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Electrochemical Oxidation of Bis(cyclopentadienyl)titanium Dichloride

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The one-electron oxidation of $(Cp)_2TiCl_2$ in acetonitrile generates $[(Cp)_2TiCl(CH_3CN)]^+$, where Cp is cyclopentadienyl anion, as characterized by ^{1}H NMR spectroscopy and electrochemical and spectroelectrochemical methods. This is a direct method for generation of cationic bis(cyclopentadienyl) group(IV) species from $(Cp)_2TiCl_2$. Photochemical generation[1] of $[(Cp)_2Ti(CH_3CN)_2]^{+\,2}$ from $(Cp)_2TiI_2$ and chemical generation[2–5] of several mono and dicationic bis(cyclopentadienyl)zirconium(IV) complexes of relevance to mechanistic studies of Ziegler–Natta catalysts have been reported. It has been shown that replacement of CH_3CN with weaker coordinating solvents enhances the reactivity of the cationic species.[2–5] Hence electrochemical oxidation of $(Cp)_2TiCl_2$ in CH_2Cl_2 was also performed, and the generation of $[(Cp)_2TiCl(CH_2Cl_2)]^+$ is discussed.

Despite the extensive electrochemical examinations[6–9] of the reduction of $(Cp)_2TiCl_2$ and reports[10] of the oxidative electrochemistry of bimetallic complexes containing the $(Cp)_2Ti$ fragment, the oxidative electrochemistry of $(Cp)_2TiCl_2$ has not been determined. However as shown in Figure 1a, which gives cyclic voltammetric data for $(Cp)_2TiCl_2$ in CH_3CN containing TBAP,[11–13] an oxidation process is found with $E_{pa} = 1.90 \pm 0.02$ V vs SCE (wave 1, Figure 1a) at a scan rate of 100 mV/s. Wave 1 is characterized by a value of $E_p - E_{p/2}$ of 83 mV, a constant ratio of the peak current to the square root of the scan rate ($i_p/v^{1/2}$) from 10 to 1000 mV/s, and a positive shift of E_{pa} with increasing scan rate. A coupled reduction process is not found for wave 1 even with multiple scans and/or fast scan rates, and there is no indication of electrode passivation. Hence, wave 1 is a diffusion-controlled process (over the scan rates examined) and represents either an $E_{rev}C$ or an E_{irr} mechanism.[14] Bulk electrolysis at potentials positive of wave 1 give 1.1 ± 0.28 electrons per Ti with a change in solution color from red to yellow. Similar results are obtained when the supporting electrolyte is either $NaClO_4$ or $TBA(BF_4)$,[15] demonstrating that the oxidative response is independent of the supporting electrolyte. Furthermore, similar results are found in CH_2Cl_2 containing TBAP, and in this solvent E_{pa} for wave 1 is 2.06 ± 0.02 V vs SCE at a scan rate of 100 mV/s.

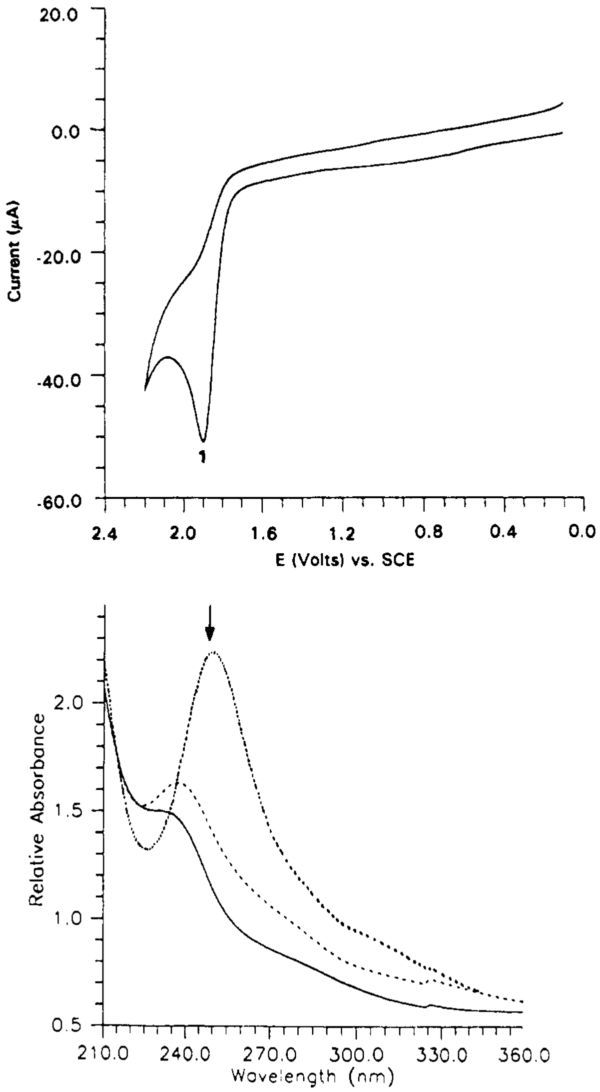

Figure 1. Top: (a) Cyclic voltammogram of a solution of 0.0052 M $(Cp)_2TiCl_2$ in CH_3CN, containing 0.13 M TBAP, scanning from 0.10 to 2.20 V vs SCE, with a scan rate of 100 mV/s bottom: (b) Spectroelectrochemical data for 0.0030 M $(Cp)_2TiCl_2$ in 0.13 M CH_3CN, containing TBAP. Oxidation was at 2.20 V vs Pt wire reference for $T = 0$, initial complex (···), $T = 20$ s (- - -), and $T = 1$ min (—) in the spectral range of 360 to 210 nm.

Figure 1b shows the UV–visible spectroelectrochemical data for the oxidation of $(Cp)_2TiCl_2$ in acetonitrile containing TBAP. Under our conditions $(Cp)_2TiCl_2$ has absorption bands at 250 (Figure 1b) and 389 nm (not shown in Figure 1b) which decrease upon oxidation with the concomitant formation of a band at 240 nm (Figure 1b). Hence, the electrogenerated titanium product is characterized by an absorption band at 240 nm. Application of a potential negative of wave 1 (up to –0.10 V) to the oxidized solutions results in no spectral changes.

Analysis of the oxidation reaction following preparative electrochemical generation was performed by ^{1}H NMR and UV–vis methods. After bulk electrolysis of $(Cp)_2TiCl_2$ in CH_3CN containing $NaClO_4$ at potentials positive of wave 1, the sample

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(11) TBAP is tetrabutylammonium perchlorate. For a full description of the electrochemical and electrochemical experiments, see refs 12 and 13. Ferrocene, added as an internal standard, has a value of $E_{1/2}$ of 0.40 V vs SCE and a ΔE_p of 90 mV.

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(15) $TBA(BF_4)$ is tetrabutylammonium tetrafluoroborate.

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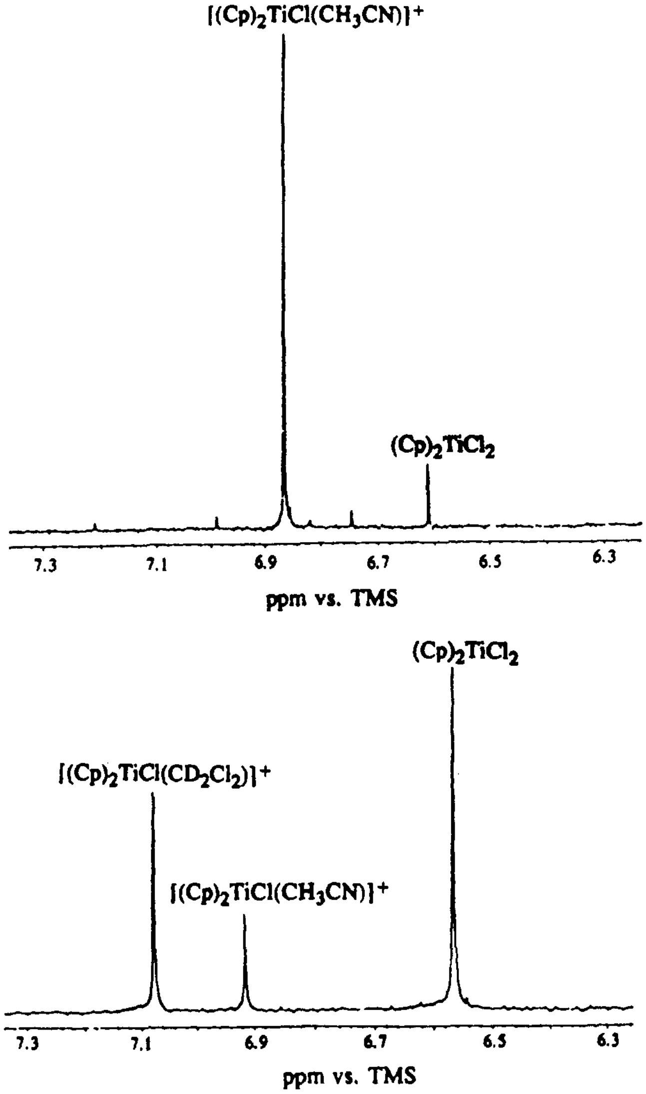

Figure 2. Top: (a) ^{1}H NMR data for [(Cp)$_2$TiCl(CH$_3$CN)]$^+$ in CD$_3$CN. Bottom: (b) ^{1}H NMR data for [(Cp)$_2$TiCl(CH$_3$CN)]$^+$ in CD$_2$Cl$_2$. Note enhancement of the peak at 6.57 ppm due to reaction with CD$_2$Cl$_2$. Reaction time was approximately 15 min.

was vacuum dried and reconstituted in CD$_3$CN, and typical results are shown in Figure 2a. The sample is characterized by a singlet in the cyclopentadienyl region at 6.85 ± 0.01 ppm. Only one additional small peak is observed at 6.59 ± 0.01 ppm between 5.0 and 8.0 ppm and is due to unoxidized (Cp)$_2$TiCl$_2$.[16] Integration of the peaks at 6.85 to 6.59 ppm gave a relative area ratio of 9.7. A large multiplet centered at 1.94 ppm is observed due to CD$_3$CN which prohibited the possible observation of resonances due to coordinated CH$_3$CN. Similar data were obtained when either TBAP or TBA(BF$_4$) were used in the bulk electrolysis experiments. UV-vis spectra of the oxidized bulk solution are in agreement with the spectroelectrochemical data.

Our spectroscopic and electrochemical data are consistent with the formation of [(Cp)$_2$TiCl(CH$_3$CN)]$^+$ following the one-electron oxidation of (Cp)$_2$TiCl$_2$. The observation of a singlet for the Cp resonance implies that the rings remain intact after the oxidation reaction. Furthermore, the downfield shift of the Cp resonance in the ^{1}H NMR spectrum is consistent with a decrease in electron density on the Ti due to the formal replacement of Cl$^-$ with CH$_3$CN. Finally the results are independent of the supporting electrolyte eliminating the possibility of anion (or cation) participation in the overall electron transfer reaction.

^{1}H NMR data for [(Cp)$_2$TiCl(CH$_3$CN)]$^+$ are in general agreement with spectra previously reported. For example, in the Cp region peaks at 6.38, 6.54, and 6.44 ppm were observed for [(Cp)$_2$Ti(CH$_3$CN)$_2$](PF$_6$)$_2$ in CD$_2$Cl$_2$.[1] The resonance at 6.38 ppm was assigned to [(Cp)$_2$Ti(CH$_3$CN)$_2$]$^{2+}$, while a monosolvated form was proposed to account for the peaks at 6.54 and 6.44 ppm. ^{1}H NMR data in the Cp region for [(Cp)$_2$Zr(CH$_3$CN)$_3$]$^{2+}$ and [(Cp)$_2$ZrCl(CH$_3$CN)]$^+$ show singlets located at 6.45 and 6.37 ppm in CD$_3$CN.[2-5] A singlet at 1.95 ppm was found and assigned to the coordinated CH$_3$CN of [(Cp)$_2$Zr(CH$_3$CN)$_3$]$^{2+}$.

If samples of (Cp)$_2$Ti(Cl)$_2$ are reconstituted in CD$_2$Cl$_2$ following bulk electrolysis, the ^{1}H NMR spectra has resonances in the Cp region at 6.88 ± 0.03 and 6.57 ± 0.01 ppm due to [(Cp)$_2$TiCl(CH$_3$CN)]$^+$ and (Cp)$_2$TiCl$_2$, respectively, and a new peak at 7.08 ± 0.01 ppm as shown in Figure 2b. A peak is also observed at 1.97 ± 0.01 ppm and is due to free acetonitrile.[17] The resonance at 7.08 ppm is assigned to formation of [(Cp)$_2$TiCl(CD$_2$Cl$_2$)]$^+$ by replacement of acetonitrile with CD$_2$Cl$_2$. The downfield shift of the Cp resonance for this species relative to [(Cp)$_2$TiCl(CH$_3$CN)]$^+$ is consistent with a further decrease in the electron density around the Ti due to the exchange of acetonitrile with dichloromethane.

Of note is that the signal due to (Cp)$_2$TiCl$_2$ is found to be significantly larger when the sample is reconstituted in CD$_2$Cl$_2$ compared to CD$_3$CN, as shown in Figure 2b. This is due to a slow chemical reaction between [(Cp)$_2$TiCl(S)]$^+$ and the CD$_2$Cl$_2$ to regenerate (Cp)$_2$TiCl$_2$. This reaction was verified by addition of CD$_2$Cl$_2$ to solutions of [(Cp)$_2$TiCl(CH$_3$CN)]$^+$ in CD$_3$CN which resulted in an immediate increase in the resonance due (Cp)$_2$TiCl$_2$ and a corresponding decrease in the resonances due to [(Cp)$_2$TiCl(S)]$^+$. Over time there is complete conversion of [(Cp)$_2$TiCl(S)]$^+$ to titanocene dichloride.

Formation of [(Cp)$_2$TiCl(CH$_3$CN)]$^+$ upon the one-electron oxidation of (Cp)$_2$TiCl$_2$ suggests that electron abstraction is directly from a Ti–Cl bond resulting in release of Cl$^\bullet$ upon coordination by CH$_3$CN.[18] A significant advantage of this route to cationic bis(cyclopentadienyl) group(IV) species is the relative availability of (Cp)$_2$TiCl$_2$ compared to the bis(iodide) adduct.[1,3] Not surprisingly, the slow reaction between [(Cp)$_2$TiCl(CH$_3$CN)]$^+$ and CH$_2$Cl$_2$ suggests [(Cp)$_2$TiCl(CH$_3$CN)]$^+$ is not nearly as reactive as the dicationic species. However, an alternate entry point into cationic bis(cyclopentadienyl) group(IV) chemistry has been realized and is under further investigation.

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(16) The relative ratio of the peak at 6.59 to that at 6.85 could be enhanced if the electrolysis was not run to completion. In addition, (Cp)$_2$TiCl$_2$ in CD$_3$CN, NaClO$_4$ was run as a blank and gave a single peak at 6.59 ppm.

(17) Under identical conditions, ^{1}H NMR analysis of CH$_3$CN in CD$_2$Cl$_2$ revealed a singlet at 1.97 ppm.

(18) No attempt was made to determine the fate of the Cl$^\bullet$ released in the electrolysis reaction.