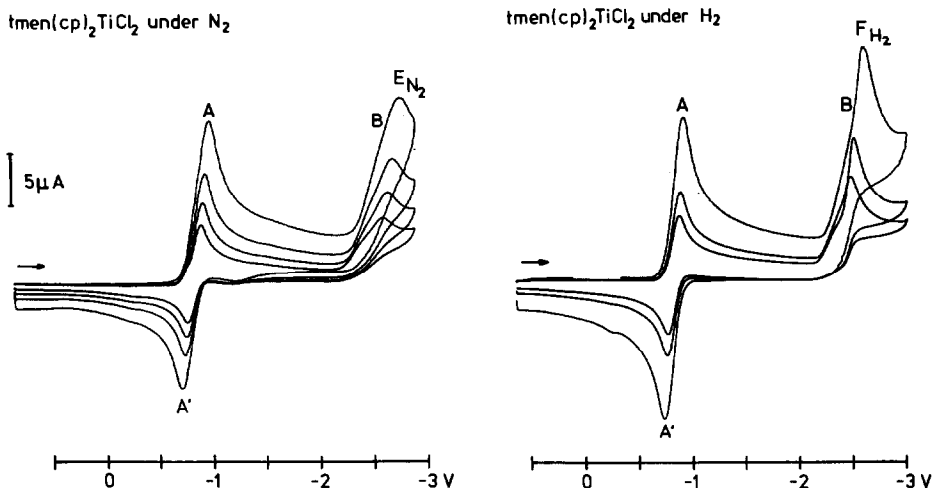


Fig. 2. Cyclic voltammograms of $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ in THF with $0.1 \text{ M TBA}^+ \text{PF}_6^-$ at 5°C , under N_2 (left; 500, 200, 100 and 50 mV/s) and under H_2 (right; 400, 100 and 50 mV/s). All voltammograms start with a reductive sweep.

V (Fig. 2): In both cases there is a new reduction peak, E_{N_2} and F_{H_2} , respectively, at a potential immediately below that of peak B, so that peak B is discernible only as a shoulder to these new signals, which have peak potentials of $E_p(E_{\text{N}_2}) - 2.64 \text{ V}$ (200 mV/s) and of $E_p(F_{\text{H}_2}) - 2.54 \text{ V}$ (200 mV/s). Both peaks are shifted to more negative potentials at higher scan rates. While the height of peak B (under Ar) relative to that of peak A is $i(B)/i(A) = 0.81$ (200 mV/s), the combined peak current of peak B plus the new, nitrogen- and hydrogen-induced peaks (at 200 mV/s) are $i(B + E_{\text{N}_2})/i(A) = 0.90$ and $i(B + F_{\text{H}_2})/i(A) = 1.35$, respectively, indicating a rather incomplete conversion, particularly with N_2 . The absence of any reoxidation peaks in the corresponding anodic sweep branches shows that the products formed at peaks E_{N_2} and F_{H_2} under nitrogen or hydrogen, like that formed at peak B under Ar, rapidly decay to species which probably contain Ti^{III} or even Ti^{IV} centres and cannot be detected by characteristic reoxidation peaks. While these observations are undoubtedly related to the reactivity of reduced titanocene systems towards N_2 , as in reductive nitrogen fixation, and towards H_2 , as in hydrogenation catalysis, we cannot at present identify the species formed at these potentials.

Preliminary studies with chemical reductants on a preparative scale have indicated, at any rate, that the products arising from reactions of $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ with Na in diethyl ether, Na naphthalide or Mg in THF, as well as ethyl- and isopropyl-Grignard or alkyllithium reagents in diethyl ether, under Ar or H_2 are reconverted into the dichloride by addition of HCl. Solutions arising from reduction under N_2 , however, yield upon hydrolysis with HCl product mixtures with a $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ content which is diminished by at least the amount corresponding to the NH_4^+ yield. Apparently N_2 -reduction is coupled here, as in similar Cp_2TiCl_2 -reduction systems [23,24] with a loss of ring ligands (Tab. 1).

3. Reduction of $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ under CO. In cyclic voltammograms of $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ obtained under an atmosphere of CO under otherwise identical

TABLE 1

REACTIONS OF $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ WITH REDUCING AGENTS UNDER N_2 (1 bar)^a

Reducing agent	mmol/mmol Ti	Solvent	Reaction time (h) ^b	NH_3/Ti after hydrolysis ^b	Fraction of $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ recovered ^b
Na metal	25/1	THF	3.5	0.74 ^c	0.18
			6	0.83 ^c	0
Mg metal (+ HgCl ₂)	44/1	THF	16	0.19	0.48
i-PrMgCl	9/1	THF	6	0.20	0.54
			18	0.56	0.39
EtMgCl	11/1	Et ₂ O	7.5	0.12	0.72
			17	0.31	0.50
n-BuLi	9/1	Et ₂ O	7.5	0.14	0.57
			17	0.20	0.51
Na naphthalide	7/1	THF	20	1.12	0

^a For comparable data with Cp_2TiCl_2 reaction systems see ref. 25 and literature cited therein. ^b Mixtures of $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ (0.5 mmol) and the respective reducing agent were stirred at room temperature for the indicated time periods, after which the reaction was quenched by adding, at -78°C , conc. aqueous HCl. NH_3 was determined by Kjeldahl distillation of the aqueous phase, N_2H_4 , measured essentially as described by Watt and Chrisp (ref. 26), was less than 0.005 mmol/mmol Ti, except where indicated; residual $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ was isolated from the organic phase. ^c Hydrazin present in addition to NH_3 in ratios of 0.01–0.015 mmol N_2H_4 /mmol Ti.

conditions, (Fig. 3), an unchanged first reduction peak *A* at $E_p(A) -0.92$ V is followed by a new, broad reduction peak *G* at a potential $E_p(G) -2.0$ V. In addition, reduction peak *B* is replaced by a new reduction peak *H* at $E_p(H) -2.8$

$\text{tmen}(\text{cp})_2\text{TiCl}_2$ under CO

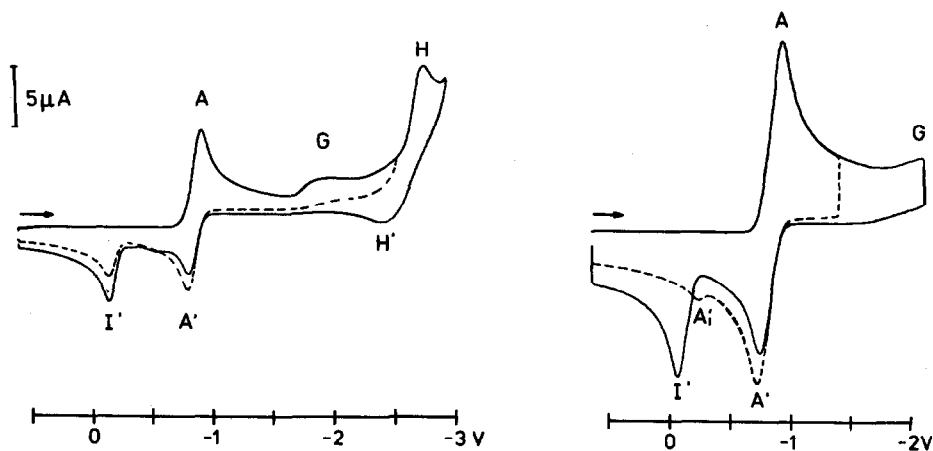


Fig. 3. Cyclic voltammogrammes of $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{TiCl}_2$, ca. 10^{-3} M in THF with 0.1 M $\text{TBA}^+ \text{PF}_6^-$ under a CO atmosphere at 5°C , starting with a reductive sweep to reversal potentials of -2.9 V (left, solid line) and -2.5 V (left, dashed line), and with waiting periods of 20 s at -2.1 V (right, solid line) and at -1.4 V (right, dashed line). Sweep rates 100 mV/s (left) and 500 mV/s (right).

V, which is accompanied by a small oxidation peak H' at a peak separation $\Delta E(H' - H)$ 0.35 V. The oxidation peak A' is partially diminished and a new oxidation peak I' appears at $E_p(I') - 0.14$ V. Peaks H and I' are associated with reduction and oxidation, respectively, of the dicarbonyl complex $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2$ (see section 4). Their appearance after reduction at peak G is evidence that electron uptake at peak G initiates formation of the dicarbonyl complex. Related observations on the formation of $\text{Cp}_2\text{Ti}(\text{CO})_2$ by reduction of Cp_2TiCl_2 under CO in this potential range have been reported previously [7,16].

We have further established that reduction under CO, at potentials between peak A and peak G , e.g. at -1.4 V, which generates $\text{tmen}(\text{Cp})_2\text{TiCl}_2^-$ and $\text{tmen}(\text{Cp})_2\text{TiCl}(\text{THF})$ in THF solution, does not lead to formation of the dicarbonyl oxidation peak I' . This is evidence that a CO-induced disproportionation of the solvated monochloride, analogous to that reported to take place with $(\text{Cp}_2\text{TiCl})_2$ and $(\text{C}_5(\text{CH}_3)_5)_2\text{TiCl}$ under CO [27,28], does not contribute to the formation of the dicarbonyl complex under the conditions of our study.

The occurrence of reduction peak G in the presence of CO is undoubtedly related to the presence of some carbonyltitanium(III) complex in the solutions. Probably the solvated monochloro complex $\text{tmen}(\text{Cp})_2\text{TiCl}(\text{THF})$ present in this potential range is in equilibrium with small concentrations of the chlorocarbonyl complex $\text{tmen}(\text{Cp})_2\text{TiCl}(\text{CO})^*$. This species, which would be more easily reduced than $\text{tmen}(\text{Cp})_2\text{TiCl}(\text{THF})$, due to the presence of the π -acceptor ligand CO, must be generated by ligand exchange to yield, at peak G , a chlorocarbonyltitanium(III) anion in the overall reaction $\text{tmen}(\text{Cp})_2\text{TiCl}(\text{THF}) + \text{CO} + e^- \rightarrow \text{tmen}(\text{Cp})_2\text{TiCl}(\text{CO})^- + \text{THF}$. Such a primary reduction product would then have to exchange ligands to form the dicarbonyl product $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2$. That this exchange is very rapid is indicated by the absence of any reoxidation peak in the potential region of reduction peak G .

A substantial decrease of the peak current at G relative to peak A , from a value of $i(G)/i(A) = 0.21$ at low sweep rates (50 mV/s) to 0.11 at a higher sweep rate of 500 mV/s, is further evidence for the view that the formation of the carbonyl product at peak G is kinetically controlled, probably by the kinetics of a CO-uptake reaction.

If reduction is continued beyond peak G , generation of Ti^{II} species in the potential region of B^{**} would certainly also be followed by ligand exchange with CO to form $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2$.

4. *Electrochemical characterization of $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2$.* Solutions of the dicarbonyl complex in THF (ca. 10^{-3} mmol/ml) with tetra-*n*-butylammonium hexafluorophosphate (ca. 0.1 mmol/ml) as supporting electrolyte, under an Ar atmosphere, yield cyclic voltammograms as represented in Fig. 4. Starting with a reductive sweep at -1.5 V, one obtains a prominent reduction peak H at a potential of $E_p(H) - 2.78$ V (200 mV/s). This peak is assigned to the one-electron-reduction of $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2$ to the dicarbonyl monoanion $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2^-$.

In the oxidative back-sweep, an oxidation peak H'_1 occurs at a peak separation of

* At elevated CO pressures, formation of the complex $\text{Cp}_2\text{Ti}(\text{CO})\text{Cl}$ is indicated by an IR absorption at 2068 cm^{-1} (ref. 29).

** If saturation of the solutions with CO is incomplete, peak B is observable between G and H .

$\text{tmen}(\text{cp})_2\text{Ti}(\text{CO})_2$ under Ar

without Cl^-

with excess Cl^-

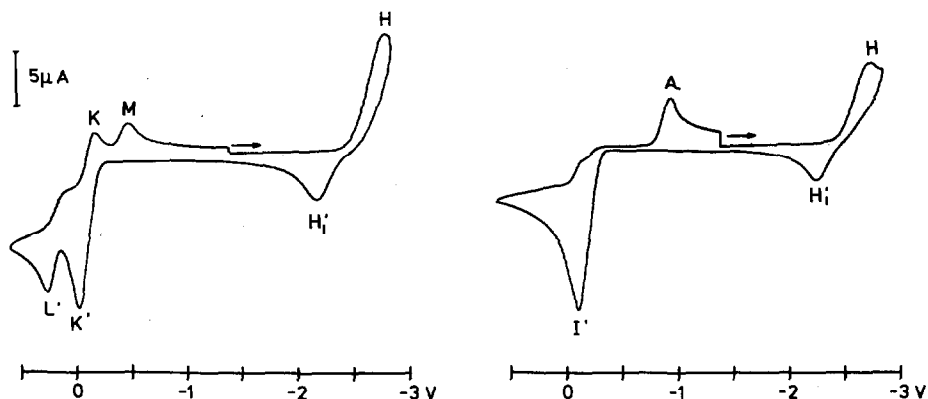


Fig. 4. Cyclic voltammogrammes of $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Ti}(\text{CO})_2$, ca. 10^{-3} M in THF with 0.1 M $\text{TBA}^+ \text{PF}_6^-$ under Ar at 5°C , without added Cl^- (left, 500 mV/s) and in the presence of ca. 0.02 M $\text{TBA}^+ \text{Cl}^-$ (right, 200 mV/s). Both voltammogrammes start at -1.4 V with a reductive sweep.

$\Delta E(H'_1 - H)$ 0.54 V (200 mV/s). The height of this peak H'_1 , relative to that of peak H , approaches unity at low sweep rates or after a waiting period of 30 s at the reversal potential (-2.85 V). Peak H'_1 can thus be assigned to the one-electron oxidation of some secondary product arising from a decay of the dicarbonyl anion formed at H . In principle either a CO ligand or an anionic ring ligand could have been lost from the Ti coordination sphere of such a 19-electron species. Since generation of H and H'_1 does not lead to any oxidation or reduction peaks in addition to those observed upon starting the oxidative sweep at a potential of -1.5 V, we tend to assign to this peak H'_1 the oxidation of the monocarbonyl anion $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})^-$, formed by loss of a CO ligand from $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2^-$ *. Oxidation of $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})^-$ at H'_1 would regenerate the dicarbonyl complex by subsequent CO uptake.

The oxidation of $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2$ occurs by two one-electron steps at peaks K' with $E_p(K') - 0.08$ V and L' with $E_p(L') + 0.24$ V; the relative peak current at L' , $i(L')/i(K')$, increases at lower sweep rates. Subsequent reduction will now generate two reduction peaks: K with $E_p(K) - 0.20$ V and M with $E_p(M) - 0.48$ V. Peak M is dependent on the prior generation of oxidation peak L' . Further reduction yields two small, new peaks N at $E_p(N) - 1.63$ V and O at $E_p(O) - 1.88$ V.

While the first oxidation step K' is fairly certain to be associated with a one-electron oxidation of $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2$ to $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2^+$, the further fate of such a product is not clear. The increase of $i(L')/i(K')$ with decreasing sweep rates indicates that the dicarbonyl cation has to decay by loss of CO and uptake either of solvent or the PF_6^- anion before further oxidation at L' can generate some

* The observation, under an atmosphere of CO, of an oxidation peak H' , close to the potential of H ($\Delta E(H' - H)$ 0.35 V) supports this assignment; apparently excess CO suppresses loss of CO from the dicarbonyl anion.

Ti^{IV} compound, such as $\text{tmen}(\text{Cp})_2\text{Ti}(\text{THF})_2^{2+}$ or $\text{tmen}(\text{Cp})_2\text{Ti}(\text{PF}_6)_2$ (for the analogous $\text{Cp}_2\text{Ti}(\text{PF}_6)_2$ see ref. 30, 31); the latter could then give rise, either directly or after CO-induced ligand exchange, to the reduction peaks *M*, *N* and *O*.

These complications are eliminated if excess Cl^- is added to the $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2$ solution (ca. 0.02 mmol/ml of tetra-*n*-butylammonium chloride). In this case in an anodic sweep starting at -1.5 V, there is a single, strong oxidation peak *I'* at $E_p(I')$ -0.14 V, the peak current of which is close to twice that of reduction peak *H*. A reductive back-sweep after generation of *I'* generates a single reduction peak with a peak potential (-0.92 V) identical to that of peak *A* observed upon reduction of $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ under Ar (section 1). Evidently, the dichloro derivative is generated, in the presence of Cl^- , by oxidation of the dicarbonyl complex at *I'*.

The potential of *I'*, $E_p(I')$ -0.14 V is quite close to that of oxidation peak *K'*, $E_p(K')$ -0.08 V, observed in the absence of chloride, which was assigned to the oxidation of the dicarbonyl complex to its monocation. It appears that this monocation is rapidly converted by ligand exchange with excess Cl^- , into the chloro-carbonyl $\text{tmen}(\text{Cp})_2\text{TiCl}(\text{CO})$ and hence to the dichloro anion $\text{tmen}(\text{Cp})_2\text{Ti}(\text{Cl})_2^-$, either one of which will lose a second electron at the rather anodic potential prevailing at peak *I'*. Observation of a peak current ratio $i(I')/i(H)$ of close to 2 is additional evidence that the overall reaction occurring at peak *I'* is such a CO/ Cl^- -exchange coupled, two-electron oxidation of $\text{tmen}(\text{Cp})_2\text{Ti}(\text{CO})_2$ which regenerates the dichloro complex $\text{tmen}(\text{Cp})_2\text{TiCl}_2$.

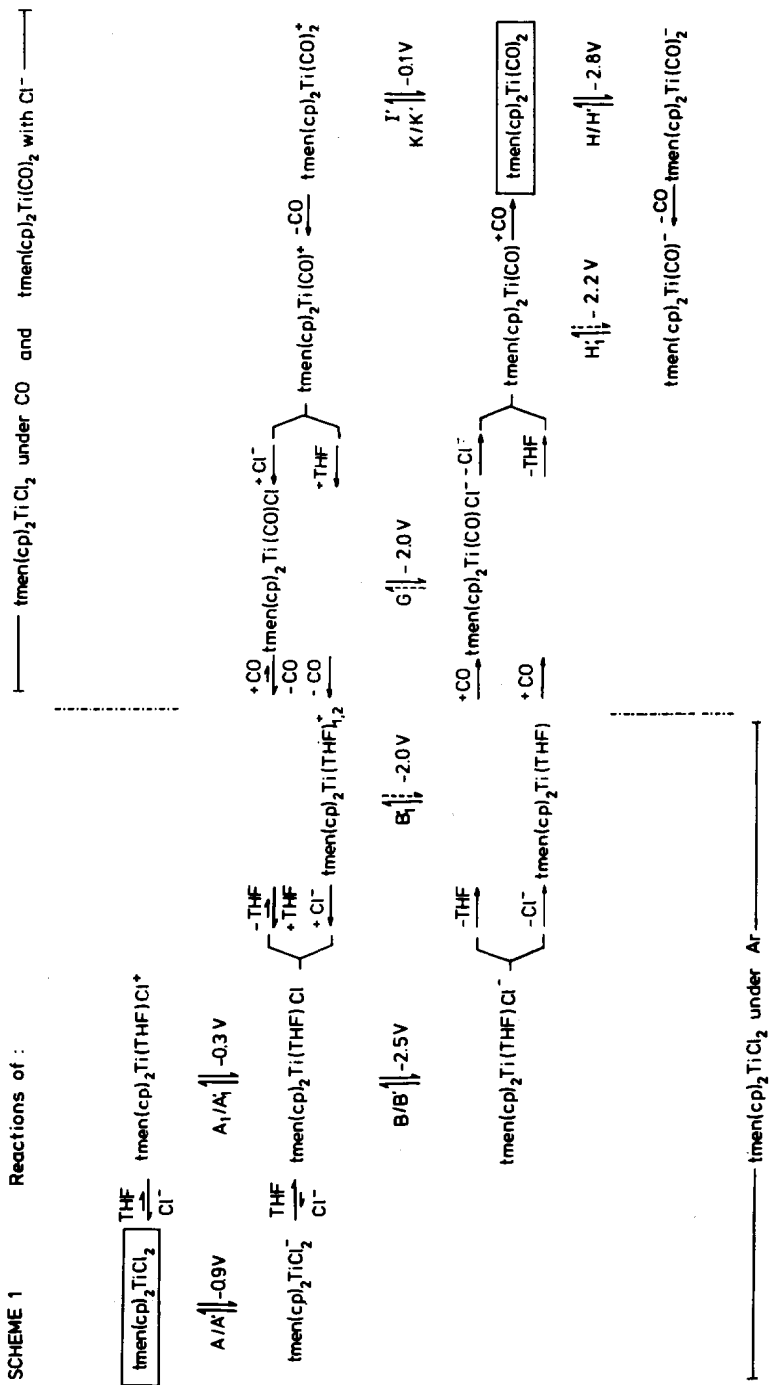
Concluding remarks

To summarize our observations on redox and ligand exchange reactions of $\text{tmen}(\text{Cp})_2\text{Ti}$ derivatives, we propose reaction Scheme 1, the left hand section of which represents electrochemical reactions of $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ under Ar, while interconversion reactions between chloride and carbonyl derivatives are summarized in the right hand section.

While some of the assignments in Scheme 1 are based on indirect evidence, its overall validity is corroborated by some additional data. Thus the potential difference of about 0.6 V between the reduction of the Ti^{IV} species $\text{tmen}(\text{Cp})_2\text{TiCl}_2$ (at *A*) and $\text{tmen}(\text{Cp})_2\text{Ti}(\text{THF})\text{Cl}^+$ (at *A*₁) implies that the equilibrium constants for THF vs. Cl^- exchange in the Ti^{IV} and Ti^{III} stages differ by a factor of about 10^{10} while neither of the two equilibrium constants is known at present, it must be assumed that concentrations of free chloride in equilibrium with the $\text{tmen}(\text{Cp})_2\text{Ti}^{\text{IV}}$ dichloride are negligible, whereas our data, like those reported by Laviron and collaborators [10–13] for Cp_2TiCl_2 , indicate that the THF/ Cl^- exchange equilibrium at the Ti^{III} stage lies predominantly on the side of the monochloro-THF adduct, which appears to be the thermodynamically favoured ligand exchange product of all Ti^{III} species, at least in the absence of excess Cl^- .

Of the THF adducts in Scheme 1, the solvated Ti^{III} cation, as most other Ti^{III} species, probably contains two ligand molecules*. The neutral Ti^{II}-THF complex, on the other hand, has undoubtedly a high-spin d^2 configuration with only one

** The complex cation $\text{Cp}_2\text{Ti}(\text{dimethoxy ethane})^+$ has been observed, by X-ray structure determination, to have two ether oxygen ligand atoms (ref. 32).



ligand site available for THF coordination [33] and is, therefore, most likely a mono-THF adduct. Its oxidation at peak B'_1 might, therefore, lead to a non-optimal configuration of the ensuing Ti^{III} species. At any rate, the potential difference between peak B' and B'_1 indicates that loss of Cl^- is highly favoured for Ti^{II} with its high-spin d^2 configuration, whereas conversion of the THF-adduct cation to the neutral monochloro complex is the preferred process at the Ti^{III} stage.

Carbonyl, on the other hand, is the preferred ligand at the Ti^{II} stage, whereas both, $tmen(Cp)_2Ti(CO)_2^+$ and $tmen(Cp)_2Ti(CO)_2^-$ suffer a rapid loss of CO. While a potential $E_p(B'_1) - 2.04$ V is assigned to the oxidation of $tmen(Cp)_2Ti(THF)$, the corresponding oxidation of $tmen(Cp)_2Ti(CO)_2$ occurs at a potential of $E_p(K') - 0.08$ V. The potential difference of almost 2 V for these two processes reflects a rather dramatic lowering of the electron occupation limit of the metallocene orbital scheme [33] in the dicarbonyl complex, which is, undoubtedly for this reason, the thermally most stable Ti^{II} derivative and the only ethylene-bridged dicyclopentadienyltitanium(II) complex observed so far.

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