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Electrochemical and density functional theory study of bis(cyclopentadienyl) mono(β-diketonato) titanium(IV) cationic complexes

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ABSTRACT

The electrochemical behaviour of fluorinated bis(cyclopentadienyl) mono(β-diketonato) titanium(IV) complexes, of general formula $[Cp_2Ti(R'COCHCOR)]^+ClO_4^-$ with Cp = cyclopentadienyl and R′, R = CF_3, C_4H_3S; CF_3, C_4H_3O; CF_3, Ph (C_6H_5); CF_3, CH_3; CH_3, CH_3; Ph, Ph and Ph, CH_3 is described. Both metal and ligand based redox processes are observed. The chemically and electrochemically reversible Ti^{IV}/Ti^{III} couple is followed by an irreversible ligand reduction at a considerably more negative (cathodic) potential. A comparison of the ligand reduction in its free and chelated state indicates that the β-diketonato ligand $(R'COCHCOR)^-$ in $[Cp_2Ti(R'COCHCOR)]^+ClO_4^-$ is electroactive at more negative potentials. A theoretical density functional theory (DFT) study shows that a highly localized metal centred frontier orbital dominates the Ti^{IV}/Ti^{III} redox chemistry resulting in a non-linear relationship between the formal redox potential ($E^{\circ\prime}$) and the sum of the group electronegativities of the R and R′ groups, $\chi_R + \chi_{R'}$, of the ligand. Linear relationships, however, are obtained between the DFT calculated electron affinity (EA) of the complexes and $\chi_R + \chi_{R'}$, the pK_a of the free β-diketones $R'COCH_2COR$ and the carbonyl stretching frequency, ν_{CO}, of the complexes. The DFT calculated electronic structure of the second reduced species $[Cp_2Ti(\beta\text{-diketonato})]^-$ shows that it is best described as Ti(III) coupled to a β-diketonato radical.

1. Introduction

Metallocene(IV) complexes are ‘bent-sandwich’ organometallic complexes where the bis(cyclopentadienyl) moieties are in a bent conformation with respect to the central metal atom. Titanocene(IV) complexes and in particular titanocene dichloride $[Cp_2Ti^{IV}Cl_2]$ exhibit various catalytic applications for example as Ziegler–Natta catalyst [1,2]. Knowledge of the activity of these complexes towards oxidation (chemical and electrochemical) or substitution is necessary to study and understand their mechanism of action during catalysis. Cyclic voltammetry (CV) is a very useful modern electroanalytical technique for the study of electroactive species [3,4]. We are interested in metallocene-β-diketones [5,6] and metallocene-β-diketonate [7] complexes and how the electronegativity of the side groups on the β-diketonate ligand influences the formal reduction potential of the metallocene couple We previously showed that the formal reduction potential of the $Ti^{III/IV}$ couple of a series of $[Cp_2Ti(CH_3COCHCOR)]^+$ complexes (R = CF_3, OCH_3, C_6H_5, CH_3 or Fc (ferrocenyl)) increased as the group electronegativity of the R group of the β-diketonato ligand increased [8], although no quantitative relationship could be establish. Here we have prepared and characterised a series of eight $[Cp_2Ti(R'COCHCOR)]^+$ complexes with different R′ and R groups and examined the redox behaviour using cyclic voltammetry. In order to predict redox potentials, enabling the design of organometallic molecules with particular redox potentials, a density functional theory (DFT) study was conducted. The “electron transfer” process was calculated in terms of the amount of energy released when an electron is added to the molecule. We have established a quantitative relationship between the electrochemical potential ($E^{\circ\prime}$) of the metal centred redox process and gas-phase electron affinity potentials in titanocene-β-diketonate complexes. Trends were also established for the interrelationships between electrochemical, spectroscopic and calculated electron affinities.

2. Experimental

2.1. General

NMR measurements were recorded on a Bruker Advance DPX 300 NMR spectrometer at 298 K. Chemical shifts are reported as

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δ values relative to $SiMe_4$ (0 ppm). Attenuated reflection infrared spectra were recorded on a Bruker Tensor 27 infrared spectrophotometer fitted with a Pike MIRacle single bounce and a diamond ATR, using the samples as is. IR absorption frequencies were measured in the solid phase. Cyclic voltammetry was performed utilizing a BAS 100 B/W Electrochemical Analyzer linked to a personal computer utilizing the BAS100W Version 2.3 software.

2.2. Cyclic voltammetry

Cyclic voltammetry measurements were performed on 0.002 mol dm^{-3} solutions of the complexes in dry acetonitrile (Aldrich, Biotech grade, 99.93+% purity, anhydrous, kept under purified argon) containing 0.1 mol dm^{-3} tetra-*n*-butylammonium hexafluorophosphate ($(^nBu_4N)(PF_6)$) (Fluka, electrochemical grade) as supporting electrolyte and under a blanket of purified argon at 25 °C. A three electrode cell, with a glassy carbon (surface area $7.07 \times 10^{-6}\,m^2$) working electrode, Pt auxiliary electrode and a Ag/Ag^+ (0.010 mol dm^{-3} $AgNO_3$ in CH_3CN) reference electrode [9] mounted on a Luggin capillary, was used [10,11]. All temperatures were kept constant to within 0.5 °C. Successive experiments under the same experimental conditions showed that all reduction and formal reduction potentials were reproducible within 5 mV. All cited potentials were referenced against the Fc/Fc^+ couple as suggested by IUPAC [12]. Ferrocene exhibited a formal reduction potential $E^{\circ\prime} = 0.084\,V$ *vs.* Ag/Ag^+, a peak separation $\Delta E_p = E_{pa} - E_{pc} = 0.066\,V$ and $i_{pa}/i_{pc} = 0.98$, under our experimental conditions. E_{pa} (E_{pc}) = anodic (cathodic) peak potential and i_{pa} (i_{pc}) = anodic (cathodic) peak current. $E^{\circ\prime}$ (Fc/Fc^+) = 0.400 V *vs.* NHE [13].

2.3. Quantum computational methods

All calculations were performed using the density functional method (DFT) with the Perdew-Wang 1991 (PW91) [14] generalized gradient approximation (GGA) as implemented in the Amsterdam Density Functional (ADF2007) package [15,16]. The Triple ζ polarized (TZP) basis, with a fine mesh for numerical integration, a spin-unrestricted (gas-phase) formalism and a full geometry optimization with tight convergence criteria, was used. No symmetry limitations were imposed during the calculations, unless indicated.

The electrochemical reduction process is modelled in terms of calculated electron affinities (EA), defined as the amount of energy released when an electron is added to a neutral atom or molecule, i.e., the energy change for the process,

$$X + e^- \rightarrow X^- + EA$$

The electron affinity is calculated as the differences between the energies of the cationic molecule (*N* electron system) and the reduced molecule (*N* + 1 electron system) at the optimized geometry of each species.

3. Results and discussion

3.1. Synthesis and spectroscopic characterisation

The bis(cyclopentadienyl) mono-β-diketonato titanium(IV) salts $[Cp_2Ti(R'COCHCOR)]^+ClO_4^-$ with Cp = cyclopentadienyl and R′, R = CF_3, C_4H_3S (1), CF_3, C_4H_3O (2), CF_3, Ph (C_6H_5) (3), CF_3, CH_3 (4), CH_3, CH_3 (5), Ph, Ph (6) and Ph, CH_3 (7) were synthesized according to an anion metathesis reaction shown in Scheme 1 and reported previously [17,18].

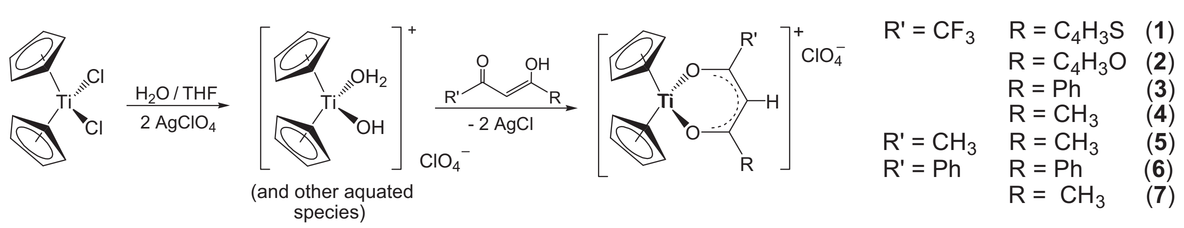
All the synthesised salts are insoluble in pure water, hexane and ether, slightly soluble in organic solvents such as chloroform, dichloromethane and soluble in acetone, THF and decomposes in ethanol. The $[Cp_2Ti(\beta)]^+$ cation is sensitive to moisture in solution, but no decomposition was detected in samples that were stored in the solid state for more than two years.

3.1.1. NMR spectra

^1H NMR spectral data of the synthesised $[Cp_2Ti(R'COCHCOR)]^+ClO_4^-$ complexes and the corresponding uncoordinated β-diketones R′COCHC(OH)R are compared in Table S1 and the ^1H NMR spectra of the CF_3-β-diketone series, complexes (1)–(4) with R′ = CF_3, are shown in Fig. 1. The ^1H NMR spectra of $[Cp_2Ti(CF_3COCHCOR)]^+ClO_4^-$ consist of three groups of signals: the cyclopentadienyl (Cp) protons (singlet, $\delta \sim 7.1$ ppm), the methine proton of the β-diketonato ligand (singlet, between δ 6.90 and 7.86 ppm) and the R group protons (C_4H_3S, C_4H_3O, Ph, CH_3). The electronic properties of the R groups of the β-diketonato ligand significantly influence the NMR shift of the methine proton which varies from δ 6.90 to 7.86 ppm for the series due to electronic communication through the C–C bonds in the β-diketonato backbone *via* conjugation. The methine proton resonance of the chelated β-diketonato ring is downfield shifted by ~0.6 ppm relative to the uncoordinated enol form of the β-diketone (see Fig. 1 and Table S1). This is due to the pseudo-aromatic system which is generated when the β-diketone chelates to the Ti(IV) metal. The study of the electrochemical behaviour of $[Cp_2Ti(\beta\text{-diketonato})]^+$ supports this view; a comparison of the cyclic voltammograms shows that the coordinated β-diketonato ligand is more electron-rich relative to its uncoordinated counterpart.

3.1.2. Infrared spectra

The infrared spectra of $[Cp_2Ti(R'COCHCOR)]ClO_4$ and the parent compound, Cp_2TiCl_2, in the 2000–600 cm^{-1} region are illustrated in Fig. 2. Infrared spectra can be used to observe successful coordination of the β-diketone R′COCHC(OH)R to the Cp_2Ti^{2+} moiety. The absence of the single carbonyl (C=O) vibration band of the uncoordinated β-diketone, in the finger print region of 1750–1650 cm^{-1} indicates coordination. The C–O stretch, ν_{CO}, of the chelated complex, is affected by the electronic properties of the R′ and R groups on the β-diketonato ligand; larger values are obtained for the fluorine containing compounds (see Table S2). The perchlorate group, ClO_4^-, exists as a counter ion (i.e., the vibration frequencies of ClO_4^- as a cation are ~1091 cm^{-1} (ν_3) and ~620 cm^{-1} (ν_4) [19]) and these values remain constant throughout the series. All the com-



Scheme 1. Synthesis of $[Cp_2Ti(R'COCHCOR)]^+ClO_4^-$ complexes.