Reversible Electron-Transfer Properties of the Titanium(II) Organometallic Species (Cp)₂Ti(bpy)

J. E. Anderson,* T. P. Gregory, C. M. McAndrews, and L. B. Kool

*Department of Chemistry, Boston College
Chestnut Hill, Massachusetts 02167*

Summary: The electrochemical and spectroelectrochemical properties of (Cp)₂Ti(bpy) in tetrahydrofuran (THF) with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte are presented. This formal Ti(II) species exhibits four reversible electron-transfer reactions on the cyclic voltammetric time scale.

We wish to report that (Cp)₂Ti(bpy), where Cp is η^5-cyclopentadienyl and bpy is 2,2'-bipyridine, can be reversibly reduced in three one-electron steps and reversibly oxidized by one electron on the cyclic voltammetric time scale. These results are based on electrochemical and UV–vis spectroelectrochemical data, which also indicate that on longer time scales chemical reaction(s) follow the oxidation process. This is the first report of electrochemical or spectroelectrochemical data for any formal titanium(II) organometallic complex.[1–3]

(Cp)₂Ti(bpy), a remarkably air- and moisture-sensitive d^2 metallocene, was prepared and characterized by comparison with literature data.[4–7] The electrochemical and spectroelectrochemical techniques used to obtain data on such species have been reported.[8] Three reduction waves at $E_{1/2} = -0.83, -1.60$, and -1.78 V (± 0.02 V) vs a Pt-wire pseudo reference electrode[9] are observed in the cyclic voltammogram of (Cp)₂Ti(bpy) in THF at a scan rate of 100 mV/s (waves 1–3, Figure 1a). The electrochemical characteristics of these waves are generally consistent with diffusion-controlled, reversible, one-electron transfers.[10,11] However, values for ΔE_p of 83, 94, and 125 mV are found for waves 1–3, respectively, which are larger than the expected[10] 57 mV. This is due to an increased solution resistance when THF is the solvent. Thin-layer bulk electrolysis (TLBE) studies show that the ratio of the charge
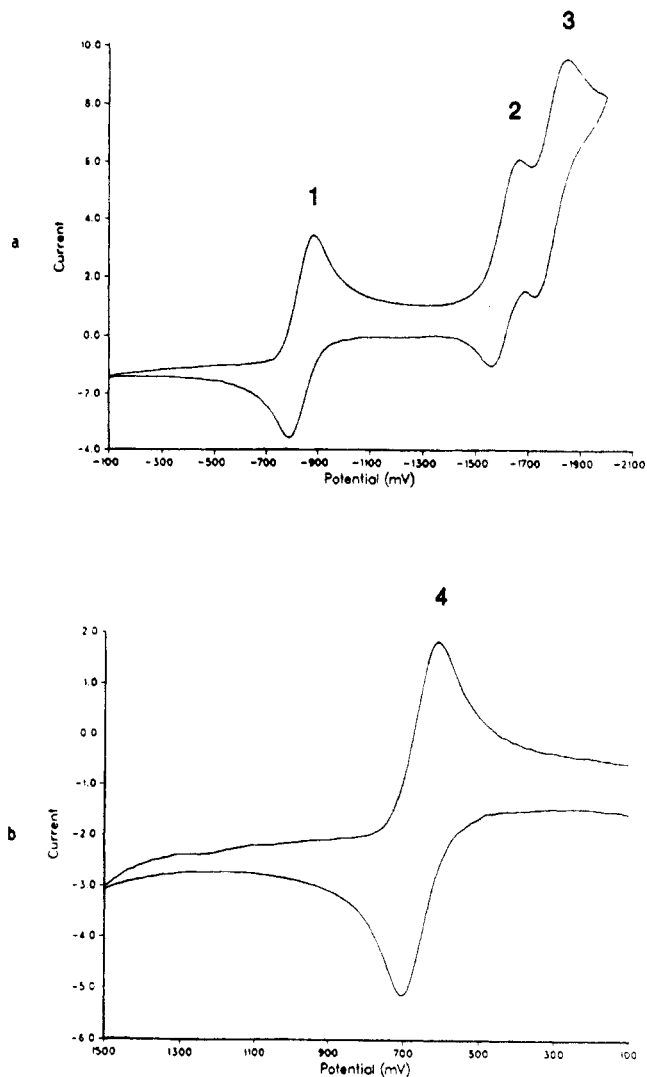

Figure 1. Cyclic voltammograms of (Cp)₂Ti(bpy) in THF at 100 mV/s with 0.2 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte: (a) scanning from −100 to −2000 mV; (b) scanning from 100 to 1500 mV. Potentials are vs a Pt-wire pseudo reference electrode. The current scale is in microamperes.

generated at a potential 100 mV past wave 3 to the charge generated 100 mV past wave 1 (i_3/i_1) is 3.1 ± 0.3 in agreement with a one-electron transfer for each process.

A reversible, diffusion-controlled, one-electron-oxidation process[10,11] (wave 4, Figure 1b) is found at $E_{1/2} = 0.66 \pm 0.02$ V at a scan rate of 100 mV/s for (Cp)₂Ti(bpy). The value of ΔE_p is 85 mV for wave 4. At slower scan rates a return wave (i_{pc}) for wave 4 is not observed, which demonstrates that chemical reaction(s) follow the oxidation. By TLBE, i_4/i_1 is 1.6 ± 0.3, which suggests further electron transfer is associated with the chemical reaction(s) following the initial one-electron oxidation.

Figure 2a illustrates the spectral changes that occur from 220 to 320 nm upon reduction of (Cp)₂Ti(bpy) at −1.10 V. In this region, (Cp)₂Ti(bpy) is characterized by two absorption bands at 243 and 238 nm due to bipyridine,[12] a shoulder at 255 nm due to cyclopentadiene, and a band at 282 nm. Upon reduction, the absorbance above 296 nm decreases and the band at 282 nm increases with an isosbestic point at 296 nm. The bands at 238 and 243 nm decrease in intensity, and an absorption band at 368 nm (not shown) is also formed. When the potential is applied

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(9) Under our conditions, the potentials are shifted cathodically by approximately 225 mV when a Pt pseudo reference electrode is used, relative to aqueous SCE. The ferrocene/ferrocenium couple, added as an internal standard, overlaps with wave 4 and is at, approximately, $E_{1/2}$ = 0.68 V. There is also indication that ferrocene reacts chemically with the neutral complex.

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(11) For waves 1–4 the value of $E_{1/2}$ is scan-rate (v) independent and $i_p/v^{1/2}$ is constant for waves 1–3 (both reduction and oxidation processes), while only $i_{pa}/v^{1/2}$ is constant for wave 4. For waves 1–3 i_{pc}/i_{pa} is unity at all scan rates, while i_{pa}/i_{pc} is unity only at scan rates >100 mV/s for wave 4. $E_{pc} - E_{pc/2}$ is 64, 55, and 66 mV for waves 1–3, while $E_{pa} - E_{pa/2}$ is 54 mV for wave 4 at 100 mV/s, and these values increase as the scan rate is increased, presumably due to solution resistance.
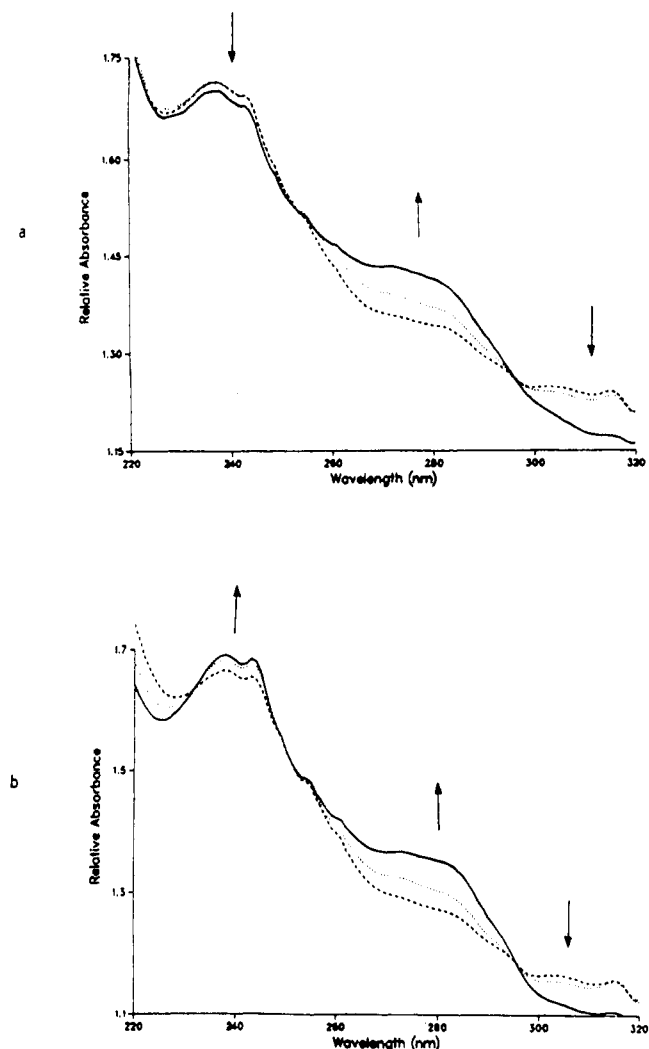
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Figure 2. Spectroelectrochemical data for (Cp)$_2$Ti(bpy) in THF, TBAP ($T = 0$; initial complex (---), $T = 20$ s (···) $T = 1$ min (—)): (a) spectral range of 220–320 nm, reduction at $E = -1.10$ V; (b) spectral range of 220–320 nm, oxidation at $E = 1.10$ V. Potentials are vs a Pt-wire pseudo reference electrode.

to 0.10 V, regeneration of (Cp)$_2$Ti(bpy) is observed, consistent with reversible electrochemical behavior.

Figure 2b shows the spectral changes that occur upon oxidation of (Cp)$_2$Ti(bpy) at 1.10 V. The absorbance above 295 nm decreases, while the absorption band at 282 nm increases with an isosbestic point at 295 nm. In addition, the bands at 238 and 243 nm show a slight increase in intensity. Re-reduction at 0.10 V does not produce any significant changes, and hence, (Cp)$_2$Ti(bpy) does not reform. This demonstrates that the oxidation is irreversible on longer time scales.

Although several metal–bipyridine complexes are known to exhibit multiple, reversible, one-electron-transfer steps,[13,14] the stability of (Cp)$_2$Ti(bpy) toward the addition or abstraction of electrons is surprising given the reactive nature of this species.[2,6] In addition, the potential for wave 1 is low, considering that (Cp)$_2$TiCl$_2$ is reduced at $E_{1/2} = -0.81$ V vs SCE under identical conditions.[15] The spectral data do not allow distinction between a metal or ligand

center for the first reduction,[12] and MO calculations suggest such a distinction is not relevant.[6]

The spectral data for the first oxidation are complicated by the subsequent chemical reaction(s). A reasonable interpretation is that free bipyridine is generated, since the bands at 238, 243, and 282 nm all increase in intensity and bipyridine has absorption bands at 280 and 235 nm. Although the monocation is not stable under our conditions, it is interesting to note that isolation of [(Cp)$_2$Ti(bpy)]PF$_6$ has been achieved[7] by addition of bpy to the Ti(III) complex [(Cp)$_2$TiCl]$_2$. Further work in our laboratories aimed at elucidating the electron-transfer properties of related low-valent early-transition-metal organometallic complexes is in progress.

(σ-Alkoxycarbonyl)(σ-vinyl)bis(triphenylphosphine)platinum(II) Complexes, Possible Models for the Metal-Catalyzed Carbalkoxylation of Electrophilic Substrates

Zhandong Zhong, Peter J. Stang, * **and Atta M. Arif**

Department of Chemistry, The University of Utah
Salt Lake City, Utah 84112

Summary: Reaction of sodium alkoxides in the corresponding alcohol solvents with (σ-vinyl)Pt^{II} carbonyl complexes, produced by the nucleophilic substitution of the corresponding labile triflate complexes with carbon monoxide, affords *trans*-(σ-alkoxycarbonyl)(σ-vinyl)Pt^{II} complexes in good yield. Key spectral features and a single-crystal X-ray structure determination are described for these novel complexes. Heating between 60 and 80 °C in a variety of solvents results in acrylate esters via reductive elimination.

The palladium-catalyzed carbalkoxylation of a variety of electrophilic substrates, such as alkyl, aryl, and vinyl halides and triflates, to esters has become an important method for the synthesis of this valuable class of organic compounds,[1] with increasing recent attention given to the reaction of triflates.[2] In principle this reaction may proceed by two main mechanisms.[3] The first is CO in-

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(15) The first reduction of (Cp)$_2$Ti(bpy) is approximately 200 mV *positive* of (Cp)$_2$TiCl$_2$ when the differences between the reference electrodes are considered.

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