Electrosynthesis of Alkyl and Aryloxy Titanium(III) Complexes; Electrochemical and Spectroscopic Characterization

By ANNIE CHALOYARD, ALAIN DORMOND, JEAN TIROUFLET, and NABIL EL MURR*†
(*Laboratoire de Synthèse et d'Electrosynthèse Organometallique, 6 Bd. Gabriel, 21100 Dijon, France*)

Summary Electrochemical or chemical reduction of mono- or dicyclopentadienyl Ti^{IV} complexes gives the corresponding radical anions which rearrange rapidly in both cases to the corresponding neutral monocyclopentadienyl Ti^{III} complexes; by a combination of electrochemical and e.s.r. techniques, it was possible to understand the mechanism of reduction of these Ti^{IV} complexes.

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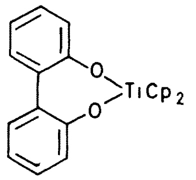
† *Present address:* Department of Chemistry, The University, Sheffield S3 7HF.

DICYCLOPENTADIENYL-TITANIUM(III) complexes are known to be of considerable interest as Ziegler-type catalysts for the polymerisation of ethylene[1,2] It has been proposed that a convenient way to obtain such complexes is by the reduction of the corresponding Ti^{IV} derivatives It was suggested that such a type of reaction could occur with elimination of Q from $(C_5H_5)_2TiQ_2$ (Q = halide,[3] alkyl,[4] or aryloxy[5]) thereby leading to neutral dicyclopentadienyl d^1 Ti^{III} compounds Recently, however, Lappert and collaborators reported that this elimination did not occur and that the reduction of some d^0 Ti^{IV} complexes led to stable solutions of d^1 dialkylmetallate(III) derivatives[6] $[M(C_5H_4R^1)_2R^2{}_2]^-$ ($M = Ti$, $R^1 = H$, $R^2 = Me$ $PhCH_2$, or Me_3SiCH_2)



(1)

We now report the electrochemical behaviour of some d^0 Ti^{IV} complexes In all cases studied [Cp_2TiR_2, $Cp_2Ti(OAr)_2$ $Cp_2Ti(OSiR_3)_2$ $CpTi(OAr)_3$ and $CpTi(OSiR_3)_3$] (Cp = cyclopentadienyl), the first electron transfer reaction led to a d^1 Ti^{III} anion but, contrary to the other studies, we noted a chemical rearrangement leading to the neutral monocyclopentadienyl Ti^{III} species

In tetrahydrofuran (THF) with $Bu_4N^+PF_6^-$ as supporting electrolyte, cyclic voltammetry at a platinum or glassy carbon electrode shows one or two monoelectronic stages (see Table) The first stage (i) is completely reversible for a scan rate of 0 1 V s^{-1} The peak spread for this first step is identical to that of the Cp_2Fe^+/Cp_2Fe system which is known to be entirely reversible in THF[7] The reversibility decreases when scan rates decrease but the system is still slightly reversible at 0 025 V s^{-1} The second reduction step, when it is detectable by cyclic voltammetry is pseudoreversible (for scan rate = 0 1 V s^{-1}), the peak spread being larger than that for the first one This implies a change in the structure or in the solvation of the molecule after the addition of the second electron[7] These results are consistent with equations (i) and (ii) where Q = R, OAr or $OSiR_3$

$$[Cp_nTiQ_{4-n}] + 1e^- \rightleftharpoons [Cp_nTiQ_{4-n}]^- \qquad (i)$$

$$[Cp_nTiQ_{4-n}]^- + 1e^- \rightleftharpoons [Cp_nTiQ_{4-n}]^{2-} \qquad (ii)$$

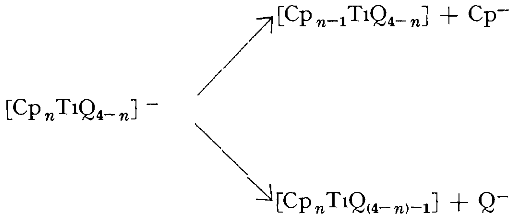
However, this had to be confirmed by electrolysis of the Ti^{IV} species Thus electrolyses at a platinum electrode, at the potential of stage (i), gave solutions which did not exhibit in their cyclic voltammograms the anodic peak corresponding to (i) In the case of the dicyclopentadienyl derivatives an anodic peak at about −0 2 V (*vs* standard calomel electrode) was then detected but this was absent in the voltammograms of the monocyclopentadienyl compounds This shows that the d^1 $Ti^{III}[Cp_2TiQ_2]^-$ anions are not chemically stable and rearrange during the electrolysis In all cases, the solutions exhibit an e s r spectral signal (see Table)

TABLE Electrochemical and e s r data on Cp_nTiQ_{4-n} in THF at 20 °C

	$-E_p$ cathodic[a] /V	g of $CpTiQ_2$[b c]
$Cp_2Ti(OC_6H_3$ 3 Me 6 $Pr^i)_2$	1 68 2 44	1 9766
$Cp_2Ti(OC_6H_4$ 4-Me$)_2$	1 70 2 48	1 9767
$Cp_2Ti(OSiMePh_2)_2$	1 40	1 9778
Cp_2Ti(biphenyl 2 2′ diyldioxy) (**1**)	1 52	1 9770
Cp_2TiMe_2	2 07	1 9789
$Cp_2Ti(CH_2Ph)_2$	1 86	1 9829[d]
$CpTi(OC_6H_4$ 4 Me$)_3$	1 63	1 9766
$CpTi(OC_6H_3$ 2 6 $Me_2)_3$	1 64	1 9801
$CpTi(OC_6H_2$ 2 4 6 $Me_3)_3$	1 74	1 9549
$CpTi(OSiMePh_2)_3$	2 1	1 9778

[a] Relative to a standard calomel electrode (s c e) [b] Values relative to diphenylpicrylhydrazyl (g = 2 0035) [c] Satellites from ^{47}Ti and ^{49}Ti are observed [d] The signal is a well defined quintuplet

The chemical rearrangement of $[Cp_nTiQ_{4-n}]^-$ can occur in two ways (Scheme) In the case of the dicyclopentadienyl compounds (n = 2), we found that the anodic peak at −0 2 V corresponded to the oxidation of the free cyclopentadienyl anion[8] This was confirmed by a bulk electrolysis followed by addition of $CoBr_2$, the cobalticinium cation $(C_5H_5)_2Co^+$ was then isolated as the hexafluorophosphate salt When n = 1 the group Q is eliminated, leading to the neutral Ti^{III} complex $CpTiQ_2$, electrolysis of Cp_2TiQ_2 affords the same compound and this is confirmed by the e s r studies



SCHEME

Our results show that the d^1 dicyclopentadienyl and d^1 monocyclopentadienyl metallates(III) are not stable chemically and that the electrochemical method of reduction affords a route to the synthesis of neutral monocyclopentadienyl Ti^{III} derivatives

E s r spectral studies, while revealing the existence of Ti^{III} complexes after reduction, do not reveal the nature of the species in solution, since there is no detectable Ti–H coupling involving the C_5H_5 rings[1]

Our results using electrochemical techniques are different from those obtained when chemical reducing agents were used[6] For this reason we have compared the electrochemical reduction of the Ti^{IV} complexes with the sodium naphthalenide reduction in THF in the presence of $Bu_4N^+PF_6^-$ (necessary to provide comparable conditions) In all cases solutions were formed which showed the same e s r spectral and electrochemical behaviour, indicating the formation of the same final products

More interesting is the behaviour of (**1**) In this case, the corresponding anion generated after chemical reduction is stable enough to be detected by e s r techniques (Figure).

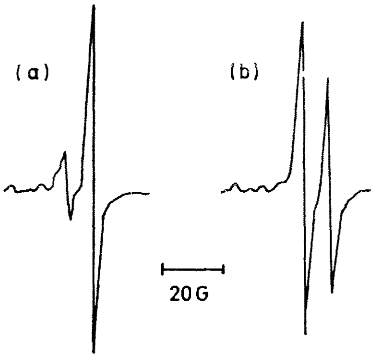


FIGURE. E.s.r. spectra of solutions obtained after reduction of (**1**) in THF at 20 °C. Spectrum (b) is recorded 10 min after (a).

The spectrum recorded immediately after addition of $Na(C_{10}H_8)$ to THF solutions of (**1**) shows two lines at $g =$ 1·9772 and 1·9709. The second line decreased in the course of time while the first one increased; after *ca.* 20 min, the spectrum showed only the first line. The electrolysis of (**1**), which lasts more than 20 min, gave a solution which has in its e.s.r. spectrum one line at $g = 1{\cdot}9770$ and its cyclic voltammogram reveals an anodic peak at $-0{\cdot}2$ V characteristic of the cyclopentadienyl anion. This is again in favour of the chemical rearrangement that we propose.

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