

ELECTROCHEMICAL BEHAVIOUR OF TITANOCENE DIHALIDES UNDER CO PRESSURE, ELECTROGENERATION OF TITANOCENE CARBONYL DIHALIDE ANIONS AND TITANOCENE DICARBONYL

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Summary

Cyclic voltammetry of Cp_2TiX_2 ($\text{X} = \text{Cl}$ and Br) in THF under CO pressure shows that a chemical reaction with CO accompanies the addition of the first electron to the titanocene dihalides. Electrolysis gave, after the transfer of one electron and a decrease of CO pressure, solutions which exhibited two ESR signals. Electrolysis of these solutions at -1.8 V gave $\text{Cp}_2\text{Ti}(\text{CO})_2$ in high yield after the transfer of a second electron and the absorption of CO. A scheme involving the generation of anions such as $(\text{Cp}_2\text{Ti}(\text{CO})\text{X}_2)^-$ is suggested to explain the results.

Reduction of Cp_2TiX_2 ($\text{Cp} = \text{C}_5\text{H}_5$, $\text{X} = \text{halide}$) has received considerable attention since it provides lower valent derivatives. For a long time it has been accepted that electrochemical reduction of Cp_2TiX_2 leads to the cleavage of the metal-halogen bond [1-9]. Recently we reported new data for the electrochemical behaviour of titanocene dihalides, and showed that in THF or DMF the one-electron transfer on Cp_2TiX_2 is electrochemically and chemically reversible and leads to the anionic species $(\text{Cp}_2\text{TiX}_2)^-$ [10,11]. When the atmosphere is controlled and very pure solvents and electrolyte support are used, the $(\text{Cp}_2\text{TiX}_2)^-$ ion is chemically stable. No cleavage of the Ti-halogen bond is observed and thus Cp_2TiX cannot be obtained by electrolytic reduction of Cp_2TiX_2 . In THF with $(\text{Bu}_4\text{N})(\text{PF}_6)$ as supporting electrolyte, electrolysis of Cp_2TiX_2 ($\text{X} = \text{Cl}$ or Br) gave solutions ($\text{X} = \text{Cl}$, yellow-green; $\text{X} = \text{Br}$, green) of the stable radical anion $(\text{Cp}_2\text{TiX}_2)^-$. These solutions are stable for up to one day at room temperature in the absence of moisture or oxygen.

A few years ago, Green and coworkers [12] found that $(\text{Cp}_2\text{TiCl})_2$ did not react with CO, and could not prepare $\text{Cp}_2\text{Ti}(\text{Cl})\text{CO}$. More recently, Teuben and coworkers [13] found that the monomer Cp_2TiCl also does not react with

CO, in contrast with the corresponding bis(pentamethylcyclopentadienyl)-titanium chloride which reacts with CO to give the adduct $(C_5Me_5)_2Ti(Cl)CO$. In order to compare the properties and reactivities of Cp_2TiX and $(Cp_2TiX_2)^-$ we studied the generation of the latter anions under CO pressure, and we report the result below and present evidence for the generation of new titanium carbonyl species, $(Cp_2Ti(CO)X_2)^-$ which are reduced under CO pressure to give $Cp_2Ti(CO)_2$.

Results and discussion

The ESR spectra (25°C) of tetrahydrofuran (THF) solutions of electrolytically generated $(Cp_2TiX_2)^-$ radical anions exhibit one line when $X = Cl$ ($g = 1.9789$, line width = 10 G) and an ill-defined septuplet when $X = Br$ ($g = 1.9899$, line width = 22 G). Addition of $PPhMe_2$ to these solutions causes these signals to split into doublets (22 G) owing to the interaction of the unpaired electron with ^{31}P . Recently Schore and Hope [14] observed a similar effect in the zirconium series, when $Cp_2Zr(Cl)CH_2P(Ph)_2$ was reduced by Na/Hg in THF; they postulated the formation of an anionic complex in which the zirconium is surrounded by two cyclopentadienyl, one methylene, one chloride and one phosphine group. Similarly for the adduct obtained by addition of $PPhMe_2$ to $(Cp_2TiX_2)^-$ we suggest a structure in which the metal would have a 19-electron configuration if both rings are still pentahapto. It is also possible however that one or both rings in this phosphine adduct become tri- or even mono-hapto. The possibility that one chloride leaves the Ti coordination sphere cannot be definitively excluded. ESR and electrochemical techniques cannot, of course, reveal the true nature of this species, but we do know that the phosphine adduct is electrochemically oxidisable and that the final product of the oxidation is the titanocene dihalide. While this is insufficient to confirm that in the phosphine adduct the titanium is surrounded by two cyclopentadienyls and two halogenes besides the phosphine ligand, in view of the results obtained in the zirconium series [14] we consider such a structure to be a reasonable possibility, and are currently investigating other methods of structural characterisation. Nevertheless, in order to find out if such an adduct could be obtained with ligands other than phosphines, we carried out an electrochemical study of titanocene dihalides under CO, using a special cell which allowed us to perform cyclic voltammetry and electrolyses under pressure.

Cyclic voltammetry of Cp_2TiCl_2 , in THF, with $(Bu_4N)(PF_6)$ as supporting electrolyte, under an argon stream (atmospheric pressure) or under argon pressure (3 bars) shows, at a glassy carbon electrode, the well-known three peaks A, B and C at -0.86 , -2.12 and -2.44 V. At a scan rate of 0.1 Vs^{-1} the first electron transfer reaction (peak A) is highly reversible, while the other two transfers are only slightly reversible. Under CO pressure (3 bars) a drastic change in the cyclic voltammogram occurs. The peaks B and C disappear, the reversibility of A decreases, and two new cathodic peaks D and E appear at about -1.7 and -2.8 V. The heights of A, D and E are in the order $A > E > D$. These preliminary results showed that a reaction with CO follows the addition of the first electron to Cp_2TiCl_2 (see Fig. 1).

Electrolysis of Cp_2TiCl_2 at potentials corresponding to A under CO pressure

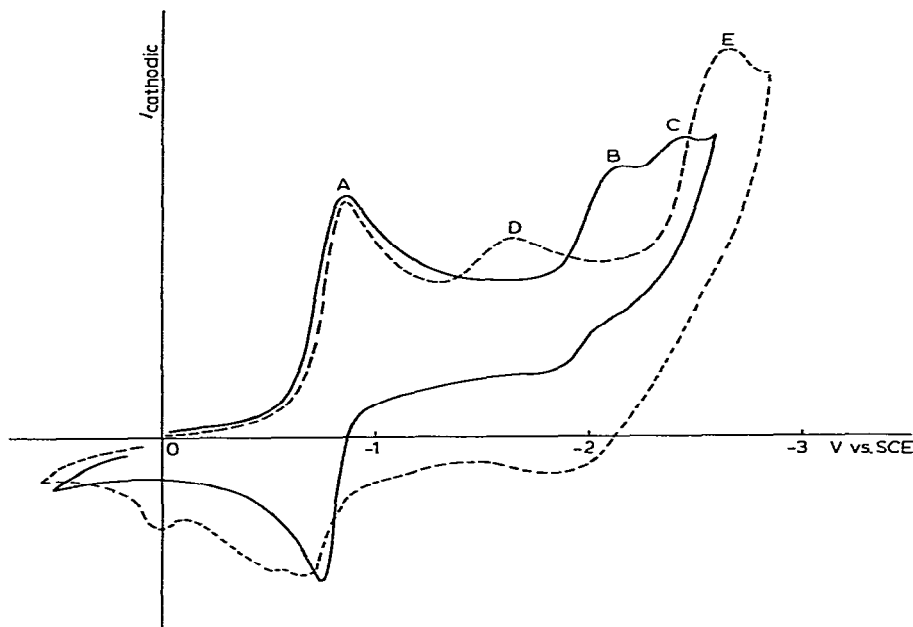


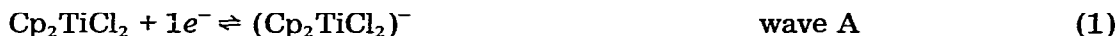
Fig. 1. Cyclic voltammogram of Cp_2TiCl_2 , in THF, 0.2 M Bu_4NPF_6 , 50 mV/sec, carbon electrode. (—) at 3 bars Ar pressure; (---) at 3 bars CO pressure.

(3 bars) gave, after the transfer of one electron, a brown solution which exhibited two ESR signals $g_1 = 1.9789$ and $g_2 = 1.9755$, the first corresponds to $(\text{Cp}_2\text{TiCl}_2)^-$ and the second a new signal not observed when electrolysis is performed under argon. During electrolysis the CO pressure decreases by an amount corresponding to 0.55 mole of CO per mole of Cp_2TiCl_2 . Cyclic voltammetry then shows the reverse anodic peak corresponding to A and the new peak D. The IR spectrum of THF solution shows a broad absorption $\nu(\text{CO})$ at 1950 cm^{-1} . When the brown solution is left in the sealed ESR tube, under argon the ESR signal at $g_2 = 1.9755$ decreases while that at $g_1 = 1.9789$ increases. After 12 h the signal corresponding to $(\text{Cp}_2\text{TiCl}_2)^-$ is virtually the only one present.

After the transfer of one electron and absorption of 0.55 mole of CO, electrolysis of the brown solution at potentials corresponding to D (electrolysis performed at -1.8 V) gave, after the transfer of a second electron, a red solution; 1.45 mole of CO is absorbed during this electrolysis and the red solution does not show any ESR signal. Cyclic voltammetry reveals the presence of peak E, and IR reveals absorptions at 1880 and 1960 cm^{-1} . Comparison with an authentic sample shows that electrolysis leads to the formation of $\text{Cp}_2\text{Ti}(\text{CO})_2$.

Bulk electrolysis of Cp_2TiCl_2 under CO pressure performed at -1.8 V confirmed the formation of $\text{Cp}_2\text{Ti}(\text{CO})_2$. The current yield for this synthesis is 100% (two Faradays per mole of Cp_2TiCl_2) and the yield based upon the conversion into isolated product is 80%. The electrolysis under argon at the same potential needs one Faraday per mole and generates the corresponding radical anion, and no titanium(II) is formed (the second reduction step of Cp_2TiCl_2 is at -2.12 V).

We consider a scheme such as eqs. 1–3 to offer a reasonable interpretation of the electrochemical results under CO pressure.



The key reaction in this scheme is the equilibrium 2. The ESR experiment shows that in $(\text{Cp}_2\text{Ti}(\text{CO})\text{Cl}_2)^-$ the CO is labile, and readily leaves the titanium coordination sphere at room temperature. When electrolysis is performed at potentials corresponding to D, $(\text{Cp}_2\text{Ti}(\text{CO})\text{Cl}_2)^-$ is rapidly reduced and the equilibrium 2 is then pushed over to the right, allowing the preparation of $\text{Cp}_2\text{Ti}(\text{CO})_2$ in almost quantitative yield.

Similar results are obtained when Cp_2TiBr_2 is used as starting material. The final isolated product is again $\text{Cp}_2\text{Ti}(\text{CO})_2$.

Experimental

The complexes Cp_2TiCl_2 and Cp_2TiBr_2 were obtained from Alfa Inorganics and PPhMe_2 from Fluka. Tetra-n-butylammonium hexafluorophosphate (Fluka) was recrystallized from aqueous ethanol and dried in vacuo, it was deoxygenated and dehydrated by melting under vacuum prior to use. THF (Fluka) was purified by fractional distillation from sodium benzophenone under a stream of argon. Electrochemical measurements were carried out under an argon atmosphere. Polarography and cyclic voltammetry were made with Amel Model 566-function generator in conjunction with Amel Model 552-potentiostat and with JJ Lloyd Model PL 1500 XY/t recorder. Potential control for coulometric experiments was maintained with a Amel Model 552-potentiostat. Potential values were referenced to the saturated potassium chloride calomel electrode (SCE) at $20 \pm 2^\circ\text{C}$ and were uncorrected for junction potentials. Polarographic measurements were made at a dropping mercury electrode with a dropping time of 0.5 s. Cyclic voltammetry experiments were made at a glassy carbon electrode, coulometry and preparative experiments were carried out at a 50 cm^3 mercury pool or 35 cm^3 platinum plate. The ESR spectra of THF solutions were recorded at room temperature with a Varian E-4 spectrometer.

References

- 1 Y. Mugnier, C. Moise and E. Laviron, *J. Organometal. Chem.*, 204 (1981) 61.
- 2 I.A. Karshunov and N.I. Malyugina, *Zh. Obshch. Khim.*, 34 (1964) 734.
- 3 H. Brintzinger, *J. Am. Chem. Soc.*, 88 (1966) 4305.
- 4 H. Brintzinger, *J. Am. Chem. Soc.*, 89 (1967) 6871.
- 5 S. Valcher and M. Mastragostino, *J. Electroanal. Chem.*, 14 (1967) 219.
- 6 S.P. Gubin and S.A. Smirnova, *J. Organometal. Chem.*, 20 (1969) 229.
- 7 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, *J. Am. Chem. Soc.*, 94 (1972) 1219.
- 8 E. Laviron, J. Besançon and F. Huq, *J. Organometal. Chem.*, 159 (1978) 279.
- 9 R.G. Doisneau and J.C. Marchon, *J. Electroanal. Chem.*, 30 (1971) 487.
- 10 N. El Murr, A. Chaloyard and J. Tirouflet, *J. Chem. Soc. Chem. Commun.*, (1980) 446.
- 11 N. El Murr and A. Chaloyard, *J. Organometal. Chem.*, 212 (1981) C39.
- 12 M.L.H. Green and C.R. Lucas, *J. Chem. Soc. Dalton*, (1972) 1000.
- 13 E.J.M. DeBoer, L.C. Tencate, A.G.J. Staring and J.H. Teuben, *J. Organometal. Chem.*, 181 (1979) 61.
- 14 N.E. Schore and H. Hope, *J. Am. Chem. Soc.*, 102 (1980) 4251.